12th Annual International Petroleum Environmental Conference
November 2005
Houston, TX

MONDAY, NOVEMBER 7, 2005

I. PRE-CONFERENCE WORKSHOPS

Waste Minimization in Oil and Gas Exploration and Production 9:00 am - 4:30 pm

Instructed by: Bart Sims, Railroad Commission of Texas, Austin, TX
(Registration/Sign-in begins at 8:30 am)

IPEC Soil Remediation Workshop 6:30 pm - 9:30 pm

Instructed by: Phil Spurlin, BEACON Environmental Assistance Corp., Edmond, OK
(Registration/Sign-in begins at 6:00 pm)

II. CONFERENCE REGISTRATION OPENS 5:00 pm - 7:00 pm

TUESDAY, NOVEMBER 8, 2005

CONFERENCE REGISTRATION 7:00 am - 5:00 pm

I. FULL BREAKFAST 7:30 am - 8:30 am

II. PLENARY SESSION 8:45 am - 11:30 am

WELCOME AND OPENING REMARKS 8:45 am - 9:00 am

Kerry L. Sublette, Conference Chair

PLENARY SPEAKERS:

William Hochheiser, U.S. Department of Energy, Washington, DC 9:00 am - 9:30 am

*"**Addressing Federal Lands Access Issues: Measuring Benefits from DOE's Oil and Natural Gas Environmental Research Program**"*

Sara McMillen, Chevron Texaco Energy Technology Company, Richmond CA 9:30 am - 10:00 am

"Environmental Litigation at E&P Sites: Science on Trial "

John Candler, M-I, L.L.C., Houston, TX 10:00 am - 10:30 am

"Understanding Biodiversity Protection Opportunities in the Oil & Gas Industry"

John Veil, Argonne National Laboratory, Washington, DC 10:30 am - 11:00 am

*"**Do Offshore Oil and Gas Platform Discharges Affect the Gulf of Mexico Hypoxic Zone?**"*

George Holliday, Holliday Environmental Services, Inc., Bellaire, TX 11:00 am - 11:30 am

*"**Lack of Commenting on Regulations Hurts the E&P Industry**"*

IV. CONCURRENT TECHNICAL SESSIONS 1:00 pm - 5:05 pm

- **Natural Attenuation of Petroleum Hydrocarbons**
- **Legal and Regulatory Issues**
- **Drilling Waste Management / Fugitive Air Emissions**
- **Produced Water and Wastewater Treatment**

IV. **POSTER SESSION** 5:15 pm - 6:30 pm

V. EXHIBITS OPEN 7:30 am - 6:30 pm

VI. EXHIBITOR RECEPTION 5:15 pm - 6:30 pm

VII. OPENING DINNER 6:30 pm - 9:00 pm

WEDNESDAY, NOVEMBER 9, 2005

Conference Registration 7:30 am - 12:00 noon

I. Exhibits Open 7:30 am - 12:00 noon

II. CONCURRENT TECHNICAL SESSIONS 8:00 am - 11:45 am

- **Groundwater Remediation**
- **NPDES and Best Management Practices**
- **Characterization and Remediation of Brine Impacted Soil and Groundwater**
- **Pollution Prevention and Waste Management I**

III. WORKSHOPS *(Registration/Sign-in begins at 1:00 pm)* 1:30 pm - 5:30 pm

Environmental Logistics: Applying Technology to Facilitate Management of Petroleum Impacted Sites

Instructed by: Jeffrey A. Johnson and Meng Ling, The RETEC Group, Houston, TX; Recep Ynez, Fugro Geosciences, Inc., Houston, TX; Mitchell Beard, EarthSoft, Inc.; Concord, MA; Yousheng Zeng, Providence Engineering & Environmental Group, Baton Rouge, LA

Environmental Issues in Oil and Gas Development: Working with the Regulatory Agencies

Instructed by: Pete McKone and Steve Veal, Carter & Burgess, Inc, Ft. Worth, TX

A Practical Guide to Using Bio-Trap Samplers to Assess Petroleum Hydrocarbon Degradation

Instructed by: Greg Davis and Dora Ogles, Microbial Insights, Inc., Rockford , TN; Aaron Peacock, Center for Biomarker Analysis, University of Tennessee, Knoxville, TN; Eric Raes, Engineering and Land Planning Associates, Clinton, NJ

THURSDAY, NOVEMBER 10, 2005

Conference Registration 7:30 am - 5:30 pm

I. CONCURRENT TECHNICAL SESSIONS 8:00 am - 12:00 noon

- **Phytoremediation**
- **Coalbed Natural Gas Produced Water I**
- **Environmental Management, Compliance and Auditing**
- **Remediation of Hydrocarbon Spills**

LUNCH 12:00 noon - 1:30 pm

Guest Speaker: **Chang-Ming Lee**, NATCO Group, Houston, TX

"***CFD: "Colorful" Fluid Dynamics to Brighten Your Water Treatment Woes***"

II. CONCURRENT TECHNICAL SESSIONS 1:30 pm - 5:35 pm

- **Site Characterization and Forensic Geochemistry**
- **Coalbed Natural Gas Produced Water II / Pollution Prevention and Waste Management II**
- **Restoration of Soils Impacted by Hydrocarbons and Produced Water Releases / Sustainable Energy Production: Greening of the Oil Field with Innovative Technologies**

III. NETWORKING RECEPTION 5:30 pm - 6:30 pm

FRIDAY, NOVEMBER 11, 2005

Symposium Registration 7:30 am - 8:00 am

I. **SPECIAL SYMPOSIUM** 8:00 am - 11:15 pm

In Honor of David C. White, Director, Center for Biomarker Analysis, UTK/ORNL Distinguished Scientist, University of Tennessee, Knoxville, TN:
"Using Molecular Methods in the Analysis of Subsurface Microbial Ecology at Hydrocarbon Impacted Sites"

Conference closes at 12:00 Noon

Technical Sessions

TUESDAY, NOVEMBER 8, 2005 - AFTERNOON

NATURAL ATTENUATION OF PETROLEUM HYDROCARBONS

Chair: Lisa Gieg, University of Oklahoma, Norman, OK

- **Linking Geochemical and Microbiological Approaches to Assess Natural Attenuation Processes: Examples from 20 Years of Research in a Crude-Oil Contaminated Aquifer Near Bemidji, MN**
  Isabelle Cozzarelli, USGS, Reston, VA
- ***In Situ* Rates of Hydrocarbon Biotransformation in a Gas Condensate Impacted Aquifer**
  Lisa M. Gieg, University of Oklahoma; Rob Alumbaugh, Jennifer Field, Jesse Jones, Oregon State University, Corvallis, OR; Joseph Suflita, University of Oklahoma, Norman, OK
- **Natural Attenuation of PAHs and Heterocyclic Organics in Groundwater: 10 Years of Experience with a Controlled Field Experiment**
  Jim Barker, Michelle Fraser and Fred Blaine, University of Waterloo, Waterloo, Ontario,

Canada; Caitlin Cooke, Golder Associates Ltd., Kanata, Ontario, Canada

- **Evidence for Hydrocarbon Destruction Linked to Sulfate Reduction at a Former Petroleum Refiner**Matthew Zenker and Gaylen R. Brubaker, The RETEC Group, Inc., Durham, NC; Joseph Suflita, Victoria A. Parisi and Lisa Gieg, University of Oklahoma, Norman, OK
- **Emerging and Under Utilized Assessment Technologies for Determining Degradation Rates for *In Situ* Natural Attenuation Capacity**
  Eric J. Raes, Engineering and Land Planning Assoc., Inc., Clinton, NJ; Kerry Sublette, University of Tulsa, Tulsa, OK; Jack Istok, Oregon State University, Corvallis, OR; Aaron Peacock, Universityof Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN
- **Assessment of *In Situ* Biodegradation Potential of Benzene Using 13C-Labeled Benzene and BioSep ® Beads**
  J.L. Busch-Harris, Eleanor Jennings, Zhong Zhong, and K.L. Sublette, University of Tulsa, Tulsa, OK; D.C. White and Aaron Peacock, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN; William E. Holmes, University of Michigan, Ann Arbor, MI; Ravi Kolhatkar, Atlantic Richfield (a BP affiliated company), Houston, TX; Xiaomin Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL
  IPEC FUNDED PROJECT
- **Stable Isotope Analysis in Remediation of Gasoline Oxygenates and Hydrocarbons**
  Tomasz Kuder and Paul Philp, University of Oklahoma, Norman, OK
  IPEC FUNDED PROJECT
- Natural Attenuation of Gasoline Hydrocarbons in Water
  Roger C. Prince and Thomas F. Parkerton, ExxonMobil Biomedical Sciences, Inc., Annandale, NJ

LEGAL AND REGULATORY ISSUES

Chair: Markus G. Puder, Argonne National Laboratory, Washington , DC

- **Quantifying Lease Stipulation Impacts on Federal Resource Accessibility**
  David Alleman, U.S. DOE/NETL, Tulsa, OK; John R. Duda, U.S. DOE/NETL, Morgantown, WV; William Hochheiser, U.S. DOE/Fossil Energy, Washington, DC; Jeffrey Eppink,Advanced Resources International, Inc., Arlington, VA
- **The Energy Policy and Conservation Act (EPCA) Cumulative Phase II Inventory: Sound Science to Support Energy Policy**
  Jeffrey Eppink, Advanced Resources International, Inc., Arlington, VA; Richard Watson, Bureau of Land Management, Washington, DC; Robert Johnson, Premier Data Services, Denver, CO
- **Railroad Commission of Texas Voluntary Cleanup Program: New Tools and Examples of Successful Cleanups**
  Aimee Beveridge, Railroad Commission of Texas, Austin, TX
- **Tremors in the Cooperative Environmental Federalism Arena**
  Markus G. Puder, Argonne National Laboratory, Washington, DC; Michael J. Paque, Ground Water Protection Council, Oklahoma City, OK
- **Environmental Regulatory Constraints to Natural Gas Production**

Deborah Elcock, Argonne National Laboratory, Washington, DC

- **Environmental Issues in Real Estate Transactions and New CERCLA Developments**
  Ann R. Barker, Baker Petrolite Corporation, Sugar Land, TX
- **New SPCC Integrity Test Requirements for Storage Containers and Tanks**
  Kevin Kupitz, TCI Services, Inc., Tulsa, OK
- **EPA Brownfields Program – Petroleum Grant Information and Guidance**
  Casey Luckett Snyder, U.S. EPA Region 6, Dallas, TX

DRILLING WASTE MANAGEMENT / FUGITIVE AIR EMISSIONS

Chair: Robert Babcock, University of Arkansas, Fayetteville, AR

DRILLING WASTE MANAGEMENT

- **The Application of a Salt-free High Performance Water Base Mud for Minimizing Environmental Impact in the Oriente Ecuadorian Basin**
  Mario A. Ramirez, Baker Hughes Drilling Fluids, Houston, TX; Pablo Benalcazar, Baker Hughes Drilling Fluids, Quito, Ecuador; Diego Paz, Baker Hughes Drilling Fluids, Houston, TX
- **Aspects of Computer Programs that Address Drilling Waste Management**
  William A. Piper, Piper Consulting, Stafford, TX; Catalin Ivan, M-I Swaco, Houston, TX; James B. Bloys, Chevron Corp., Houston, TX; Carole Fleming, Chevron Energy Technology Company, Houston, TX
- **Cementing Additives for Use in Environmentally Sensitive Regions**
  Samuel J. Lewis, Michael Szymanski and John M. Wilson, Halliburton Energy Services, Duncan, OK
- **Optimizing Fluid Choices for Landfarm Applications**
  Simon Seaton and John Hall, Halliburton Baroid Fluid Services, Houston, TX
- **Closed Loop Solids Handling Systems**
  Lary Parker, Controlled Recovery, Inc., Hobbs, NM

FUGITIVE AIR EMISSIONS

- **Use of Hildebrand Solubility Parameters for the Correlation of Emissions from Stock Tank Crude Oils**
  Robert E. Babcock, University of Arkansas, Fayetteville, AR; Jorge M. Plaza, Trinity Consultants, Inc., Baton Rouge, LA
- **Benzene Emissions Control for Area Sources Triethylene Glycol Dehydrators**
  George Holliday, Holliday Environmental Services, Inc., Bellaire, TX
- **Optimized Production of Biodiesel Fuel from Low Cost Feedstock, and its Potential Impact on Diesel Engine Exhaust Emissions**
  Brian Mattingly, Ed Clausen and Michael Popp, University of Arkansas, Fayetteville, AR
- **Safety Considerations for Installing Flow and Level Instrumentation in Oil Storage Tanks**

Wayne Shannon, Magnetrol, Downers Grove, IL; Randy Webb, Myers-Aubrey, Tulsa, OK

PRODUCED WATER AND WASTEWATER TREATMENT

Chair: G. Dale Wesson, FAMU-FSU, Tallahassee , FL

- **Economic Handling of Oilfield Produced Waters Using a Combined Biological Treatment and Phytoremediation System**
  Muralikrishnan Erat and John N. Veenstra, Oklahoma State University, Stillwater, OK
- **Overview of Regulations for Potential Beneficial Use of Oilfield Produced Water in California**
  Raymond Ouellette, Rajagopalan Ganesh and Lawrence Y.C. Leong, Kennedy/Jenks Consultants, Irvine, CA
- **Further Advances in Produced Water De-Oiling Utilizing a Technology That Removes and Recovers Dispersed Oil in Produced Water Two Microns and Larger**
  M.J. Plebon, Marc A. Saad and Serge Fraser, EARTH (Canada) Corporation, Montreal, Quebec, Canada
- **Chemical Conditions Impacting the Removal Efficiency of Hg and Other Toxic Trace Metals from Wastewater**
  Carl E. Hensman, Frontier Geosciences, Inc., Seattle, WA
- **Diagnosing Chemical and Mechanical Problems with Produced Water Treating Systems**
  Ted Frankiewicz, Joseph Lee and Chang-Ming Lee, Natco Group, Houston, TX
- **Generalized Models for Vapor-Liquid Equilibria Predictions**
  Khaled Gasem, D. Ravindranath, S.S. Godavarthy and R.L. Robinson, Jr., Oklahoma State University, Stillwater, OK

POSTER SESSION

Chair: Brandy Fidler, University of Tulsa, Tulsa, OK

- **Assessing Soil Ecosystem Recovery Following Managed and Unmanaged Bioremediation**
  Dan Weber, Eleanor Jennings, and Kerry Sublette, University of Tulsa, Tulsa, OK; Greg Thoma, University of Arkansas, Fayetteville, AR
  IPEC FUNDED PROJECT
- **Remediation of a Historic Brine Scar: Characterization and Development of a Remediation Protocol**
  Shoeb Munshi, Kerry Sublette, Eleanor Jennings, Ken Roberts, J. Berton Fisher, and Bryan Tapp, University of Tulsa, Tulsa, OK
  IPEC FUNDED PROJECT
- **Economic Handling of Oilfield Produced Waters Using a Combined Biological Treatment and Phytoremediation System**
  Muralikrishnan Erat and John N. Veenstra, Oklahoma State University, Stillwater, OK
- **Tracking the Fate and Recycling of 13C Hexadecane in a Captina Silt Loam**

Jill A. Baird, K.M. Greer, S.E. Ziegler, G.J. Thoma, K.J. Davis and D.C. Wolf, University of Arkansas, Fayetteville, AR

- **Biosurfactant Production and Their Application in Enhanced Petroleum Hydrocarbon Remediation**
  Thu Nguyen, Noha Youssef, Michael McInerney and David Sabatini, University of Oklahoma, Norman, OK
  IPEC FUNDED PROJECT
- **Assessing Phytoremediation of a Crude Oil-Contaminated Soil Using Nematode Diversity and Maturity Indices**
  Mary C. Savin, P.J. Tomlinson, K. Karim, G.J. Thoma, K.J. Davis and D.C, Wolf, University of Arkansas, Fayetteville, AR
- **Controlling Soil Sodicity During Irrigation with CBNG Produced Water**
  Dina E. Brown and Kevin C. Harvey, KC Harvey, L.L.C., Bozeman, MT
- **Proposing an Environmentally Friendly Welltesting Method for Iranian Oil Fields**
  Shahin Kord, National Iranian Oil Company, Ahwaz, Iran
- **Characterization of Three Creosotes with Environmental Forensic Purposes**
  Luis Torres, M.G. Urquiza and R. Iturbe, UNAM, Mexico DF, Mexico
- **Catalytic Cracking of Straight-Run Diesel Fractions (200-360 oC) of Tamsagbulag and Zuunbayan Oils, Mongolia**
  Adiya Sainbayar, National University of Mongolia, Ulaanbaatar, Mongolia; A.V. Vosmerikov, Tomsk Institute of Petroleum Chemistry, Tomsk, Russia
- **Comparison of Individual Hydrocarbons Composition of Gasoline Fractions Between Tamasgbulag and Zuunbayan Oils, Mongolia**
  Adiya Sainbayar, National University of Mongolia, Ulaanbaastar, Mongolia; A.V. Vosmerikov, Tomsk Institute of Petroleum Chemistry, Tomsk, Russia
- **Earthworms as Ecoengineers in the Restoration of Oil and Brine-Impacted Soils Following Remediation**
  Nitya Alahari, Kerry Sublette and Eleanor Jennings, University of Tulsa, Tulsa, OK; Greg Thoma and Duane Wolf, University of Arkansas, Fayetteville, AR; Kathleen Duncan, University of Oklahoma, Norman, OK; Mac A. Callaham, Jr., USDA-Forest Service, Athens, GA; Tim Todd, Kansas StateUniversity, Manhattan, KS
  IPEC FUNDED PROJECT
- **Assessment of *In Situ*Biodegradation Potential of Benzene Using 13C-Labeled Benzene and BioSep ® Beads**
  J.L. Busch-Harris, Eleanor Jennings, Zhong Zhong, and K.L. Sublette, University of Tulsa, Tulsa, OK; D.C. White and Aaron Peacock, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN; William E. Holmes, University of Michigan, Ann Arbor, MI; Ravi Kolhatkar, Atlantic Richfield (a BP affiliated company), Houston, TX; Xiaomin Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL
  IPEC FUNDED PROJECT
- **Hypothesis of a Natural Brine Pump Causing Persistent Brine Scars in the Tallgrass**

Prairie, Oklahoma
Courtney Busse-Jones, Vanessa Andrews, Melissa Barton, Teko Blanchard, Kaitlin Beam, Chelsea Coleman, Jenny Hironaga, Daniel Weber, Aaron Palke, Bryan Tapp and Winton Cornell, University of Tulsa, Tulsa, OK; Kate Key, Rhodes College, Memphis, TN; Sara Prior, University of Arkansas-Monticello, Monticello, AR

- **Trace Element Compositions of Brine Impacted Soils and Produced Water in Osage County, Oklahoma**
  Dan Weber, Eleanor Jennings, Kerry Sublette, Ken Roberts, and Bryan Tapp, University of Tulsa, Tulsa, OK

WEDNESDAY, NOVEMBER 9, 2005 - MORNING

GROUNDWATER REMEDIATION

Chair: Eleanor Jennings, University of Tulsa, Tulsa, OK

- **A Field Study of Pulsed Air Sparging for Remediation of Petroleum Hydrocarbon Contaminated Soil and Groundwater**
  Xiaomin Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL; Craig Niedermeier, The RETEC Group, Inc., Austin, TX; Dennis Beckmann, Atlantic Richfield (a BP affiliated company), Tulsa, OK; Stephanie Fiorenza, Atlantic Richfield (a BP affiliated company), Houston, TX
- **Application of Denitrification-Based Bioremediation (DBB) for *In Situ* Bioremediation of Sorbed-Phase Hydrocarbons and Source Areas**
  Eric Hince, Geovation Technologies, Inc., Florida, NY
- **Transport of Nano-C60 Particles in Soil**
  Mason B. Tomson, Xuekun Cheng, and Amy T. Kan, Rice University, Houston, TX
- ***In Situ* Treatment of Chromate in Groundwater by the Injection of Soluble Carbon Reagents**
  David B. Vance and Steve Tischer, ARCADIS, Midland, TX
- **Arsenic Removal on Magnetite Nanoparticles from Groundwater**
  Mason Tomson, Sujin Yean, Cafer T. Yavuz, Amy T. Kan, and Vicki Colvin, Rice University, Houston, TX; Lili Cong, Champion Technologies, Houston, TX
- **Modeling of LNAPL Distribution and Recovery at a Former Refinery Site**
  Tie Li, URS Corporation, Houston, TX; Xiaomin Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL

NPDES AND BEST MANAGEMENT PRACTICES

Chair: Patricia Billingsley, Oklahoma Corporation Commission, Oklahoma City, OK

- **STRONGER Guidance for State Stormwater/Erosion Control Measures at Oil and Gas Sites**

Patricia Billingsley, Oklahoma Corporation Commission, Oklahoma City, OK

- **EPA NPDES Construction Stormwater Rules and Regulations Update for Upstream Oil and Gas Operators**
  Casey Luckett Snyder, US EPA Region 6, Dallas, TX
- **NPDES Permits for Oil and Gas Stormwater**
  Janet McQuaid, Fulbright & Jaworski, L.L.P., Austin, TX
- **EPA Should Not Apply Storm Water Permit Requirements to Drill Site Construction**
  George Holliday, Holliday Environmental Services, Inc., Bellaire, TX
- **Effects of EPA Storm Water Permitting on US Oil and Gas Exploration**
  Walter Mayfield, Goldston Oil Corporation, Houston, TX
- **Reasonable and Prudent Practices for Stabilization of Oil and Gas Construction sites (RAPPS)**
  Marilyn Fish, EOG Resources, Inc., Houston, TX
- **Stormwater Management and Site Restoration, an Integral Component of Oil and Gas Exploration and Production in Pennsylvania**
  Ronald P. Gilius, Melissa L. Hack-Becker and Joseph Umholtz, Pennsylvania Department of Environmental Protection, Harrisburg, PA
- **Best Management Practices for Oil and Gas Development on Public Lands**
  Rebecca Hunt, Department of the Interior/BLM, Carlsbad, NM

CHARACTERIZATION AND REMEDIATION OF BRINE IMPACTED SOIL AND GROUNDWATER

Chair: J. Berton Fisher, University of Tulsa, Tulsa, OK

- **Geologic Controls on Surface and Subsurface Produced Water Movement at the OSPER "A" Site, Skiatook Lake, Osage County, Oklahoma**
  James K. Otton, Robert A. Zielinski, USGS, Lakewood, CO; Marvin M. Abbott, USGS, Oklahoma City, OK
- **Trace Element Compositions of Brine Impacted Soils and Produced Water in Osage County, Oklahoma**
  Dan Weber, Eleanor Jennings, Kerry Sublette, Ken Roberts, and Bryan Tapp, University of Tulsa, Tulsa, OK
- **Impacts of Produced-Water Releases on Ground Water: Results from the OSPER Sites, Osage County, Oklahoma**
  Yousif K. Kharaka and William N. Herkelrath, USGS, Menlo Park, CA; Bruce D. Smith and Robert Zielinski, USGS, Lakewood, CO, Marvin M. Abbott, USGS, Oklahoma City, OK
- **Investigation of Select Saltwater Impacts**
  William Renfro, Railroad Commission of Texas, Austin, TX
- **Case Study of Integrated Approach to the Cleanup of Ogallala Groundwater Impacted by Oilfield Brine, Haskell County, Kansas**

Kevin Hopson and Al Potter, Daniel B. Stephens & Associates, Lubbock, TX; Michael Jacobs, Pioneer Natural Resources USA, Inc., Midland, TX; Neil Blandford, Daniel B. Stephens & Associates, Inc., Albuquerque, NM

- **Restoration of Brine and Oil Contaminated Marshlands by Cationic Exchange and Chemical-Biological Stabilization**
  Randy H. Adams, J. Abisenas Alvarez R., Conrado Tinal O. and Francisco J. Guzman O., Juarez Autonomous University of Tabasco, Villahermosa Tabasco, Mexico
- **Isolation and Characterization of a Halophile that Degrades Benzene and Toluene as the Sole Carbon and Energy Source**
  Babu Z. Fathepure and Carla A. Nicholson, Oklahoma State University, Stillwater, OK

POLLUTION PREVENTION AND WASTE MANAGEMENT I

Chair: John Veil, Argonne National Laboratory, Washington , DC

- **Findings from CSB Investigations into the BP Texas Oil Refinery Vapor Cloud Explosion**
  Gary Visscher, Francisco Altamirano, Johnnie Banks, Hillary Cohen, Don Holmstrom, Bill Hoyle, Giby Joseph, Mark Kaszniak, Cheryl Mackenzie and Stephen Wallace, U.S.Chemical Safety and Hazard Investigations Board, Washington, D.C.
- **Effects of Deep Subsurface Carbon Dioxide Injection on Microbial Communities in the Frio Formation, Texas**
  Susan Pfiffner, Amanda Smithgall, Andrew Parson and Margaret Gan, University of Tennessee, Knoxville, TN; Dave Riestenberg and Tommy Phelps, Oak Ridge National Laboratory, Oak Ridge, TN
- **Best Practices in Integrated Subcontractor Management to Elevate EHS Performance in the Petroleum Industry**
  James J. Colbert, The RETEC Group, Inc., Fort Collins, CO; Jessica Cassens and Daniel Anguiano, The RETEC Group, Inc., Austin, TX
- **Offsite Commercial Disposal of E&P Wastes**
  John Veil and Markus Puder, Argonne National Laboratory, Washington, DC
- **Effective Storm Water and Sediment Control During Pipeline Construction Using New Filter Fence Concept**
  Sandeep Yeri, Jeyarathan Arjunan, Khaled Gasem, Ellen Stevens and Bill Barfield, Oklahoma State University, Stillwater, OK
  IPEC-FUNDED PROJECT
- **Proactive Safety and Pollution Prevention**
  Nathan Walters and Quinn Holtby, Katch Kan Limited, Edmonton, Alberta, Canada
- **Determination of Mercury and 22 Other Metals in Hydrocarbon Matrices at Trace Level Concentrations Using a Novel Digestion Method**
  Carl E. Hensman and Deborah Cussen, Frontier Geosciences, Inc., Seattle, WA
- **Solidifiers – Changing the Face of Oil Spills on Water**
  Thomas R. Hanley, Auburn University, Auburn, AL; Terry Masters and Dan Parker, Immediate

Response Spill Technologies, Louisville, KY

THURSDAY, NOVEMBER 10, 2005 - MORNING

PHYTOREMEDIATION

Chair: Greg Thoma, University of Arkansas, Fayetteville, AR

- ***In Situ*Measurement of Rhizosphere Degradation Kinetics**
  Greg Thoma, Thanh B. Lam, Pei-Ting Hsu, Khursheed Karim, Duane Wolf and Susan Ziegler, University of Arkansas, Fayetteville, AR
- **Effect of Petroleum-Tolerant Grasses on Biodegradation of Weathered Hydrocarbons in Soil**
  James L. Brown, Lockheed Martin/REAC, Edison, NJ; Harry Allen, U.S. EPA, Edison, NJ
- **A Five-Year Field Study to Evaluate Phytoremediation of a Crude Oil-Contaminated Soil**
  Khursheed Karim, G.J. Thoma, D.C. Wolf, P.M. White, Jr., O. Alba and K.J. Davis, University of Arkansas, Fayetteville, AR
  IPEC-FUNDED PROJECT
- **Field Testing of Soil Bioremediation Guidelines for Small, Independent Oil Producers in New York and Pennsylvania**
  James L. Brown, Lockheed Martin/REAC, Edison, NJ; Harry Allen, U.S. EPA, Edison, NJ
- **Phytoremediaton of Pyrene-Contaminated Soil: Nitrogen Additions and Plant Root Parameters**
  Oriana Alba, D.C. Wolf, J.D. Mattice, K.J. Davis and G.J. Thoma, University of Arkansas, Fayetteville, AR
- **Cost Comparisons of Phytotechnologies to Other Remedial Approaches**
  David T. Tsao and Barb Padlo, Atlantic Richfield (a BP affiliated company), Warrenville, IL
- **Plant/Ground-Water Interactions at a Petroleum-Hydrocarbon Contaminated Site**
  James E. Landmeyer, USGS, Columbia, SC

COALBED NATURAL GAS PRODUCED WATER I

Chair: Deidre Boysen, BC Technologies Ltd., Laramie, WY

- **Coalbed Natural Gas Development in the Powder River Basin: Local Objections vs National Impacts**
  J. Daniel Arthur and Bruce Langhus, ALL Consulting, L.L.C., Tulsa, OK
- **Use of Coalbed Methane Produced Water for Power Plant Cooling In the San Juan Basin**
  Barbara Carney, U.S. DOE/NETL, Morgantown, WV; Thomas Feeley, U.S. DOE/NETL, Pittsburgh, PA; John Duda, U.S. DOE/NETL, Morgantown WV; Kent Zammit, EPRI, Palo Alto, CA
- **Opportunities and Limitations of CBNG Produced Water Management Alternatives in the**

Powder River Basin
Thomas J. Osborne, HydroSolutions, Inc., Billings, MT; Joel E. Adams, HydroSolutions, Inc., Red Lodge, MT

- **Managed Irrigation Systems for the Beneficial Use of CBNG Produced Water**
  Kevin C. Harvey, Dina E. Brown and Aaron DeJoia, KC Harvey, L.L.C., Bozeman, MT
- **Coalbed Production…Topsoil Management, Sampling and Analytical Procedure**
  Kate Forsting, Energy Laboratories, Inc., Casper, WY
- **Assimilative Capacity in the Powder River, WY for Discharge of Coal Bed Natural Gas Produced Water**
  Jeffrey T. Cline, Anadarko Petroleum Co., Houston, TX; Arthur O'Hayre, Applied Hydrology Inc., Denver, CO; Glen Maynard, Devon Energy Corporation, Oklahoma City, OK

ENVIRONMENTAL MANAGEMENT, COMPLIANCE AND AUDITING

Chair: Deborah Elcock, Argonne National Laboratory, Washington, DC

- **Best Practices for Environmentally Driven Capital Projects**
  Robert A. Brown, Jr., Independent Project Analysis, Ashburn, VA; Allen Kufert, BP Products, Texas City, TX
- **Petroleum Environmental Data from the Field to the Map**
  David W. Rich, Geotech Computer Systems, Inc., Englewood, CO
- **State Electronic Commerce Initiatives: Produce More Oil and Gas and Increase Environmental Protection**
  Paul Jehn, Ground Water Protection Council, Oklahoma City, OK; Stan Belieu, Nebraska Oil and Gas Commission, Sidney, NE; Mark Bohrer, North Dakota Industrial Commission, Bismark, ND; Tom Richmond, Montana Board of Oil and Gas, Billings, MT
- **HSE Auditing: Challenges of Management System Integration with Compliance Measurement**
  Ann Potten, Baker Petrolite Corporation, Sugar Land, TX
- **Cleanup Goals and Site Closures – The South Dakota Triad Challenge**
  John Sohl and Ned Tillman, COLUMBIA Technologies, Baltimore, MD; Dennis Rounds, South Dakota Petroleum Release Compensation Fund, Pierre, SD
- **Technology Transfer in Environmental Remediation**
  Russell R. Sirabian, Batelle Memorial Institute, New Rochelle, NY; Myriam Amezcua Allieri, Cintia Mosler Garcia and Victor Martinez Martinez, Instituto Mexicano del Petroleo, Mexico City, Mexico
- **Waste Management Challenges at Petrobras E&P**
  Lucia de Toledo Camara Neder, Edgard Rangel Pessanha, Ricardo Caselli Moni, Denise de Almeida Pires do Rosario and Janete Teixeira Brandao, PETROBRAS, Rio de Janeiro, Brasil

REMEDIATION OF HYDROCARBON SPILLS

Chair: Jeffrey A. Johnson, The RETEC Group, Inc., Houston, TX

- **What Has Been Learned From Sites With Difficult Lithologic Conditions Where Controlled In-Situ Chemical Oxidation Processes Are Being Used To Reduce Petroleum Contaminants**
  Thomas Douglas, Advanced Environmental Technologies, L.L.C., Pensacola, FL; William Lundy, DeepEarth Technologies, Inc., Oak Forest, IL; Eric Nuttall, University of New Mexico, Albuquerque, NM
- **Innovative Remediation Technology for Pipeline Releases**
  David B. Vance, ARCADIS, Midland, TX
- **LNAPL Management: Moving Toward Site Specific Clean-up Goals**
  Jeffrey A. Johnson, The RETEC Group, Inc., Houston, TX
- **Evaluation of Polycyclic Aromatic Hydrocarbons in Historic Exploration and Production Waste and Associated Impacted Soil**
  Heidi Bojes, Railroad Commission of Texas, Austin, TX
- **Surfactant Enhanced Washing of Soils Contaminated with Three Mexican Crude Oils. Use of Nonionic and Ionic Surfactants With or Without Salts**
  Luis Torres, X. Lumus and R. Iturbe, UNAM, Mexico, D.F. Mexico
- **Optimization of a Crude Hydrocarbons Biodegradation Process in Soil, Using a Native Biostimulated Bacteria Consortium in a Static Pilot Biopile**
  Alfonso C. Espitia, Rocio Jimenez, Virginia Torrecilla, Rocio Cruz and Karina Uribe, UAM, Mexico, D.F.
- **The Application of Jet Recycle Technology in the Treatment of Oily Sludge from Oil Lakes of Kuwait**
  Al-Hashem, A. Al-Muttawa and E. Al-Muhameed, Petroleum Research and Studies Center, KISR, Safat, Kuwait

THURSDAY, NOVEMBER 10, 2005 - AFTERNOON

SITE CHARACTERIZATION AND FORENSIC GEOCHEMISTRY

Chair: Peter Pope, Railroad Commission of Texas, Austin, TX

- **An Evaluation of Total Petroleum Hydrocarbon (TPH) Cleanup Levels for Abandoned Oil and Gas Exploration and Production Facilities**
  Peter G. Pope and Heidi K. Bojes, Railroad Commission of Texas, Austin, TX
- **Improve Hydrocarbon Contamination Assessment and Conceptualization Using Visual Imagery Technology and LIF Data**
  Meng Ling and Jeffrey Johnson, The RETEC Group, Inc., Houston, TX
- **Using Chemical and Process Forensics to Identify Refined Products in Complex Environmental Samples**
  Phillip W. Beall, Batelle Memorial Institute, Houston, TX; Yakov Galperin, Batelle Memorial Institute, Moorpark, CA

- **Alternative Methods to Evaluate Volatile Organic Compounds in Soil: A Mexican Case Study**
  Alfonso C. Espitia and Nina Kondratenko, UAM, Mexico, D.F.; Jose Luis Luna Baez, PGPB, Mexico, D.F.
- **Delineation of a Petroleum Release Using the Soil Conductivity/Membrane Interface Probe**
  Roger Lamb, Maxim Technologies, Kansas City, KS
- **The Integration of the Membrane Interface Probe with In Situ Remediation Injection Technology to Facilitate Cost Effective Treatment of Groundwater**
  Eliot Cooper, Vironex, Golden, CO
- **The New DRET Test to Predict Heavy Metal Release During a Resuspension of Anoxic Sediments**
  Mason B. Tomson, Heather J. Shipley, Yan Gao, and Amy T. Kan, Rice University, Houston, TX

COALBED NATURAL GAS PRODUCED WATER II / POLLUTION PREVENTION AND WASTE MANAGEMENT II

Chair: John Boysen, BC Technologies, Ltd., Laramie, WY

COALBED NATURAL GAS PRODUCED WATER II

- **Capacitive Deionization Desalination Technology for Coal Bed Methane Produced Water, Treatment and Rangeland Rehabilitation**
  Mike Hightower, Allan Sattler, Richard Kottenstette, Charlie Hanley, Ryan Donahe, Emily Wright and Sam Wallace, Sandia National Laboratories, Albuquerque, NM
- **Methane in Water Wells, San Juan Basin, Colorado: Analysis of Data Submitted in Response to COGCC Orders 112-156 & 112-157**
  Anthony W. Gorody, Universal Geoscience Consulting, Inc., Houston, TX; Debbie Baldwin and Cindy Scott, Colorado Oil and Gas Conservation Commission, Denver, CO

POLLUTION PREVENTION AND WASTE MANAGEMENT II

- **Investigating Variations of Mercury and Trace Metal Analytical Results by Interrogation of a 55-gallon Barrel of Light Crude**
  Carl E. Hensman and Deborah Cussen, Frontier Geosciences, Inc., Seattle, WA
- **Nitrogen Rejection Membranes to Increase Gas Heating Value – A Wellhead Process**
  Ankur Jariwala and Kaaeid A. Lokhandwala, Membrane Technology & Research, Inc., Menlo Park, CA
- **New Approach in Rating Environmental Compliance Using a Weighted Optimal Life Cycle Analysis in Offshore Oil and Gas Exploration and Production Development**
  Kingsley Abhulimen, University of Lagos, Lagos, Nigeria
- **CO 2 Reduction by Green Algae**

Young Hoon Choi and Omar Barkat, McNeese State University, Lake Charles, LA

- **Countermeasure to Global Warming**
  Yoshihiro Tsukita, Kyushu Institute of Technology, Kitakyushu, Japan; Masaki Iijima, Mitsubishi Heavy Industry, Yokohana, Japan

RESTORATION OF SOILS IMPACTED BY HYDROCARBONS AND PRODUCED WATER RELEASES / SUSTAINABLE ENERGY PRODUCTION: GREENING OF THE OILFIELD WITH INNOVATIVE TECHNOLOGIES

Chair: David Friday, The RETEC Group, Inc., Austin, TX

RESTORATION OF SOILS IMPACTED BY HYDROCARBONS AND PRODUCED WATER

- **Earthworms as Ecoengineers in the Restoration of Oil and Brine-Impacted Soils Following Remediation**
  Nitya Alahari, Kerry Sublette, and Eleanor Jennings, University of Tulsa, Tulsa, OK; Greg Thoma and Duane Wolf, University of Arkansas, Fayetteville, AR; Kathleen Duncan, University of Oklahoma, Norman, OK; Mac A. Callaham, Jr., USDA-Forest Service, Athens, GA; Tim Todd, Kansas State University, Manhattan, KS
  IPEC FUNDED PROJECT
- **United States Business Council for Sustainable Development Green Brownfields Initiative**
  David D. Friday, The RETEC Group, Inc., Austin, TX; Andrew Mangan, U.S. Business Council for Sustainable Development, Austin, TX; Margaret Roy, URS, Austin, TX; Brad Raffle, Baker Botts, Houston, TX
- **Oil, Gas and Coal Bed Methane Reclamation and Financial Assurance Guide**
  James R. Kuipers and Kimberly Machardy, Kuipers & Associates and Western Organization of Resource Councils, Butte, MT; Victoria Lynne, Blue Sky Technical Services, Elliston, MT
- **Oil Pollution of West Kazakhstan Soil by Oil and Gas Companies**
  Yedil Zhanburshin, Karaganda State University, Aktau, Republic of Kazakhstan; E.A. Buketov, Kazakh National University, Almaty, Republic of Kazakhstan; Aithazha B. Bigaliev, Karaganda State University, Aktau, Republic of Kazakhstan

SUSTAINABLE ENERGY PRODUCTION: GREENING OF THE OILFIELD WITH INNOVATIVE TECHNOLOGIES

- **Windmill Potholes**
  Jim Myers, Chevron Energy Technology Company, Houston, TX; Jim Neaville, USFWS (retired), Anahuac, TX
- **Mother Nature: An Industrial Application**
  Tony Pace, Parsons Corporation, Cleves, OH; Jim Myers, Chevron, Houston, TX
- **Crude Oil Production & Geothermal Technology Transfer Using the Natural Energy**

Engine
Brian Hageman, Deluge, Inc., Phoenix, AZ

- **A New Meme for the Hydrocarbon/Energy Industry**
  Douglas B. Swift, MWS, L.L.C., Midland, TX; Sovani Meksvanh and Ronald Whelan, MWS, L. L.C., Bethesda, MD; Richard Erdlac, Jr., University of Texas, Odessa, TX; Anthony Swift, DOT, Washington, DC
- **Restoring Greenspace for Wildlife Habitat Conservation**
  Stephen Archer, Wildlife Habitat Council, La Porte, TX

SPECIAL SYMPOSIUM
FRIDAY, NOVEMBER 11, 2005

USING MOLECULAR METHODS IN THE ANALYSIS OF SUBSURFACE MICROBIAL ECOLOGY AT HYDROCARBON IMPACTED SITES

In Honor of David C. White, Center for Biomarker Analysis, UTK/ORNL Distinguished Scientist, University of Tennessee, Knoxville, TN

Chairs: Kerry L. Sublette, University of Tulsa, Tulsa, OK

- **Assessment of In Situ Biodegradation Potential of MTBE Using 13C-Labeled MTBE and Bio-Sep ® Beads**
  Jennifer Busch-Harris, Kerry Sublette, Ken Roberts and Eleanor Jennings, University of Tulsa, Tulsa, OK; Aaron Peacock and D.C. White, University of Tennessee, Knoxville, TN; Greg Davis, Microbial Insights, Inc., Rockford, TN; William Holmes, University of Michigan, Ann Arbor, MI; Xiaomin Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL
  IPEC FUNDED PROJECT
- **Investigation of Microbial Consortia Stimulated by Denitrification-Based Bioremediation in a Gasoline-Contaminated Aquifer via DGGE, Real-Time PCR and Multi-Color Fluorescence*In Situ* Hybridization ("mFISH")**
  Eric Hince, Geovation Consultants, Inc., Florida, NY; Dora Ogles, Microbial Insights, Inc., Rockford, TN
- **Monitoring Subsurface Microbial Ecology in a Sulfate-Amended Gasoline-Contaminated Aquifer**
  Kerry Sublette, University of Tulsa, Tulsa, OK; Aaron Peacock and D.C. White, University of Tennessee, Knoxville, TN; Greg Davis and Dora Ogles, Microbial Insights, Inc., Rockford, TN; Dave Cook, GeoEngineers, Inc. Bellingham, WA; Ravi Kolhatkar, Atlantic Richfield (a BP affiliated company), Houston, TX; Xiaomin Yang, Atlantic Richfield (a BP affiliated company), Warrenville, IL; Dennis Beckmann, Atlantic Richfield (a BP affiliated company), Tulsa, OK
- In Search of the Truth? Genetic Potential (rDNA) Versus Expression (mRNA) for Understanding Microbial Responses
  Greg Davis and Dora Ogles, Microbial Insights, Inc., Rockford, TN; Aaron Peacock, University

of Tennessee, Knoxville, TN

- **Utility of Lipid Biomarkers in Support of Bioremediation Efforts at Army Sites**
  D. B. Ringelberg and C.M. Reynolds, U.S. Army ERDC-CRREL, Hanover, NH
- Molecular Genetic Detection & Enumeration of Aromatic Oxygenase Genes at Gasoline-Contaminated Sites
  Loring Nies, Cindy H. Hakatsu, Jennifer Nebe and Brett Sutton, Purdue University, West Lafayette, IN; Brett R Baldwin, University of Tennessee, Knoxville, TN
- **Development of a RTQ-PCR Protocol for Quantification of Anaerobic Benzene Degraders**
  Marcio LB da Silva and Pedro Alvarez, Rice University, Houston, TX

MEASURING BENEFITS FROM DOE'S OIL AND NATURAL GAS ENVIRONMENTAL RESEARCH ON FEDERAL LANDS

H. William Hochheiser
U.S. Department of Energy

David Alleman
National Technology Energy Laboratory/DOE

Jeffrey F. Eppink, Ramon Alvarado, and Michael Godec
Advanced Resources International, Inc.

Presented at the 12th Annual International Petroleum Environmental Conference
Houston, Texas, November 8, 2005

ABSTRACT

The benefits from the Department of Energy's (DOE's) Oil and Natural Gas Environmental Research Program were assessed using the recently-expanded Energy Policy and Conservation Act (EPCA) Inventory datasets and GIS model. In the EPCA Inventory, the analysis of constraints to oil and gas development centers on whether the lands are open or closed to leasing and the degree of constraint to development resulting from lease stipulations on open lands. The analysis focused on the Rocky Mountain region, where most lower-48 onshore Federal oil and gas resources are located. For the analysis, the EPCA model was supplemented to explicitly analyze the impact of resource depth on the ability to drill a well in a single season in areas with timing limitations. The expected results of DOE's research activities, which are associated with improvements in land use planning and science-based stipulations, were analyzed to determine how they might improve access to oil and gas resources as well as decrease annual costs and delays in drilling. The analyses show that the modest investment represented by the DOE Program can result in significant increases in access to Federal oil and gas resources.

PURPOSE AND BACKGROUND

Objectives of this Study

Many of the Oil and Natural Gas Environmental Program activities in the Department of Energy's Office of Fossil Energy (DOE/FE) are focused on Federal lands aim to find ways to streamline regulatory processes and to fund research providing alternative strategies to manage oil and gas development and minimize environmental impacts. To assist the Program in its R&D planning activities and to aid in program justification, the Energy Policy and Conservation Act (EPCA) Inventory data and model were used to provide an analysis of potential benefits from the DOE's Environmental Program, whose mission is to promote a reliable, affordable supply of oil and gas by supporting a cost effective, risk based environmental regulatory framework, providing cost effective compliance technologies, and improving environmental protection.

In the analysis, attempts were made to quantify the impact of current and planned R&D activities on:

- Access to Federal oil and gas resources by lessening restrictions on drilling operations on Federal leases;
- Costs that the industry must bear in order to comply with lease requirements for drilling operations associated with Federal lands; and
- Project delays associated with drilling operations conducted on Federal lands.

EPCA Inventory Background

Reauthorized in 2001 by Congress, the Energy Policy and Conservation Act (EPCA), among other things, mandates that an inventory of all oil and gas resources underlying onshore Federal lands be conducted to identify the "nature of their restrictions or impediments" to the development of those resources.

Federal oil and gas leases are governed by multiple statutory and regulatory requirements, which can have many purposes, ranging from the protection of environmental, social, historical, or cultural resources or values, to the payment of rents and royalties. These often take the form of stipulations, derived from land use planning documents or National Environmental Policy Act (NEPA) requirements, to the leasing of Federal minerals.

The EPCA Inventory provides estimates of undiscovered technically recoverable resources and proved reserves of oil and gas and the extent and nature of potential limitations to their development.

In the EPCA Inventory, the geographies of the stipulations from the Federal land management agencies, primarily the Bureau of Land Management (BLM) and the U.S. Forest Service (USFS), along with the oil and gas resources provided by the U.S. Geological Survey (USGS), and a land status layer, detailing Federal, state and private land ownership, are spatially intersected to present a snapshot detailing the oil and gas resources and the potential impediments to their development. The inventory is being conducted in phases: the EPCA Phase I Inventory was released in January 2003, and Phase II will be published in late 2005.

Between the Phase I and Phase II basins, the bulk of the oil and natural gas resources—approximately 21 billion barrels of oil and 182 trillion cubic feet (TCF) of natural gas—under Federal ownership in the onshore United States were considered in the EPCA Inventory. Within these basins, analysis of constraints to oil and gas development centers on two factors that affect access to oil and gas resources on Federal lands:

- Whether the lands are open or closed to leasing; and
- The degree of constraint to development resulting from lease stipulations on lands open to leasing.

U.S. Hydrocarbon Resource Basins Assessed to Date in the EPCA Inventory

The EPCA Inventory covers eleven basins across the U.S., including Alaska, which contain most of the onshore oil and natural gas under Federal ownership.

The EPCA Phase I Inventory was released in January 2003 and covers the following areas (shown in blue in Figure 1):

- Uinta-Piceance Basin (Colorado and Utah)
- Paradox-San Juan Basins (Colorado, New Mexico, and Utah)
- Montana Thrust Belt (Montana)
- Powder River Basin (Montana, Wyoming, South Dakota and Nebraska)
- Greater Green River Basin (Colorado, Utah, and Wyoming)

Phase II of the EPCA Inventory, which is cumulative, incorporates Phase I basins and also includes the following areas (shown in red in Figure 1):

- Northern Alaska (ANWR and NPRA)
- Wyoming Thrust Belt (Wyoming, Utah and Idaho)
- Denver Basin (Colorado, Wyoming, South Dakota and Nebraska)
- Florida Peninsula (Florida)
- Black Warrior Basin (Mississippi and Alabama)
- Appalachian Basin (New York, Pennsylvania, New Jersey, Ohio, West Virginia, Virginia, Maryland, Tennessee and Kentucky)

The EPCA model overlays all the stipulations at a given geographic point and computes the cumulative restriction. For example, big game winter range stipulations may be added to spring stipulations for sage grouse and the total number of month of drilling prohibition is displayed. Federal land and resources are then binned into nine

categories and include the complete range of access restrictions associated with oil and gas leasing. Table 1 shows the categorization hierarchy and a description of each category is listed below.

1. **No Leasing Statutory/Executive Order (NLS)** are areas that cannot be leased due to Congressional or Presidential action. Examples include national parks, national monuments, and wilderness areas.

2. **No Leasing Administrative (NLA)** are areas in which leasing does not occur based on discretionary decisions made by the Federal land management agency. NLA areas include endangered species habitat and historical sites.

3. **No Leasing Administrative, Pending Land Use Planning or NEPA Compliance (NLA/LUP)** are Federal administrative areas that have not yet undergone or are currently undergoing land use planning or NEPA analysis, and that are generally not available for leasing. In cases where there is no land use plan in effect, non-Federal mineral estate underlying Federal land is categorized as NLA/LUP in this analysis to reflect the fact that, as a practical matter, access to mineral estate can be allowed through the NEPA process.

4. **Leasing, No Surface Occupancy (NSO) (Net NSO for O&G Resources)** are areas that can be leased but where stipulations prohibit surface occupancy for natural gas and oil drilling activities. These stipulations protect identified resources such as special status plant species habitat. Access relative to NSO resources is incorporated by consideration of an extended drilling zone which accounts for the ability to drill directionally to reach a target. In this study, therefore, the NSO land categorization reflects areas covered by NSO stipulations; however to determine *access to oil and gas*, the NSO resource categorization incorporates access generally afforded by an EDZ and hence is "Net NSO" (NNSO). The access impact of NNSO resources is similar to that associated with NLA areas.

5. **Leasing, Cumulative Timing Limitations (TLs) of > 9 Months** are areas that can be leased, but stipulations limit the time of the year when oil and gas exploration and drilling can take place. Timing limitation stipulations prohibit surface use during specified time intervals to protect identified resources such as sage grouse habitat or elk calving areas.

6. **Leasing, Cumulative Timing Limitations (TLs) of > 6 to ≤ 9 Months**

7. **Leasing, Cumulative Timing Limitations (TLs) of > 3 to ≤ 6 Months**

8. **Leasing, Controlled Surface Use (CSU)** are areas where stipulations control the surface location of natural gas and oil exploration and development activities by excluding them from certain (typically small) portions of the lease. For example, a CSU stipulation could require an operator to develop a specialized mitigation plan based on the presence of moderate steep slopes within a lease area. This category also includes areas that have timing limitations with an impact of less than three months. These areas are minimal.

9. **Leasing, Standard Lease Terms (SLT)** comprise areas that can be leased and where no additional stipulations are added to the standard lease form. Standard lease terms, however, still dictate that the lessee must comply with a number of environmentally protective and other requirements.

The inventory also includes consideration of exceptions/waivers/modifications to stipulations granted after a review of on-the-ground conditions and the use of modern technologies such as directional drilling.

The DOE environmental R&D program conducts research to provide sound science for land management decision making and also develops tools to help streamline the planning, leasing, and permitting process on public lands. The EPCA Inventory model and datasets provide a useful tool to assess the benefits of DOE's Environmental Program relative to surface restrictions, or stipulations, on Federal lands. Where leasing can occur, specific stipulation parameters in the EPCA Inventory model that are available for adjustment, based on assumed outcomes of DOE R&D activities, are geography (e.g. the area of a big game stipulation), timing limitations (the time of the year activities are restricted due to a stipulation) and the percentage of the time where a waiver/modification/exception is made to a stipulation or an "exception factor." Between the two phases of the EPCA Inventory conducted to date, approximately 2,100 stipulations were analyzed.

QUANTIFYING THE BENEFITS OF CURRENT AND PLANNED R&D PROGRAM ACTIVITIES

Development of Program Cases

The benefits associated with Federal lands access issues were assessed using a probabilistic approach. An "expected value" was used to estimate the impact of program activities in terms of changes in resource access, costs of stipulation and condition of approval (COA) compliance for exploration and development wells, and project delays.

In carrying out this approach, three cases were defined at the outset:

- *Case 1:* A "without DOE R&D" or "industry only" case;
- *Case 2:* A "with DOE R&D Budgeted" case, which assumes a historic level of funding; and
- *Case 3:* A "with DOE R&D Planning" case, which assumed a higher level of funding.

Assessment of Federal Land Access Issues that Could Impact Oil and Gas Exploration and Production Activities

The issues that affect access to Federal oil and gas resources can be placed into several broad categories. A discrete number of Federal land access issues were identified that are the subject of DOE-funded research:

- Wildlife habitat impacts
- Surface impacts (water and soils)
- Cultural impacts
- Analytical tools/data base development
- Process streamlining
- Air impacts
- Aesthetic impacts

Two of the issues listed (air and aesthetic impacts) were determined not to be appropriate for modeling with EPCA Inventory data because they cannot be mapped as affecting discrete geographic areas and, in the case of air impacts, affect non-Federal lands as well. These issues were accounted for in other parts of the Environmental Program benefits categorization process. The balance of the Federal lands issues were used to develop metrics indicators for the assessment of benefits, as shown in Table 2.

Individual Oil and Natural Gas Environmental Program Project Managers and Principal Investigators were contacted to determine potential benefits associated with specific research projects. Table 3 shows how individual projects in DOE's Oil and Natural Gas Environmental Program relate to the Federal lands access issues evaluated. This portfolio of DOE's projects related to Federal lands access issues was reviewed to discern the outcomes that have occurred, or could occur as a result of project activities.

Principal investigators of individual projects in the Environmental Program were contacted to discuss the project, timing, objectives, results (to date or anticipated), and implementation in time and geography. For specific leasing stipulations, project leaders were generally asked to qualitatively assess impacts of the project as low, medium or high. Those with impacts were then correlated to stipulation geography, exception factors, and timing limitations based upon Advanced Resources' experience with the EPCA Inventory dataset.

Oil and Gas Resource Categorization

Oil and gas resources were analyzed based on the most recent USGS assessment units or plays. The resource types analyzed were undiscovered, technically recoverable resources. Proved reserves were not analyzed as they are already in production and would not be affected by DOE program activities focused on Federal land access issues. The resource category called reserves growth, or the anticipated growth in proved reserves likely to result from delineation drilling and the application of new technologies, would only apply to costs and delay impacts. Further, the Energy Information

Administration (EIA) is currently assessing reserves growth, for EPCA Inventory Phase I and II basins; such data have not been considered in the inventory to date.

Determining the Appropriate Geography of Research Benefits

Since the great majority of oil and gas resources on on-shore Federal land in the lower-48 are located in the Rocky Mountain region, and most DOE Federal land research is conducted in this region, this analysis was applied to the following Rocky Mountain basins:

- Paradox-San Juan Basin
- Uinta-Piceance Basin
- Greater Green River Basin
- Powder River Basin
- Wyoming Thrust Belt
- Denver Basin
- Big Horn Basin
- Wind River Basin

For all basins except the Big Horn and Wind River basins, plays were modeled directly using EPCA Inventory data. The Big Horn and Wind River, because they are not in the EPCA Inventory datasets, were assessed based on analogy with assessed plays. The Big Horn was compared to the Powder River, and the Wind River was compared with the Greater Green River Basin.

Examination of the above basins captures potential impacts on the majority of undiscovered Federal oil and gas resources in the lower-48 states (estimated to be in excess of 85 percent).

Incorporation of Drilling Depth Considerations Relative to Access

In a significant advancement in the EPCA Inventory methodology, DOE incorporated limitations due to drilling depth in this analysis to capture the effect of the leasing stipulations on the drilling season, and identify areas where the oil and gas resources may be too deep to drill within a single drilling season.

For this task, deep-horizon maps, stratigraphic charts, and cross-sections were obtained for each basin. The relevant maps were digitized, and edged-matched to develop a composite Rocky Mountain-wide depiction of the Lower Cretaceous (Dakota Formation or equivalent, which are the most regionally available mapped strata). The appropriate structural depths for the average play objectives were delineated relative to the Lower Cretaceous based on cross-sections. The product of this exercise was an average structural objective depth criteria for each play in each study area.

With industry input (three operators and two drilling contractors), basin-specific drilling time curves were developed. Based upon discussions with industry, Advanced

Resources integrated the curves to produce a drilling depth vs. time correlation for Rocky Mountain basins (Figure 2).

Subsequently, based upon the Lower Cretaceous structure maps, a digital elevation model was used to determine a composite drill depth map to the Lower Cretaceous (Figure 3). Based on the Lower Cretaceous, the average drilling times required for each play were assessed. It should be noted that some plays (especially coalbed methane) have lesser drilling times; deeper strata can have significantly longer drilling times. Drilling time was determined for each play independently.

Costs and Delays Associated with Federal Lands Access

Costs associated with access to oil and gas resources from Federal lands were estimated based upon data from the National Petroleum Council's (NPC) 2003 natural gas study, *Balancing Natural Gas Policy: Fueling the Demands of a Growing Economy* supplemented by Advanced Resources' data and experience.

In the analysis, NPC costs for wildlife surveys, cultural surveys, etc., were weighted relative to EPCA Inventory access categories to determine per well costs and delays associated with exploration and development on Federal lands. Costs were configured based on the NPC data by:

Increasing well cost according to the number of months of seasonal restrictions

- Deriving percent of wells by cost category (exploratory and development wells) and months of seasonal restrictions; and
- Deriving percent of wells by cost category and processing delay.

The data were then integrated and average figures were computed according to EPCA Inventory criteria to derive:

- Weighted average of the added well cost; and
- Weighted average of the delay in months to drill a well

For resource objectives that may be too deep to be reached in one drilling season, an additional $95,000 for added mobilization/demobilization activities were allocated. Further, 12 months of delay were added. Cost information for the Wyoming Thrust Belt and Denver Basin were not available from the NPC, but were estimated by analogy. Summary costs and delay, by basin, are shown in Table 4.

Development of Alternative Scenarios and Possible "Outcomes"

Program outcomes focus on the geographic, temporal and surface attributes of lease stipulations (e.g., timing and geography of big game winter range) that impact Federal lands access and subsequent incremental resources, costs, and project delay. Within the EPCA Inventory model, there are three major aspects of resource access decision-making processes that could be influenced by the results of the DOE program activities:

- Changes to leasing stipulations themselves
- Recategorization of resources due to planning improvements (EPCA NLA/LUP resources)
- Recategorization of resources due to process streamlining (e.g., quicker lease and APD processing)

With regard to changes to leasing stipulations, in turn, there are three adjustments that could be made in the EPCA Inventory model, specifically changes to: (1) areas of specific stipulations, (2) exception factors for stipulations, and (3) timing limitations for stipulations. Use of such adjustments is consistent with BLM's current program for adaptive management.

As a result of the assessment of DOE's portfolio of projects (from Table 3), appropriate changes in geography, exception factors, and delays for various stipulations were determined. Table 5 presents the composite outcomes determined for analysis in the EPCA Inventory model based on individual DOE projects. In compiling the chart, a relatively conservative approach was undertaken, especially when extrapolating project benefits to the entire Rocky Mountain region. Consequently, outcome estimates are relatively conservative.

Next, changes were made to the EPCA Inventory datasets and model, where there are over 1,300 stipulations, with accompanying GIS, in the EPCA Inventory Phase I and II datasets for the Rocky Mountains. To implement the changes according to the criteria above, the area of the stipulations locally or Rocky Mountain-wide, and/or the exception factors or timing limitations, were adjusted.

To change the area of a stipulation that is affected by research results, as it is impossible to determine what areas would actually be reduced by the DOE R&D projects, it was decided to randomly remove areas from the stipulation based on the percentage determined by the DOE project portfolio and shown in Table 5. To do this, the GIS was overlain with a 400 meter grid and randomly selected grid cells were deleted from the stipulation (Figure 4). By this process, the areas of stipulations were changed using a randomized GIS process to reduce footprint based on the percentage reduction in each stipulation. Note that, typically, the geographic extent of stipulations were changed. If , in addition, it was determined that individual R&D projects affected stipulation exception factors or timing limitations, these were also changed. (These last two elements do not exist for all stipulations).

Scenario Development

To estimate program benefits, three scenarios were defined:

- **Baseline Scenario**. This scenario is based on the EPCA Inventory conducted to date, i.e., the regulatory environment relative to oil and gas resources represented in EPCA Inventory Phases I and II for Rocky Mountain basins. The EPCA Inventory datasets and models were run, by play, to provide this assessment. In addition, the portion of the resources by basin that cannot be effectively drilled in a single season was modeled as a function of land access categorization. This activity comprised modeling

the EPCA Inventory land access categorization against play-specific drilling time maps to determine resources that are timing-limited due to drilling concerns (as opposed to regulation-limited).

- **Scenario 1**. This scenario includes the Baseline, plus impacts due to DOE activities applied to local BLM field offices. The assumption here is that the impacts of the project would be rapidly disseminated throughout similar stipulations in a field office. For example, sage grouse habitat may be defined more rigorously resulting in reduced area for stipulations in the BLM Buffalo Field Office.
- **Scenario 2**. This scenario includes Scenario 1, plus impacts from general application of DOE-funded research results to all Rocky Mountain basins where such stipulations occur. (Examples: Big game winter range timing limitations are reduced, land use plan revisions accelerated, etc. in all Rocky Mountain basins where they occur.) Scenario 2 also makes allowance for future, as yet unspecified, research activities that DOE may undertake.

Broader impacts from DOE activities, i.e., accelerating land use planning and streamlining of the regulatory process via improved information flow, etc., were also modeled. For the EPCA NLA/LUP category, resources were distributed to lower EPCA category levels at a constant rate of 15 percent. For streamlining projects with broad impacts, that do not operate on specific stipulations (e.g., a project for web-hosting of lease stipulations), benefits were captured by broadly adjusting resources among EPCA Inventory categories. To capture the process streamlining, recategorization of resources subsequently was made at a constant rate across leasable EPCA Inventory categories based on a fixed percentage (15 percent). Both recategorizations consider relevant projects in aggregate to represent the cumulative impacts of DOE activities.

Program Expected Value Determination

Assessment of the benefits associated with DOE's Environmental Program efforts with regard to Federal lands access issues used a probabilistic approach, where an "expected value" provides an estimate of the impact of the program in terms of changes to resource access, costs of exploration and development, and project delay.

As indicated previously, three cases were developed:

- Case 1: "Without DOE R&D" or "Industry only" case
- Case 2: "With DOE R&D Budgeted"
- Case 3: "With DOE R&D Planning"

Table 6 presents the program expected value determination probabilities and timing matrix. The cases are assumed to be independent. The differences between the first and second DOE cases are directly attributable to DOE activities performed at a level consistent with historic program budgets; the differences between the second and third DOE cases reflect the implementation of potential activities above and beyond the base program at a higher budget level. Timing of implementation reflects immediate implementation in the DOE cases, with a 4 year lag for region-wide application, and a time lag of five years for case 1, to account for the ability of industry to accomplish similar objectives over time without DOE assistance.

The EPCA Inventory model was run to provide estimates of changes to the amount of oil and gas resources in each EPCA access category as a result of program activities. Impacts in terms of costs and delays were then estimated.

Data Structure

DOE uses EIA's National Energy Modeling System (NEMS) to estimate benefits for all of its Fossil Energy programs. Use of NEMS required a simplification of the EPCA Inventory results. Specifically, the data structure for the categorization of benefits in NEMS required that the EPCA access categories be collapsed into three: inaccessible (no leasing), accessible with restrictions, and standard lease terms. Table 7 shows how the EPCA access categories were mapped into each of the three NEMS categories.

Table 8 presents the data structure for this analysis. The data were reported for each USGS play by case (i.e., "Without DOE R&D", etc.), with associated resources, costs, and delays.

Incorporation into NEMS

As a final step, the impacted resources, incremental costs, and anticipated delays were incorporated into the existing structure of NEMS to appropriately represent these impacts within the NEMS analytical process. Only one NEMS region, the Rocky Mountain region, was affected, with separate representations for the conventional oil and gas, coalbed methane, tight gas, and gas shales resource categories in this region. These changes were incorporated into the representation of the entire Oil and Gas Environmental Program (including areas of the program beyond those just associated with issues on Federal lands). The Oil and Gas R&D Program was then run in NEMS with and without the Federal lands R&D component to determine the impact of the R&D.

Aggregated Results

Aggregated results are as shown in Table 9. Assuming a DOE Program costs of $5 million/year (Case 2) and $10 million/year (Case 3), this works out to a modest R&D investment of roughly $0.045 to $0.050, per incremental MCF-equivalent made accessible as a result of DOE Program activities, respectively, assuming development over 25 years and an irreducible gas saturation of 30 percent.

The implications of the analysis were used to set up a second analysis which is addressed in the companion paper for this conference: *Quantifying Lease Stipulation Impacts on Federal Oil and natural Gas Resource Accessibility.*

References

National Petroleum Council, 2003, *Balancing Natural Gas Policy–Fueling the Demands of a Growing Economy*. See http://www.npc.org/

U.S. Departments of the Interior, Agriculture, and Energy, January 2003, *Scientific Inventory of Onshore Federal Lands' Oil and Gas Resources and Reserves and the Nature of Restrictions or Impediments to their Development.*

Table 1. EPCA Inventory Categorization Hierarchy

Level	Access Category	Comments
1	No Leasing (Statutory/Executive Order), (NLS)	Status set by Law or Executive Order; drilling prohibited
2	No Leasing (Administrative), general category (NLA)	Status set by Federal surface management agency; drilling prohibited
3	No Leasing (Administrative), Pending Land Use Planning or NEPA Compliance (NLA/LUP)	Status set by Federal surface management agency; drilling prohibited pending planning
4	Leasing, No Surface Occupancy (NSO) (Net NSO for O&G Resources)	Not accessible for drilling except for resources within an extended drilling zone
5	Leasing, Cumulative Timing Limitations (TLs) on Drilling >9 Months	Categorized by the cumulative effect of seasonal leasing stipulations during which drilling is prohibited, generally for protection of wildlife
6	Leasing, Cumulative Timing Limitations (TLs) on Drilling >6 - ≤9 Months	
7	Leasing, Cumulative Timing Limitations (TLs) on Drilling >3 - ≤6 Months	
8	Leasing, Controlled Surface Use (CSU)	Drilling permitted, specialized mitigation plan required for CSU this categorization includes Cumulative Timing Limitations (TLs) on Drilling ≤3 Months, which are minimal.
9	Leasing, Standard Lease Terms (SLTs)	Drilling permitted, mitigation plan required

Table 2. Federal Lands Access Issues Relative to DOE Environmental Program Projects

Federal Lands Access Issue	EPCA Modeling Parameter
Wildlife Habitat Impacts	**Apply to stipulations**
Surface Impacts (Water and Soils)	**Apply to stipulations**
Cultural Impacts	**Recategorize leasable resources**
Analytical Tools/Data Base Development	**Apply to NLA/LUP resources**
Process Streamlining	**Recategorize leasable resources**
Air Impact	**Non EPCA**
Aesthetic	**Non EPCA**

NLA/LUP = No leasing administrative pending land use planning
Identification and Characterization of Program Activities Focused on Federal Lands Access Issues

Table 3. Relation between Federal Land Access Issues and EPCA Modeling

Issue	NPC NG study--1999	Upland Erosion--Largo Canyon	Wildlife Habitat Assessment	Comprehensive COAs	CBM Impact on WLH in PRB	GIS Database--WY	Plover Study--WY, MT	Visual Impacts--O&G Develp.	LUP--Web-based System	Soil Recov.-Geoph. Explor.	Road Drainage--Erosive Soils	1:24,000 scale--Soil Surveys	NEPA ToolKit	Habt. Loss and Fragmentation	Lesser Prairie Chicken Habitat	Dry Creek Basin--Envn. Enhan.	Annotated Biblio.--Lower 48	NPC NG Study--2003	Best Management Practices	N. Slope Sci. Infrastr.	Low Impact NG & Oil	IOGCC access to O&G data	RMEC Survey	Sage Grouse--WY, MT	EPCA Inventory	Argonne NL--RMPs	Permit Primer	GWPC--Web-based Stipulations	NM/WY Cult. Res. Modeling
Wildlife Habitat Impacts			X				X							X	X	X			X		X			X					
Surface Impacts (Water and Soils)		X						X		X	X	X				X					X								
Cultural Impacts																X													X
Analytical Tools/Data Base Development					X				X					X		X		X		X		X	X		X		X		
Process Streamlining	X			X	X	X			X				X				X					X			X	X	X	X	

Table 4. Incremental Costs Associated with EPCA Categorization by Basin

Exploration (costs)	Exploration well, costs/well ($)										Inputs
EPCA Category	1, 2 & 4	5	3,5	6	6	7	7	8	8	9	
USGS Province	NLA, NLS, NSO net	TLS>9--DD_TL	NLA/LUP, TLS>9	TLS 6-9--DD_TL	TLS 6-9	TLS 3-6--DD_TL	TLS 3-6	TLS <3--DD_TL, CSU, SLT	TLS <3, CSU	SLT	Non Federal
(20) Uinta-Piceance	$ -	$ 230,735	$ 135,735	$ 238,937	$ 143,937	$ 260,548	$ 165,548	$ 236,524	$ 141,524	$ 46,703	$ -
(22) Paradox-San Juan	$ -	$ 168,050	$ 73,050	$ 125,630	$ 30,630	$ 169,421	$ 74,421	$ 158,766	$ 63,766	$ 21,043	$ -
(33) Powder River	$ -	$ 198,854	$ 103,854	$ 196,468	$ 101,468	$ 210,473	$ 115,473	$ 203,035	$ 108,035	$ 35,652	$ -
(34) Big Horn	$ -	$ 218,545	$ 123,545	$ 220,142	$ 125,142	$ 231,543	$ 136,543	$ 221,892	$ 126,892	$ 41,874	$ -
(35) Wind River	$ -	$ 277,619	$ 182,619	$ 291,163	$ 196,163	$ 294,753	$ 199,753	$ 278,462	$ 183,462	$ 60,542	$ -
(36) Wyoming Thrust Belt	$ -	$ 300,311	$ 205,311	$ 319,686	$ 224,686	$ 323,822	$ 228,822	$ 301,079	$ 206,079	$ 68,006	$ -
(37) Greater Green River	$ -	$ 330,130	$ 235,130	$ 354,292	$ 259,292	$ 350,939	$ 255,939	$ 328,746	$ 233,746	$ 77,136	$ -
(39) Denver Basin	$ -	$ 225,109	$ 130,109	$ 228,033	$ 133,033	$ 238,566	$ 143,566	$ 228,178	$ 133,178	$ 43,949	$ -

Development (costs)	Development well, costs/well ($)										
EPCA Category	1, 2 & 4	5	3,5	6	6	7	7	8	8	9	
USGS Province	NLA, NLS, NSO net	TLS>9--DD_TL	NLA/LUP, TLS>9	TLS 6-9--DD_TL	TLS 6-9	TLS 3-6--DD_TL	TLS 3-6	TLS <3--DD_TL, CSU, SLT	TLS <3, CSU	SLT	Non Federal
(20) Uinta-Piceance	$ -	$ 205,443	$ 110,443	$ 196,952	$ 101,952	$ 211,493	$ 116,493	$ 192,417	$ 97,417	$ 32,147	$ -
(22) Paradox-San Juan	$ -	$ 155,415	$ 60,415	$ 124,730	$ 29,730	$ 151,304	$ 56,304	$ 149,229	$ 54,229	$ 17,896	$ -
(33) Powder River	$ -	$ 155,636	$ 60,636	$ 149,173	$ 54,173	$ 160,529	$ 65,529	$ 152,228	$ 57,228	$ 18,885	$ -
(34) Big Horn	$ -	$ 161,114	$ 66,114	$ 156,877	$ 61,877	$ 164,912	$ 69,912	$ 155,997	$ 60,997	$ 20,129	$ -
(35) Wind River	$ -	$ 177,546	$ 82,546	$ 179,990	$ 84,990	$ 178,060	$ 83,060	$ 167,304	$ 72,304	$ 23,860	$ -
(36) Wyoming Thrust Belt	$ -	$ 196,140	$ 101,140	$ 199,460	$ 104,460	$ 196,271	$ 101,271	$ 181,874	$ 86,874	$ 28,668	$ -
(37) Greater Green River	$ -	$ 192,153	$ 97,153	$ 200,534	$ 105,534	$ 189,748	$ 94,748	$ 177,355	$ 82,355	$ 27,177	$ -
(39) Denver Basin	$ -	$ 162,940	$ 67,940	$ 159,445	$ 64,445	$ 166,373	$ 71,373	$ 157,254	$ 62,254	$ 20,544	$ -

Exploration (delay)	Exploration well, delay (months)										
EPCA Category	1, 2 & 4	5	3,5	6	6	7	7	8	8	9	
USGS Province	NLA, NLS, NSO net	TLS>9--DD_TL	NLA/LUP, TLS>9	TLS 6-9--DD_TL	TLS 6-9	TLS 3-6--DD_TL	TLS 3-6	TLS <3--DD_TL, CSU, SLT	TLS <3, CSU	SLT	Non Federal
(20) Uinta-Piceance	No Access	23	11	23	11	23	11	23	11	4	-
(22) Paradox-San Juan	No Access	20	8	20	8	20	8	20	8	3	-
(33) Powder River	No Access	20	8	20	8	20	8	20	8	3	-
(34) Big Horn	No Access	21	9	21	9	21	9	21	9	3	-
(35) Wind River	No Access	23	11	23	11	23	11	23	11	4	-
(36) Wyoming Thrust Belt	No Access	25	13	25	13	25	13	25	13	4	-
(37) Greater Green River	No Access	26	14	26	14	26	14	26	14	4	-
(39) Denver Basin	No Access	21	9	21	9	21	9	21	9	3	-

Development (delay)	Development well, delay (months)										
EPCA Category	1, 2 & 4	5	3,5	6	6	7	7	8	8	9	
USGS Province	NLA, NLS, NSO net	TLS>9--DD_TL	NLA/LUP, TLS>9	TLS 6-9--DD_TL	TLS 6-9	TLS 3-6--DD_TL	TLS 3-6	TLS <3--DD_TL, CSU, SLT	TLS <3, CSU	SLT	Non Federal
(20) Uinta-Piceance	No Access	21	9	21	9	21	9	21	9	3	-
(22) Paradox-San Juan	No Access	19	7	19	7	19	7	19	7	2	-
(33) Powder River	No Access	25	13	25	13	25	13	25	13	4	-
(34) Big Horn	No Access	26	14	26	14	26	14	26	14	5	-
(35) Wind River	No Access	30	18	30	18	30	18	30	18	6	-
(36) Wyoming Thrust Belt	No Access	29	17	29	17	29	17	29	17	6	-
(37) Greater Green River	No Access	32	20	32	20	32	20	32	20	7	-
(39) Denver Basin	No Access	27	15	27	15	27	15	27	15	5	-

Table 5. Changes to EPCA Datasets as a Function of DOE's Environmental Program Project Portfolio

Stipulated Environmental Resource	Impacts on Habitats or Mapped Areas			Exception Factor Changes		Timing Limitation Changes
	Local BLM Office Jurisdiction of Project	Rocky Mountain-wide				
Big Game	**-5%**	**-5%**	and	**5%**		
Eagle roosting	**-10%**	**-10%**	and	**10%**		
Ferruginous hawk	**-5%**	**-5%**	and	**5%**	or	**2 wks**
Historic trails, Native American Sites	**-15%**	**-15%**				
Lesser Prairie Chicken	**-10%**	**-10%**				
Plover	**-15%**	**-15%**				
Sage Grouse (4 projects)	**-10%**	**-10%**	and	**5%**	or	**2 wks**
Soils (5 projects)	**-5%**	**-10%**				
Soils, seismic (1 project)	**-15%**	**-10%**				
White tailed prairie dog	**-5%**	**-5%**	and	**5%**	or	**2 wks**

Table 6. Program Expected Value Probabilities and Timing Matrix

Federal Lands Access						
	Case 1 "Without DOE R&D" Case		Case 2 "With DOE R&D Budgeted" Case		Case 3 "DOE R&D Planning" Case	
SCENARIOS	Prob.	Timing	Prob.	Timing	Prob.	Timing
Baseline Scenario. Regulatory environment relative to O&G resources represented in EPCA Inventory Phases I & II for Rocky Mountain basins, adjusted for deep drilling.	70%	2006	30%	2006	20%	2006
Scenario 1. Baseline Scenario, plus impacts due to DOE activities applied locally. Example: Sage grouse habitat defined more rigorously resulting in reduced area for stipulations.	25%	2013	50%	2008	45%	2008
Scenario 2. Scenario 1, plus impacts from general application of DOE-funded research results to all Rocky Mountain basins, where applicable. Examples: Big game winter range timing limitations reduced, land use plan revisions accelerated, etc.	5%	2015	20%	2010	35%	2010

Table 7. Metrics Categorization Relative to the EPCA Inventory

Metrics Categorization		EPCA Equivalence
A.	Inaccessible	No access by Federal statute or directive (EPCA categories 1, 2, & 3) or unreachable NSO areas (category 4)
B.	Accessible with Restrictions	Leasable with restrictions (EPCA categories 5-8)
C.	Accessible under Standard Lease Terms	Leasable with standard lease terms (EPCA category 9)
D.	Non Federal	Non Federal

Table 8. Data Structure for Oil and Gas Resources, Cost and Delay Reporting

		By Play				
		Oil and Gas Resources by Case	Estimated Incremental Cost		Estimated Incremental Delay	
			Expl.	Devel.	Expl.	Devel.
Metrics Categorization		MMbbl or TCF	($/well)	($/well)	Mo.	Mo.
A.	Inaccessible					
B.	Accessible with Restrictions					
C.	Accessible under Standard Lease Terms					
D.	Non Federal					

Table 9. Analytical Results in Sum

Changes relative to Case 1			
Case 2	Gas	1,621	Bcf
Case 3	Gas	2,797	Bcf
Case 2	Oil	53	MMBbl
Case 3	Oil	92	MMBbl

Figure 1. U.S. Hydrocarbon Resource Basins Assessed to Date in the EPCA Inventory

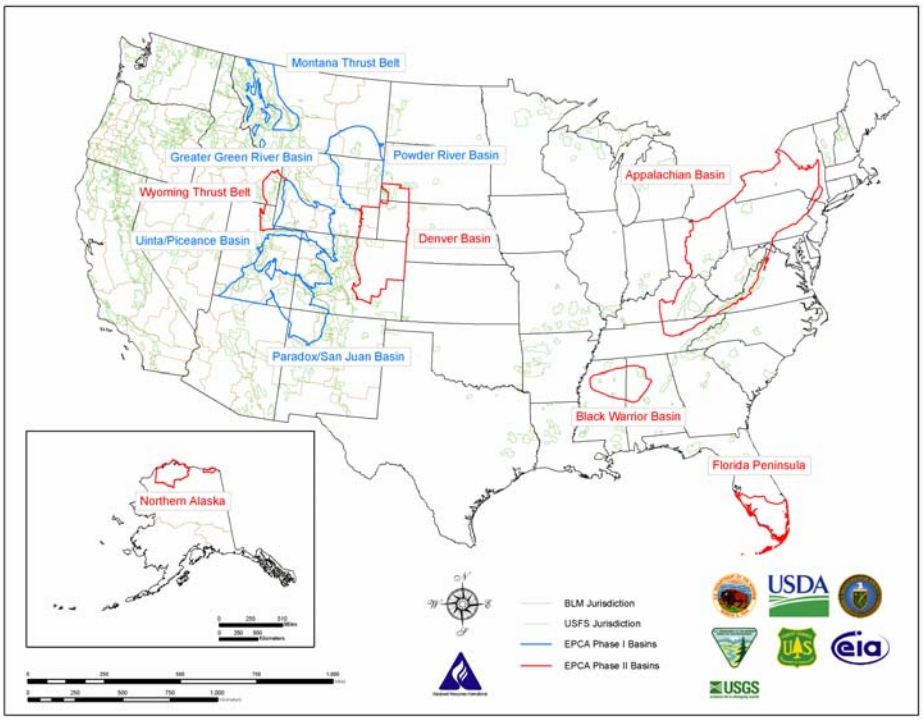


Figure 2. Drilling Depth vs. Time Correlation—Rocky Mountain Basins

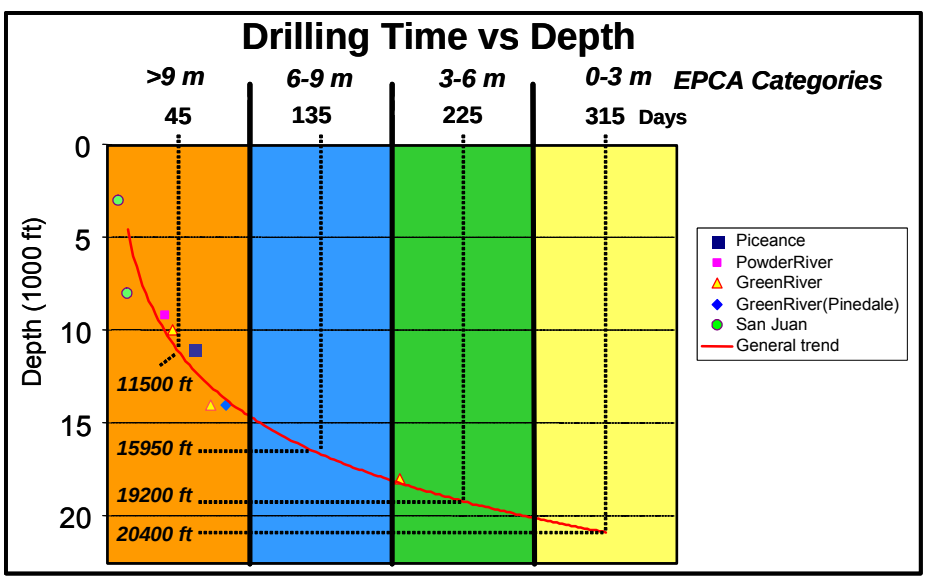


Figure 3. Drill Depth Map Illustrating Time to Drill "Representative" Wells in the Basins Analyzed

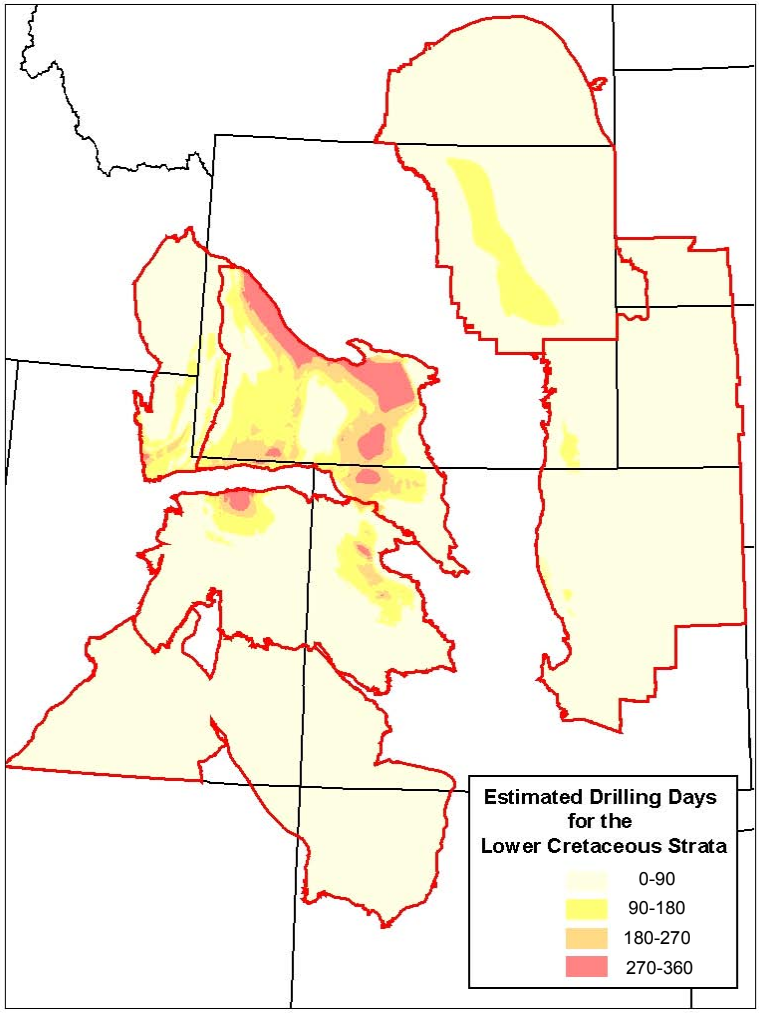
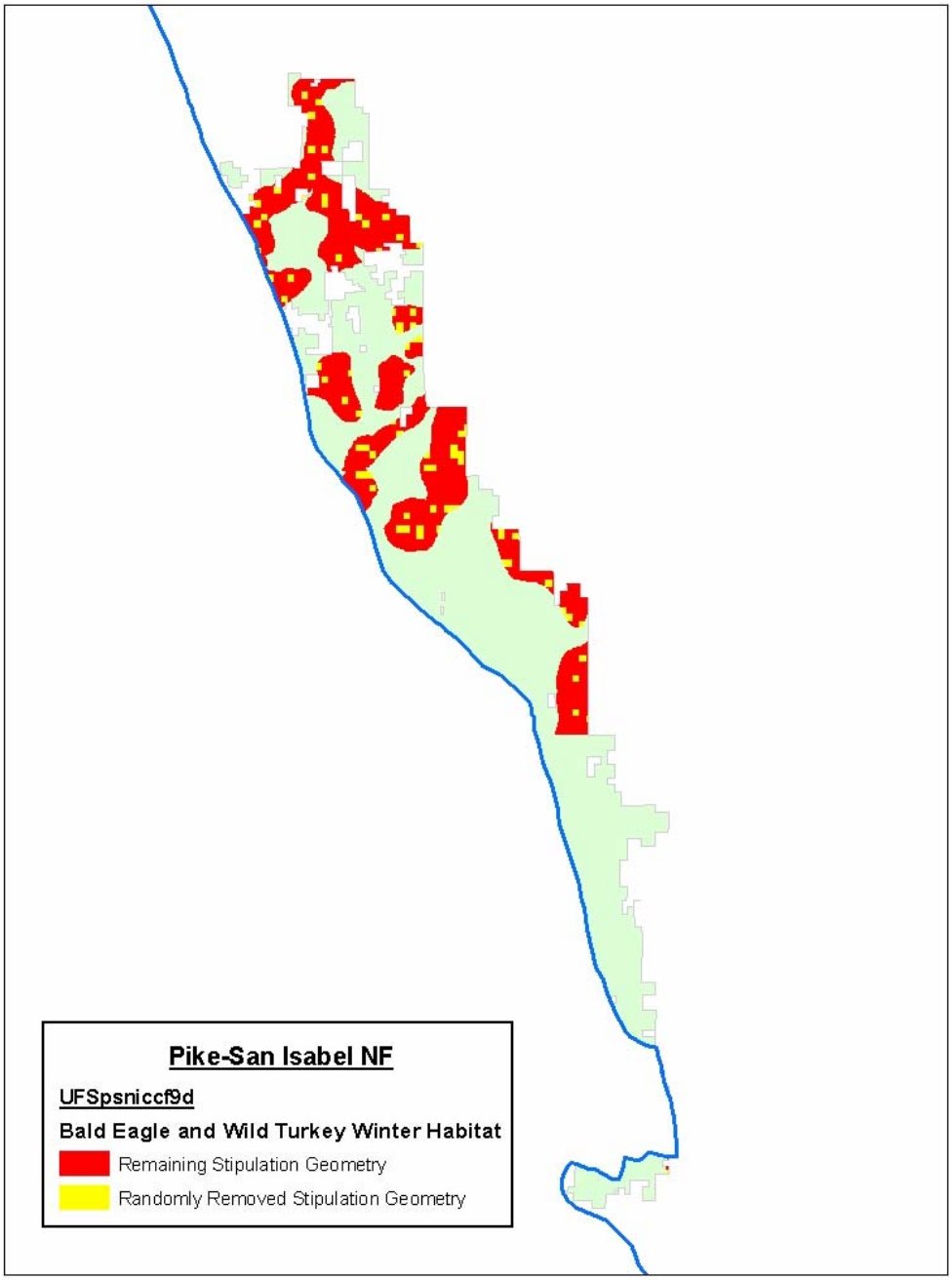
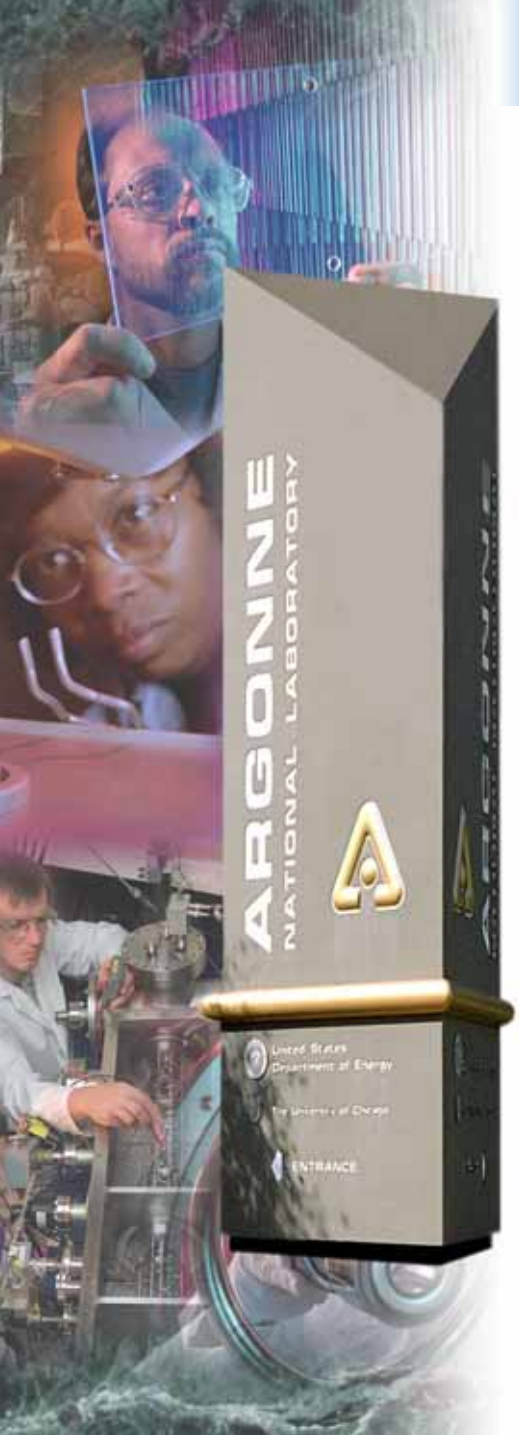


Figure 4. Example of a Randomized GIS Layer to Represent the Impact of DOE R&D Activities to Modify Stipulation Conditions





ARGONNE NATIONAL LABORATORY

Do Offshore Oil and Gas Platform Discharges Affect the Gulf of Mexico Hypoxic Zone?

John A. Veil

Argonne National Laboratory

Washington, DC

Presented at the 12th International Petroleum Environmental Conference

Houston, TX

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  - Kent Satterlee, Shell

Topics for Discussion

- What is produced water?
- What is oxygen demand and the hypoxic zone?
- Why was produced water sampled?
- How was the sampling program designed and implemented?
- What were the results?
- How do platform discharges compare to other nutrient input sources?

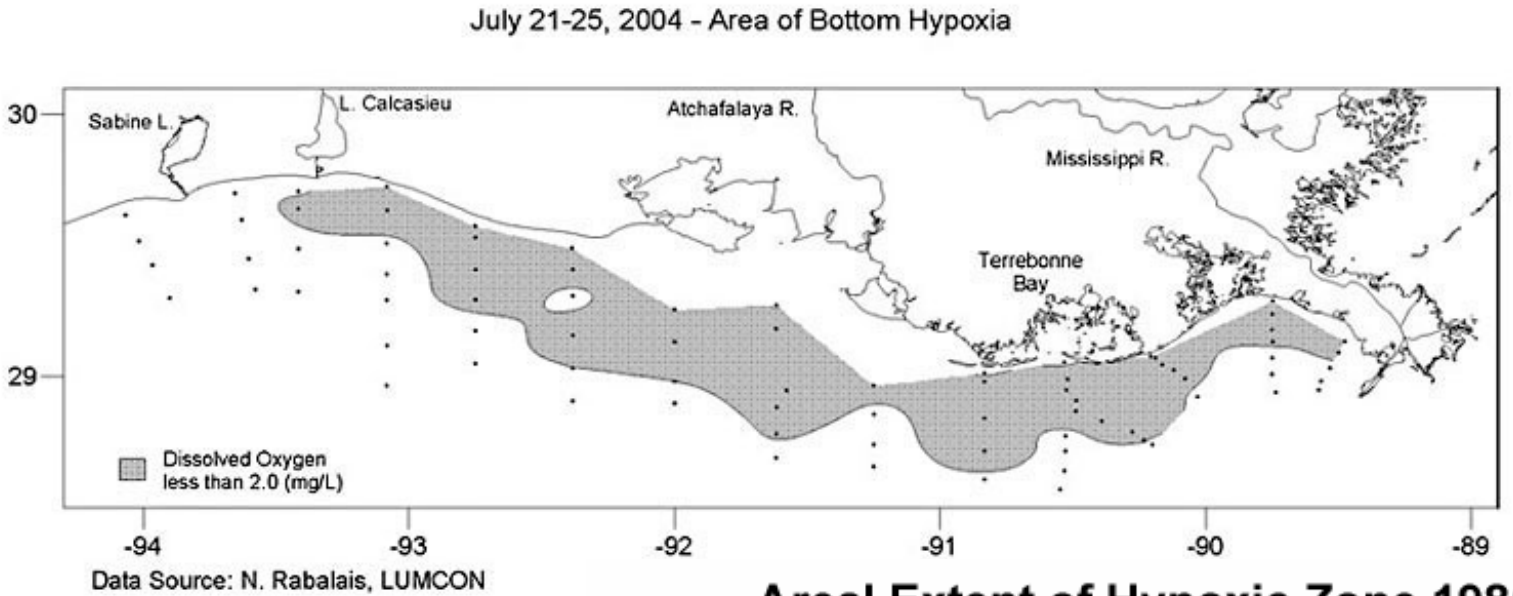
What is Produced Water?

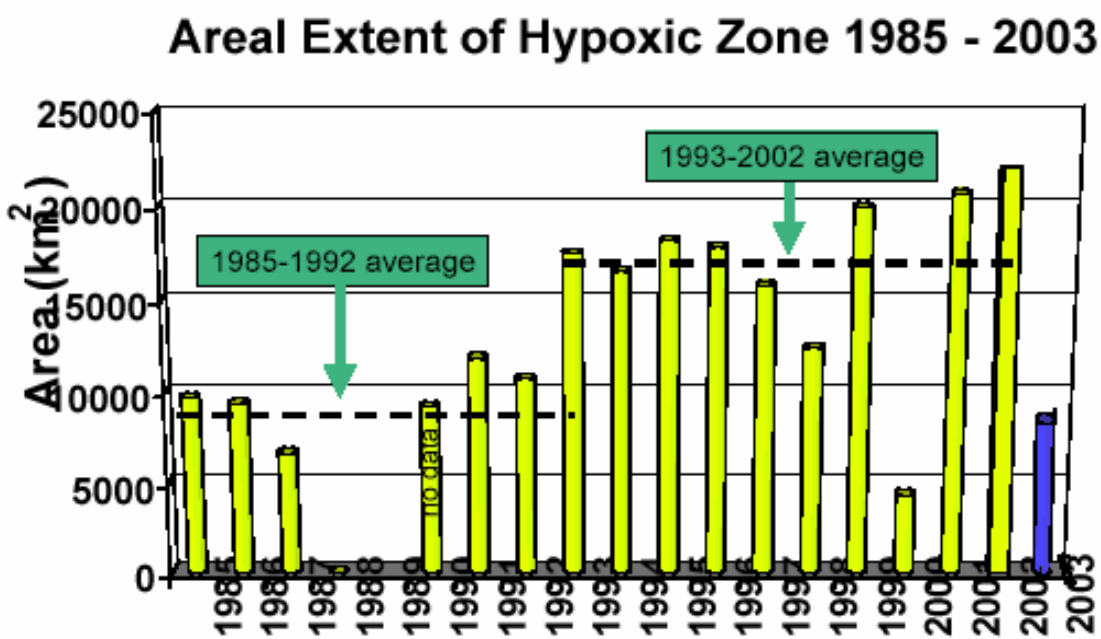
- Water that comes to the surface with oil and gas
- Contains many chemical constituents
  - Salt content (salinity, total dissolved solids [TDS], electrical conductivity)
  - Oil and grease
    - *Composite of many hydrocarbons and other organic materials*
  - Toxicity from various natural inorganic and organic compounds or chemical additives
  - NORM
  - Some oxygen demanding materials

What Is Oxygen Demand?

- The amount of oxygen that is consumed through microbial biodegradation of materials in a water sample
  - Typically measured as biochemical oxygen demand (BOD_5)
  - Can be caused by many chemical constituents
    - *Carbon*
    - *Nitrogen*
    - *Phosphorus*
- High oxygen demand can deplete oxygen in surface or bottom waters
  - Creates an unhealthy environment for marine life

How Does This Affect Offshore Oil and Gas?

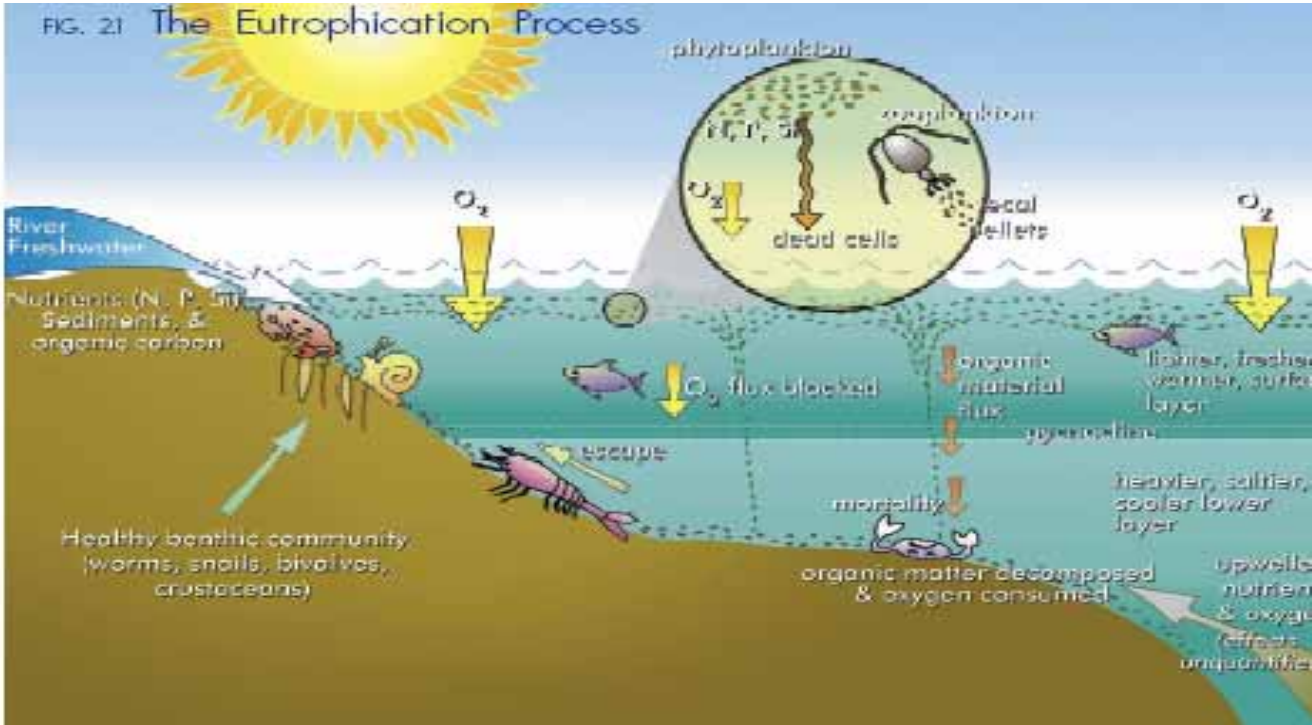




- Each year, a large hypoxic zone forms in the near-shore Gulf of Mexico
- Size of zone appears to be increasing

How Is the Hypoxic Zone Formed?

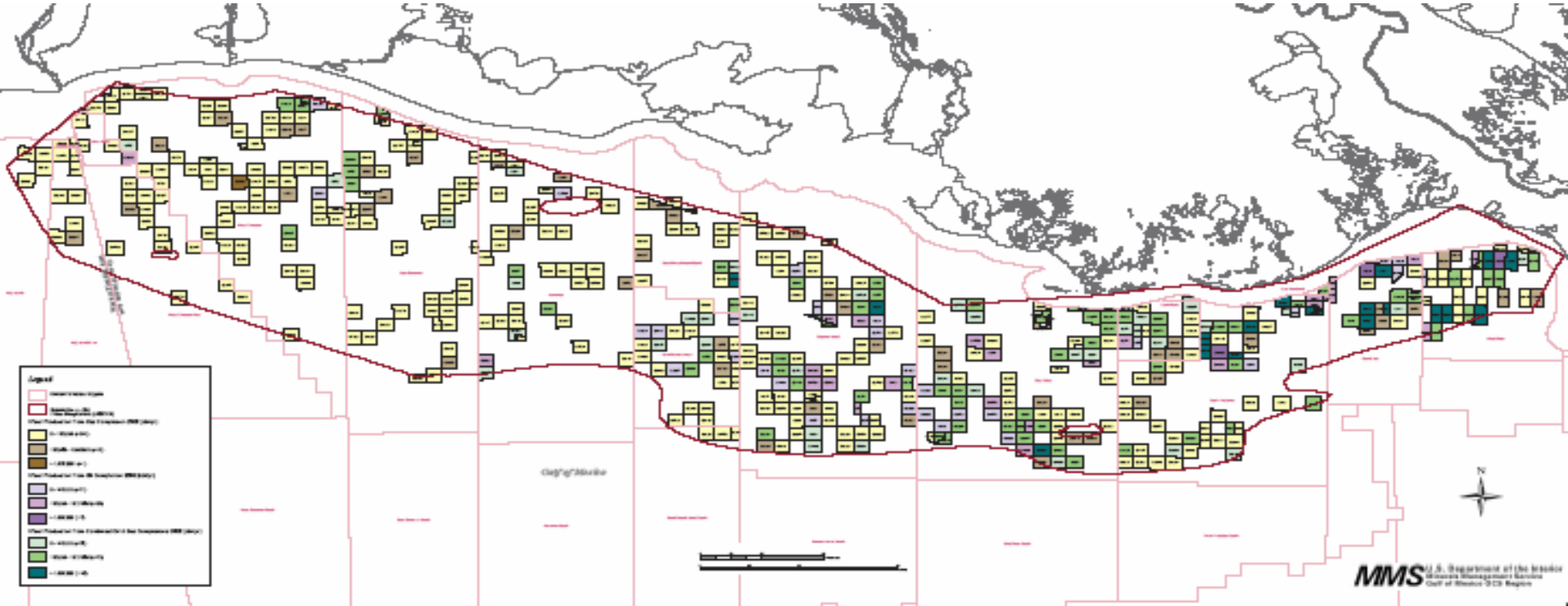
- Primary contribution to hypoxic zone is nutrient inputs from Mississippi River and Atchafalaya River
  - Other sources may be important too
- Nutrients cause rapid growth of phytoplankton
- Later these die off and sink to the bottom where they are decomposed by microorganisms
  - This depletes the available oxygen



Source: NOAA

Why Is Produced Water Being Sampled?

- Numerous offshore produced water discharges enter the hypoxic zone
  - The red line outlines the zone that experiences <2 mg/l oxygen more than 25% of the time – our study area
- EPA is concerned that offshore discharges make a significant contribution to oxygen demand
  - The offshore contribution had not previously been quantified



Project Goal

- Provide information on the concentration of nutrient and oxygen demanding chemicals present in Gulf of Mexico produced water discharges
- Estimate loadings of those parameters from all platforms in the hypoxic zone
- Compare loadings to other sources of pollutants that contribute to hypoxic zone

U.S. Regulatory Requirements for Discharging

Laws

- *Clean Water Act*

Discharge Regulations

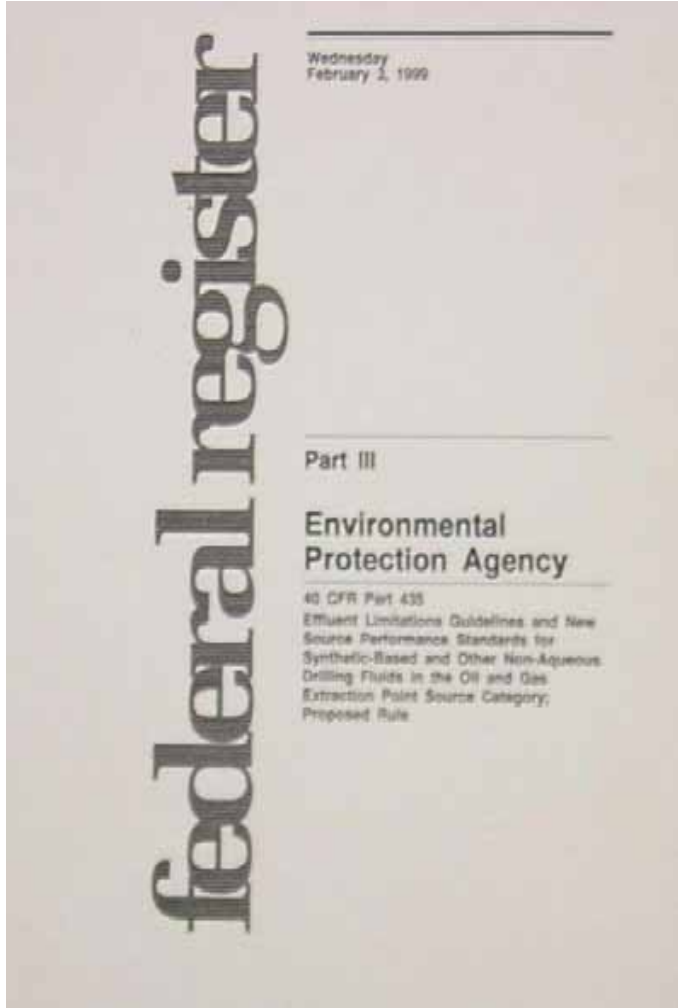
- *National Pollutant Discharge Elimination System (NPDES) program*
- *Effluent limitations guidelines (ELGs)*

Permits and Guidance

- *Environmental Protection Agency (EPA) or delegated states issue NPDES permits for discharges*

Offshore and Coastal ELGs

- Best Available Technology (BAT) for offshore produced water:
  - Oil and grease limits before discharge
    - *29 mg/l monthly average*
    - *42 mg/l daily maximum*
- Zero discharge for coastal waters (except Cook Inlet)
- No other national requirements
  - Permit writer can select additional controls


federal register

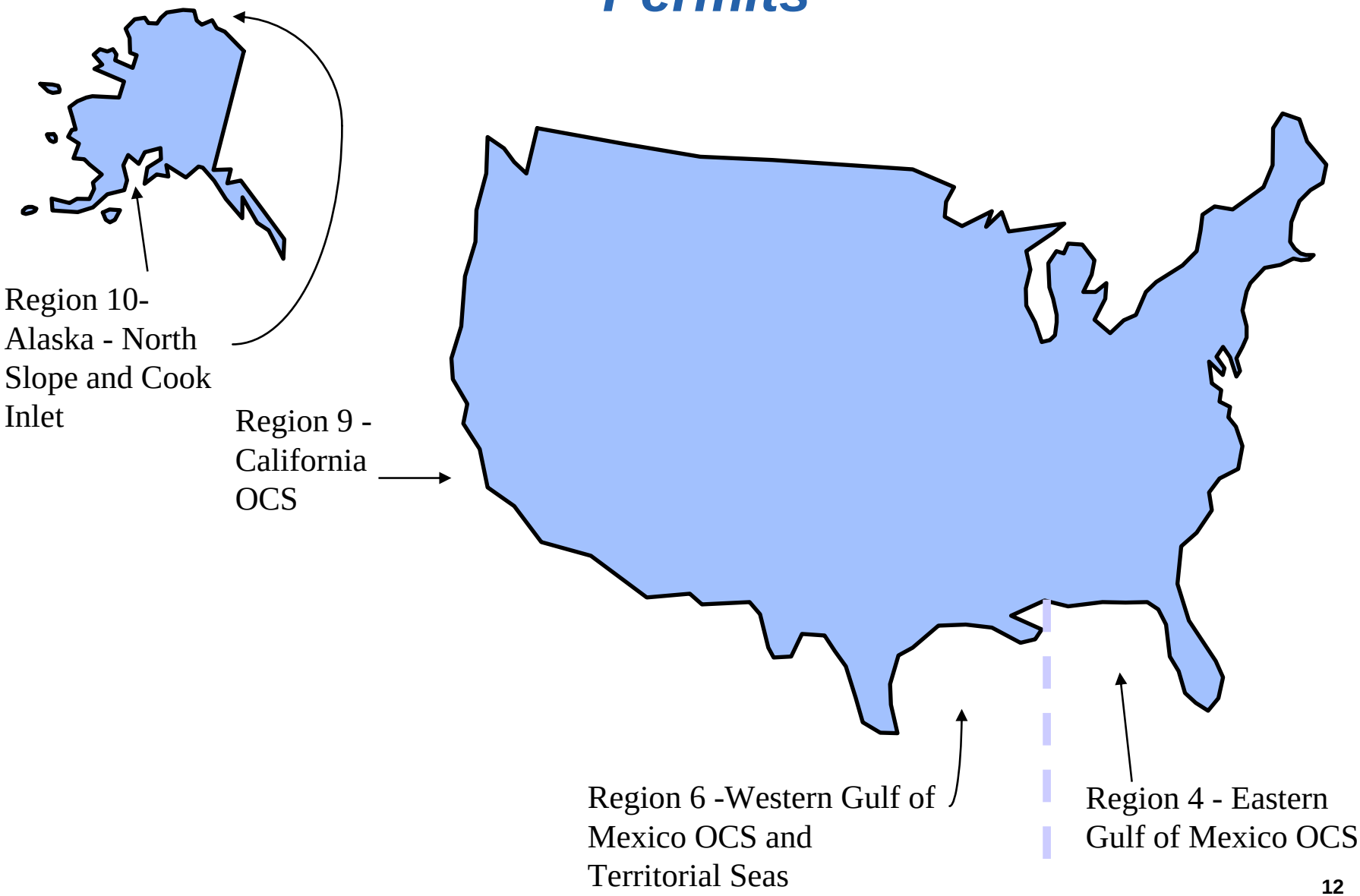
Wednesday
February 3, 1999

Part III

Environmental Protection Agency

40 CFR Part 435
Effluent Limitations Guidelines and New Source Performance Standards for Synthetic-Based and Other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category; Proposed Rule

EPA Regions Issuing Offshore General Permits



EPA Actions

- EPA began work on renewing the NPDES general permit for Outer Continental Shelf (OCS) in central and western Gulf in 2003
- Proposed permit conditions include language to control produced water oxygen demand inputs:
  - New or increased produced water discharges to the hypoxic zone would be prohibited unless a comparable amount of BOD is removed from other produced water discharges
  - Proposed a web-based trading program

EPA Actions - continued

- Industry and MMS strongly objected during winter and spring 2004
- EPA agreed to remove the proposed conditions and require an industry sampling program
  - All discharges located in hypoxic zone would sample individually or the industry could undertake a joint study
- Permit was issued for 3 year-term rather than the usual 5 years
  - Would allow for the permit to be renewed following collection of new data

The Players and Their Roles

EPA – Issued permit; will decide future regulatory actions based on the study results

MMS – Responsibility for offshore activities; maintains extensive data collections and sponsors research

DOE – Concerned about maintaining energy supplies from offshore production; funded sampling program support and Argonne's work

Argonne – DOE contractor; designed sampling program; coordinated sampling, interpreted results, and prepared report

API – funded the laboratory analytical work

Offshore Operators Committee – assisted with selection of sampling locations; many member companies were sampled or offered to be sampled

Two analytical laboratories – one coordinated preparation of sample kits and delivery of samples to second lab; second lab conducted tests

Companies Participating in Hypoxic Zone Study

Apache	Dominion	J.M. Huber	Remington
Arena Offshore	El Paso	Kerr-McGee	Seneca Resources
ATP Oil & Gas	Energy Resource Technol	Linder	Shell Offshore
BHP Billiton	Eni	Marathon	Spinnaker
Bois dArc Offshore	EOG Resources Inc.	Mariner Energy	SPN Resources
BP	Exxon Mobil	Murphy	Stone Energy
Callon Petroleum	Forest Oil	Newfield	Houston Exploration
Calpine	Gryphon Exploration	Nexen	Unocal
Century Exploration	Helis	Northstar Gulfsands	W&T Offshore
Chevron	Hunt Oil Company	PetroQuest Energy	
Devon	Hunt Petroleum (AEC)	Pioneer	

Objectives of Sampling Program

- Sample a representative subset of the produced water discharges in the study area
- Determine average and range of BOD and nutrients from produced water discharges
- Estimate variability within the same discharge
- Follow good scientific procedures
- Complete study by August 2005

Chronology of Events

- **Summer of 2004** – DOE funded Argonne to conduct study
  - Argonne began working with industry to develop draft sampling plan
- **Aug 2004** – meeting of all stakeholders to establish goals
- **Sept 2004** – meeting with water quality modelers to identify the sampling parameters needed for model inputs
- **Oct 2004** – EPA issued permit with a deadline for study submittal in Aug 2005
- **Nov 2004** - developed sampling plan and went through several rounds of review and comment
- **Dec 2004** – final sampling plan approved; developed QA/QC plan; selecting sites for first round of testing
- **Jan 2005** – selected and notified sites to be sampled and developed sampling schedule
- **Feb-June 2005** – conducted sampling
- **July 2005** – prepared draft report
- **Aug 2005** – submitted final report

Sample Design and Schedule

- Sampled 10% of approximately 500 discharges in the hypoxic zone
  - 16 platforms sampled three times
  - 34 platforms sampled one time
- Parameters tested

Measure Indirect Oxygen Demand

ammonia

nitrate

nitrite

total Kjeldahl nitrogen (TKN)

total phosphorus

orthophosphate

Measure Direct Oxygen Demand

BOD

TOC

Other Parameters

pH

conductivity

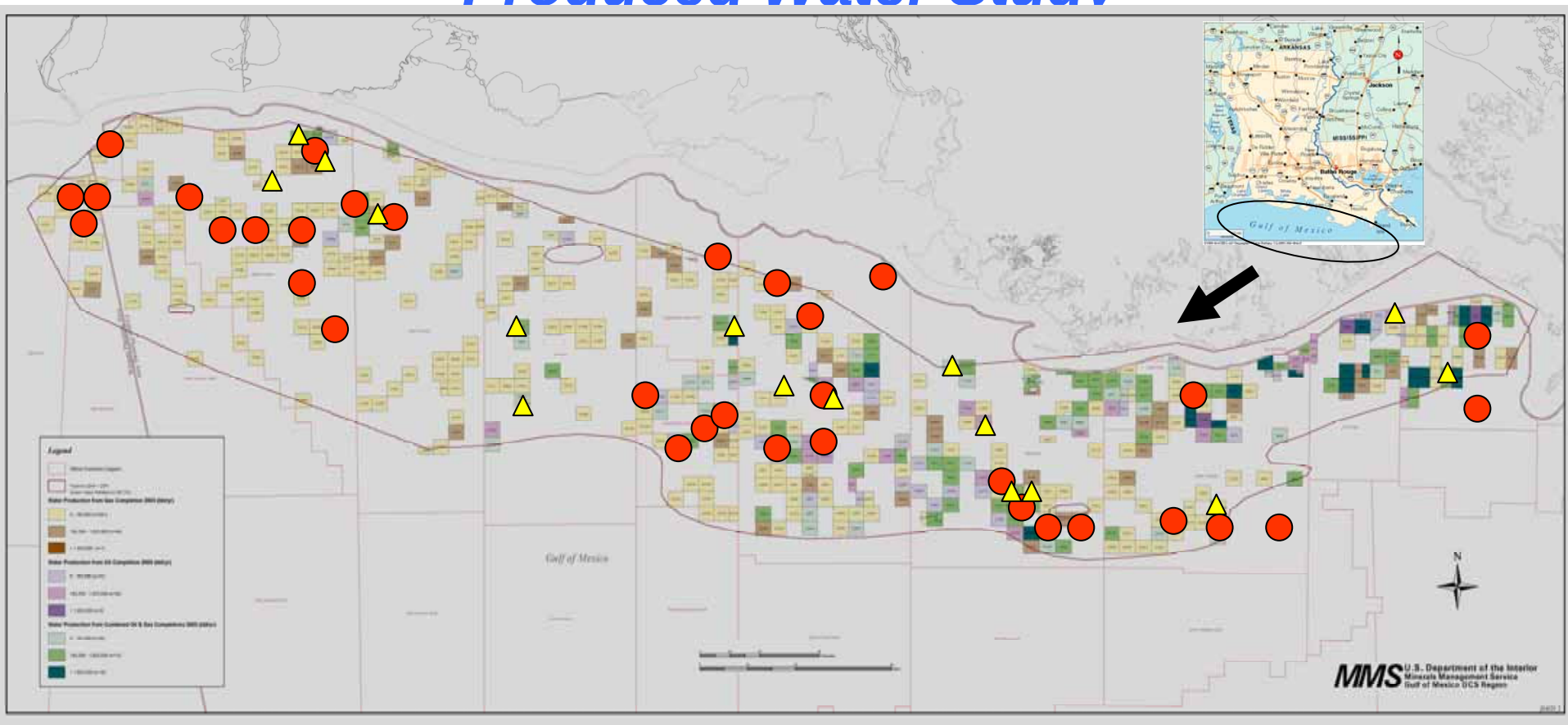
salinity

temperature

Selection of Sampling Sites

- For the 16 sites tested 3 times, subdivide hypoxic zone lease blocks into 3 water production rate classes (< 500 bbl/day, 500 – 5,000 bbl/day, >5,000 bbl/day) and 3 hydrocarbon production type classes (oil completions, gas completions, both types of completions)
  - Select at least 1 facility from each of the 9 subcategories
- For the 34 sites tested one time, select locations at random
- Issue
  - Neither EPA nor MMS had accurate data of number and identify of produced water discharges
  - Decided to use MMS data on leases that produce both water and oil or gas (496 leases in study area)

Location of Platforms Sampled for Hypoxic Zone Produced Water Study



Platforms sampled one time and selected at random

Platforms sampled three times and selected based on discharge volume and type of hydrocarbon produced

Sample Collection and Transportation

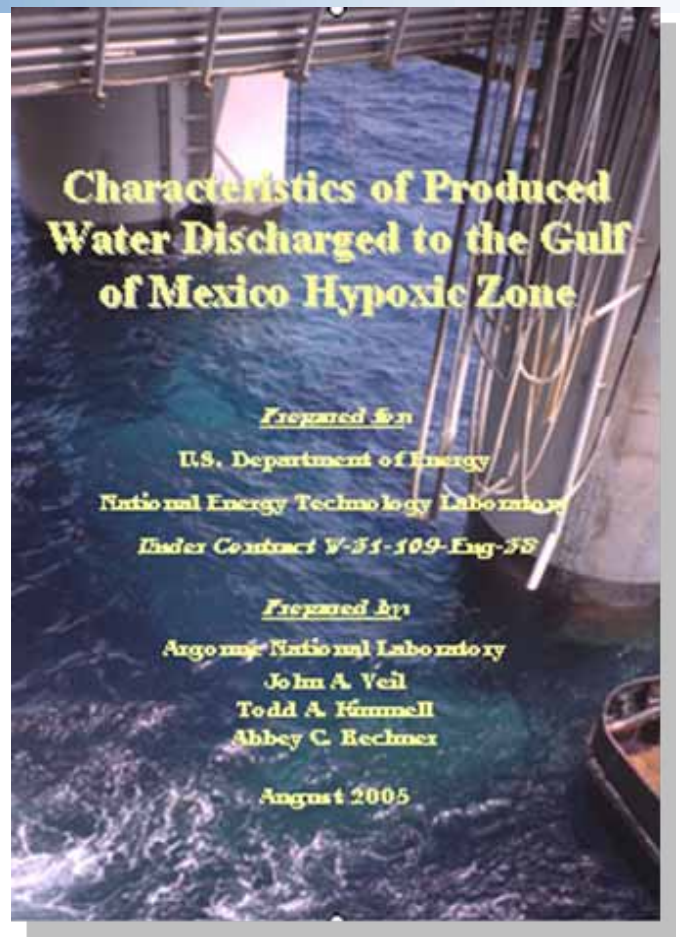
- Sample kits were delivered to shore bases in advance of sampling date
- Platform personnel collected samples according to instructions and placed them in a cooler with ice
- Coolers were taken to helicopter pilot who delivered them to the shore bases
- Laboratory couriers collected coolers at shore bases and delivered to lab
- All transfers were documented on Chain of Custody form
- Issues
  - Tests must be started within 48 hours of sample collection
  - Complex scheduling and coordination
    - *Weather could impact schedule*

QA/QC Measures

- QA plan was developed before sampling begins
  - Sampling measures
    - *Blanks*
    - *Duplicates*
  - Analytical measures
    - *Calibration*
    - *Matrix samples*
    - *Blanks*

Current Status

- The hypoxic zone report was completed in August 2005 and subsequently submitted to EPA
- EPA modelers are scheduled to use the data from this report as inputs to water quality models
- Results are shown on the following slides

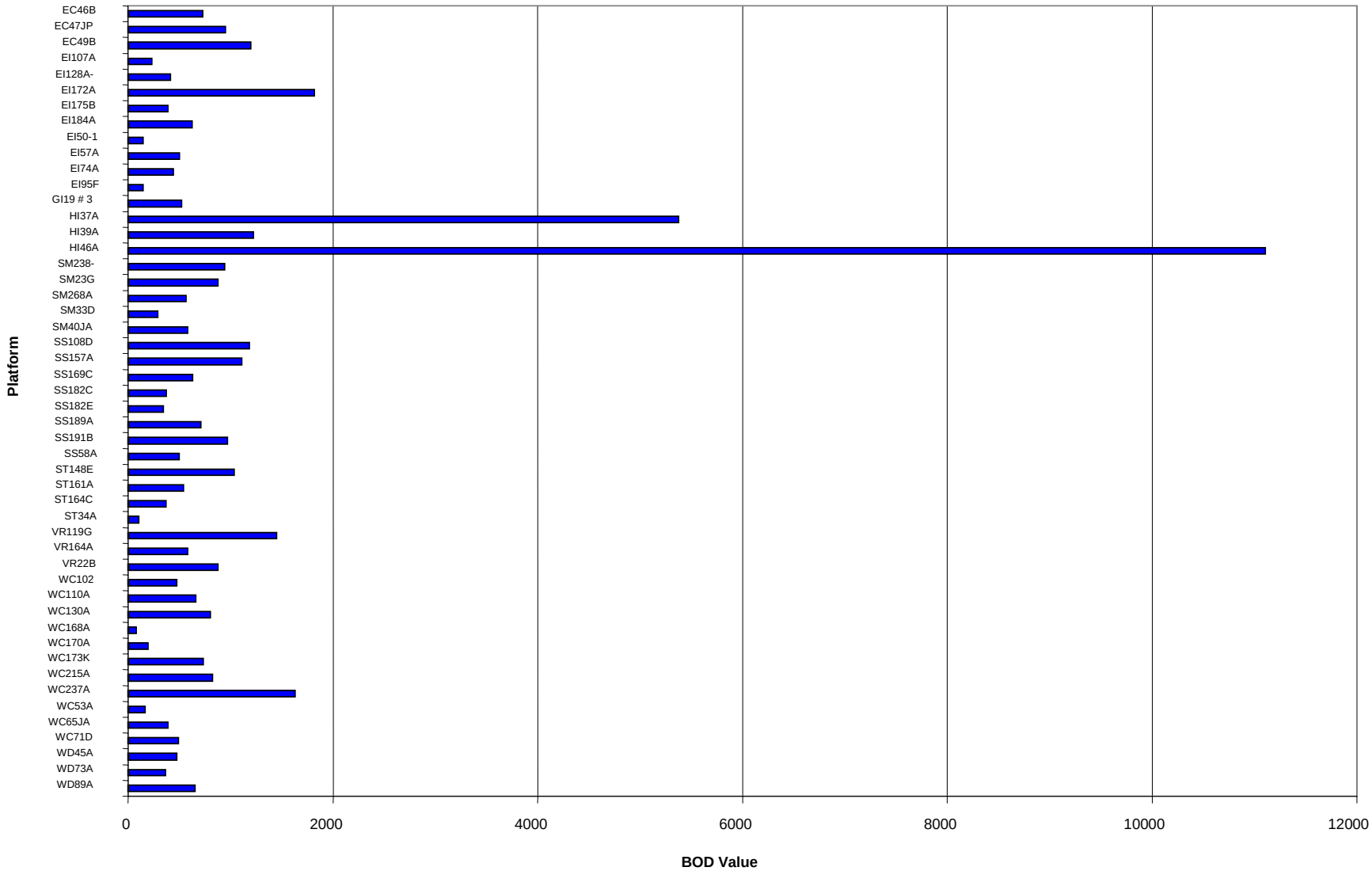


Download report at:
www.ead.anl.gov/pub/dsp_detail.cfm?PubID=1874

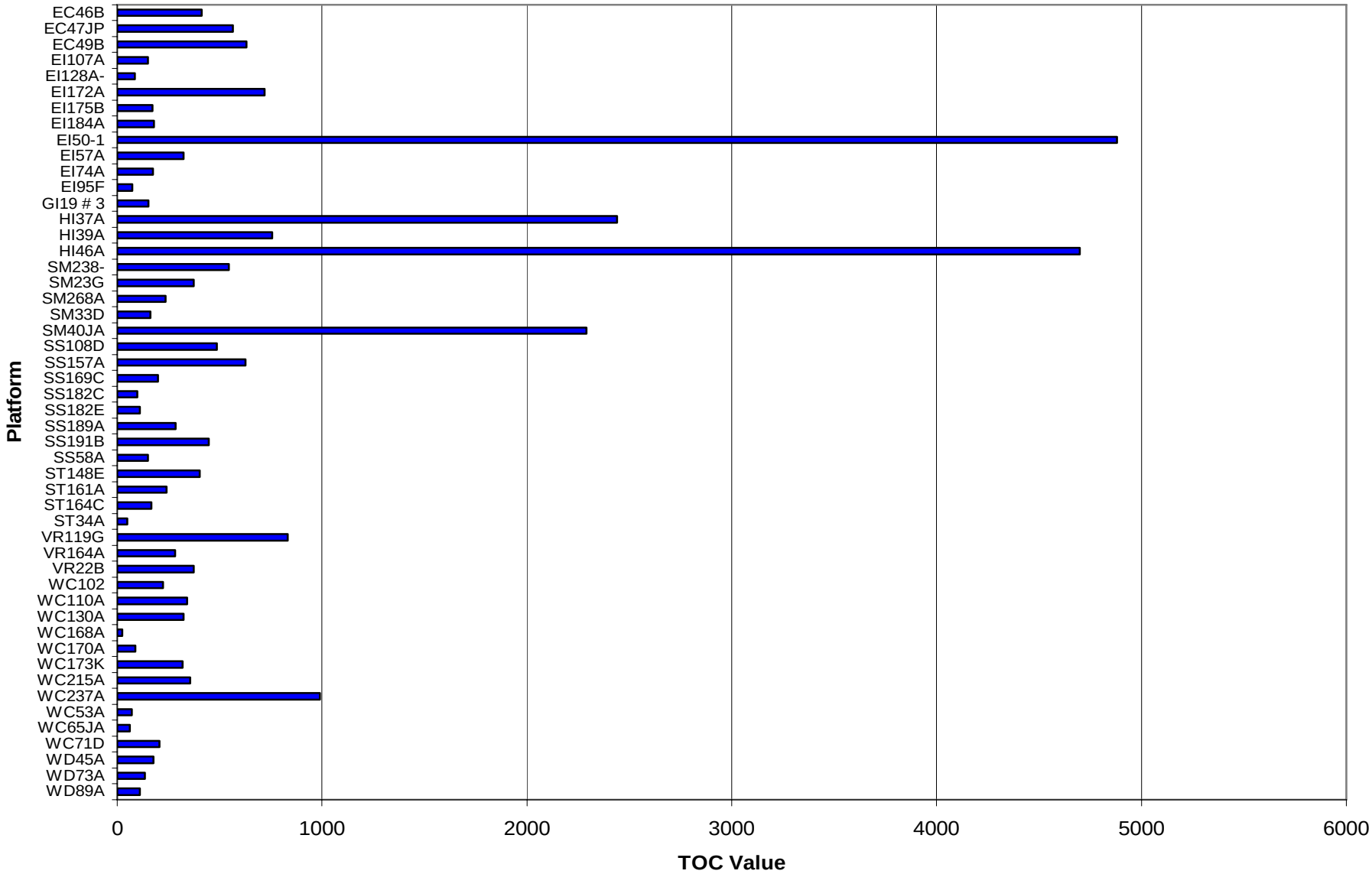
Summary of Analytical Data

Parameter	Mean	Median	Maximum	Minimum
BOD, mg/L	957	583	11,108	80
Dissolved BOD, mg/L	498	432	1,128	132
Suspended BOD, mg/L	76	57	146	16
TOC, mg/L	564	261	4,880	26
Dissolved TOC, mg/L	216	147	620	67
Suspended TOC, mg/L	32	13	127	5
Nitrate, mg/L	2.15	1.15	15.80	0.60
Nitrite, mg/L	0.05	0.05	0.06	0.05
Ammonia, mg/L	74	74	246	14
TKN, mg/L	83	81	216	17
Orthophosphate, mg/L	0.43	0.14	6.60	0.10
Total phosphorus, mg/L	0.71	0.28	7.90	0.10
Conductivity, umhos/cm	87,452	86,480	165,000	360
Salinity, ppt	100	84	251	0
Temperature, ^{o}C	38	32	80	20
pH, SU	6.29	6.50	7.25	1.77

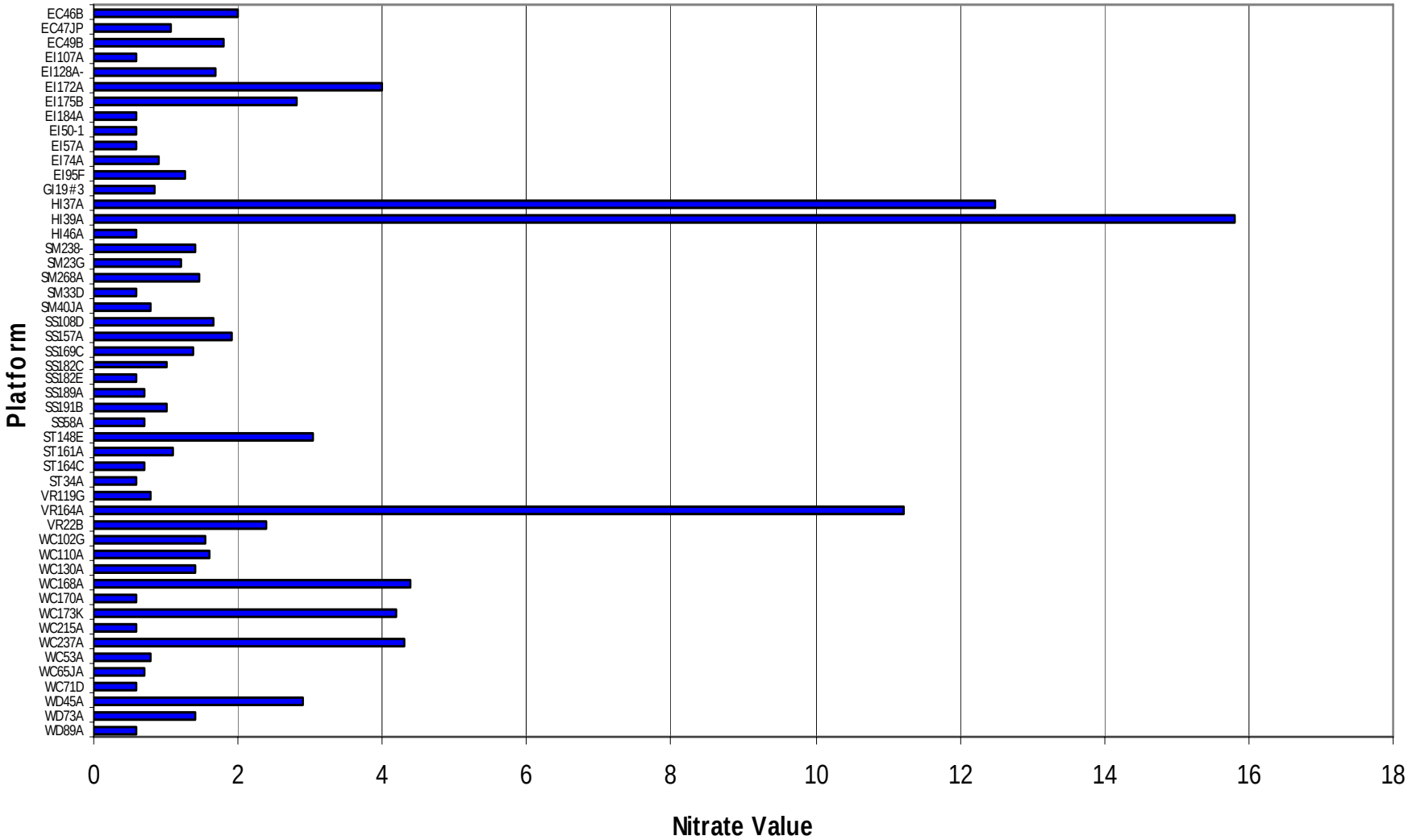
BOD Results from All Platforms (in mg/L)



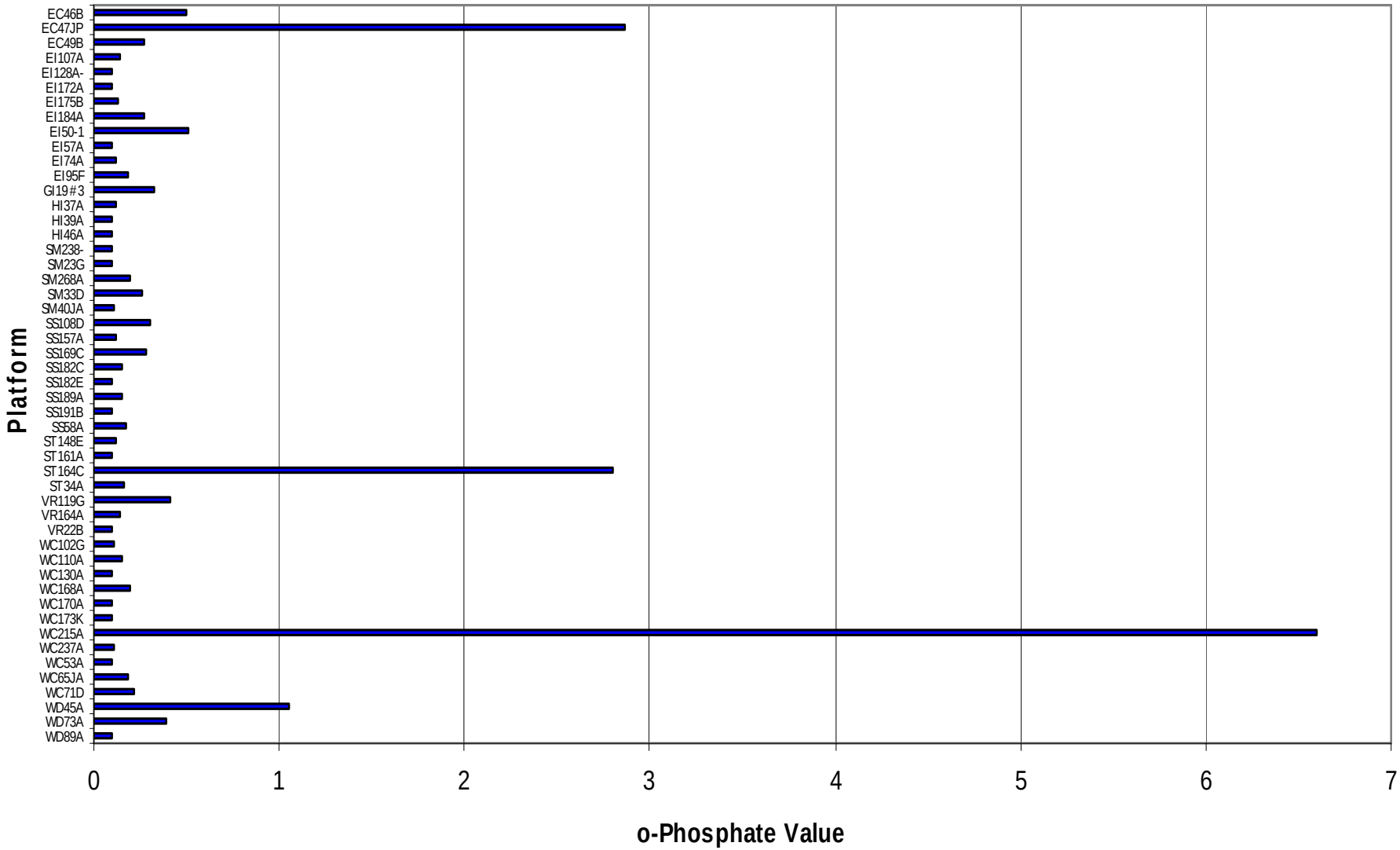
TOC Results from All Platforms (in mg/L)



Nitrate Results from All Platforms (in mg/L)



Orthophosphate Results from All Platforms (in mg/L)



Total Phosphorus Results from All Platforms (in mg/L)

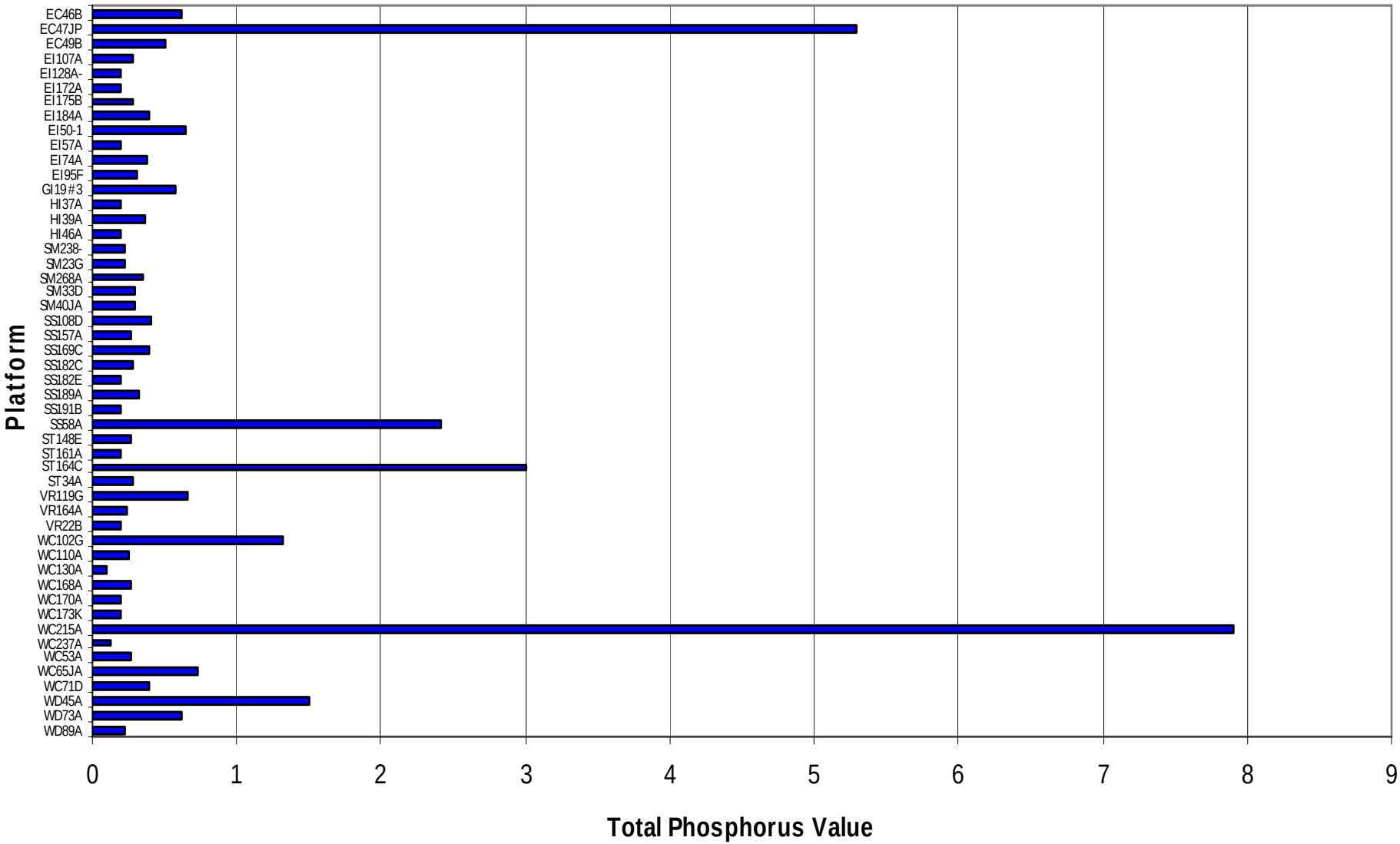


Table ES-2 – Loading Estimates for 50 Platforms and Entire Hypoxic Zone

Parameter	Loading from Sampled Platforms (lb/day)	Estimated Loading for Entire Hypoxic Zone (lb/day)
BOD	36,000	104,000
TOC	14,100	40,700
Nitrate	68.3	197
Nitrite	3.07	9
Ammonia	4,770	13,800
TKN	5,140	14,900
Orthophosphate	22.6	65
Total phosphorus	37.6	109

- **The mass loadings from offshore oil and gas discharges to the entire hypoxic zone were estimated by multiplying the 50-platform loadings by the ratio of total water generated to 50-platform discharge volume.**

Table 23 – Comparison of Nutrient Loadings from Produced Water Discharges and Riverine Inputs

Nutrient	Mean Flux (lb/yr) from Mississippi and Atchafalaya Rivers (Goolsby et al. 1999)	Estimated Annual Mass Loading (lb/yr) from Produced Water Discharges to the Hypoxic Zone	Ratio of Produced Water Loading to Riverine Loading
Ammonia	68,355,000	5,030,000	[a]
Organic N	1,278,900,000	389,000 (calculated as TKN – ammonia)	[a]
Nitrate	2,100,000,000	71,900	[a]
Nitrite	0	3,285	[a]
Total N	3,460,000,000	5,500,000	0.00159
Orthophosphate	92,100,000	23,700	[a]
Particulate phosphate	209,000,000	0	[a]
Total P	301,000,000	39,800	0.00013

[a] The key ratios are total nitrogen and total phosphorus. Ratios for the other component comparisons are not shown.

nitrogen - 0.16%

phosphorus 0.013%

Conclusions

- Designing and conducting the sampling program was a cooperative effort among many players
- The program was complex but was completed in a short time frame to meet EPA needs
- These data from 50 platforms represent the most complete and comprehensive effort ever undertaken to characterize the amount and potential sources of the oxygen demand in offshore oil and gas produced water discharges.

Conclusions (continued)

- Results were scientifically sound
- Discharges of oxygen-demanding pollutants and nutrients are collectively large, but they represent less than 1% of the contribution of the same pollutants from the Mississippi and Atchafalaya Rivers
- The offshore environment tends to rapidly assimilate surface oxygen demand through wind and wave activity

LACK OF COMMENTING ON REGULATIONS HURTS THE E&P INDUSTRY

George Holliday*
Holliday Environmental Services, Inc.
P. O. Box 2508
Bellaire, TX 77402
Voice: 713-668-7640
Fax: 713-668-5184
Email: ghh@houston.rr.com

United States E&P operators are not protecting themselves from over regulation. Instead, they rely on trade associations to provide comments regarding the impact of proposed regulations. The actions of letting others take the responsibility for commenting results in erroneous information, partial information or inadequate input to agencies. Recent examples include the Sediment Toxicity Testing (40 CFR Part 435), Spill Prevention, Control and Countermeasure (SPCC) Plan rule (40 CFR Part 112) and the Storm Water National Pollutant Discharge Elimination System Permit rule (40 CFR Part 122). Implementation of these rules has the potential to result in continuous noncompliance of offshore wells, and premature abandonment of marginal onshore wells. In many cases independent operators are not aware of the proposed rules. When the operators are aware of the rules, they do not avail themselves of the opportunity to comment, because they fear retaliation by the agency or prefer to rely on the trade associations to fill that function. The trade associations perform a valuable service, but there is no substitute for information presented by the affected party.

This paper discusses the development of an industry wide communication system, and submission of extensive, factual comments by field oriented operators.

THE APPLICATION OF JET RE-CYCLE TECHNOLOGY IN THE TREATMENT OF OILY SLUDGE FROM OIL LAKES OF KUWAIT

A. Al-Hashem, A. Al-Muttawa and E. AlMuhameed
Petroleum Research and Studies Center
Kuwait Institute for Scientific Research
P.O.Box 24885
13109 Safat, Kuwait
Email:ahashem@prsc.kisr.edu.kw

ABSTRACT

In this investigation, a pilot testing plant was used to feed oily polluted soils and oil sludge to prove the adaptability of the jet recycle system to treat and possibly recover valuable oil contained in the wastes. The capacity of the pilot plant was 0.2 tons/ hour. The practical application of the system in actual treatment and decontamination of the various oily sludge and oil-polluted soils by the jet recycle technique was investigated. Results have confirmed that the evaporation of hydrocarbons contained in the sludge is highly achievable, at less than 1 wt % of the residual oil content in the treated solid, by applying a proper treating temperature in the chamber of the pilot plant according to the properties of the sludge. It was also verified that the expected carbonization of hydrocarbons contained in the sludge is possible to minimize, by adjusting the temperature, and shortening the retention time in the chamber. The API gravity of the recovered oils from oily sludge, oily water sludge and oily sand were in the range of 9.5 to 26.6 at temperatures of 300 to 500C. This method was also found to be cost effective, when compared to other treatment methods available in the market. Based on a processing capacity of 20-40 tons per day, the treatment cost is estimated at 20-36 KD/ton.

INTRODUCTION

System Summary

Feature

The system utilizes the Jet Burner Technology, with sufficient functions capable of separating liquid and solid in the sludge material (1).The high efficient separation of hydrocarbon mixtures from the sludge, which seemed difficult to accomplish, is achieved through the peculiar functions as follows:

(1) Pulverization and uniform mixing of the solid by high turbulences and shock waves, generated by jet steam of pressurized combustion gas.
(2) Instantaneous vaporization of hydrocarbons, by direct heating with high temperature combustion gas, which contributes high efficient heat transfer.
(3) Separation of hydrocarbons from the material, in a lack of oxygen (non-combustion of hydrocarbons).
(4) Saving heat energy requires for vaporization of hydrocarbons by the decreasing boiling points of hydrocarbons due to the effect of partial pressure of the combustion gas component mixtures.

Moreover, the treatment system applied to the Jet Re-cycle System is engineered based on the

defined basic philosophies of sludge treatment, which are to;

- recover valuable materials in the waste,
- decontaminate various types of waste, and reuse of the final products,
- minimize waste for final disposal,
- conform with environmental regulations/standards in Kuwait,
- achieve high treatment without any additive,
- minimize energy consumption for treatment
- simplify the system and operation

System Configuration and Process Description-General

Configuration of the System is outlined in Figure 1 and 2. The description of the system is summarized below as follows:

(1) Mixture of fuel (oil or gas) and compressed air is fired into the Jet Burner located on the top of the Jet Re-cycle Chamber, where high temperature and high pressure combustion gas is developed into the chamber.

(2) The sludge is fed into the Jet Re-cycle Chamber by Sludge Feeder, and the slurry sludge is fed into the chamber by Slurry Pump at a specified rate. The sludge fed in the chamber is pulverized into small particles, and the hydrocarbon and water contents in the sludge are evaporated quickly, by the jet stream generated by Jet Burner. Carbonization and combustion of hydrocarbons does not occur in this process, due to the lack of oxygen in the chamber.
The temperature and time necessary for processing the material in the chamber is automatically controlled in accordance with the volume, properties of material and the quality of the products specified.

(3) The vapors are discharged together with the flue gas, and the dried solid particles are passed to a solid separation section, consisting of a Gravity Separator and Cyclone Separator. The larger particles of solids are descended in the vessel, and discharged from the bottom as treated (de-contaminated) sludge. Furthermore, the smaller solid particles, which passed through the Gravity Separator, are separated from the gas stream by Cyclone Separator.

(4) Gas mixture (hydrocarbon and water vapors, and flue gas) is introduced into the Condenser and the liquefied hydrocarbon and water separated from flue gas are recovered.
Furthermore, water is separated from the liquid recovered, and the hydrocarbon is recycled as a valuable resource.

(5) The flue gas are induced by a Blower, and sent to the Flue Gas Chamber, further eliminating the slight residual hydrocarbon vapor in the gas exhausted.

Principle of Jet Re-cycle System

Functions of Jet Re-cycle Chamber (JR Chamber)

The JR Chamber, which is the main equipment of the system, evaporates the liquid contained in the feed material, and separates the liquid from solid by direct heating. The extremely high velocity and high temperature Jet Stream (generated by the Jet Burner) creates turbulence in the chamber, which pulverizes the material in small particles. Such action increases the surface area (heat transfer area) of the material, causing the material to dry quickly. The basic functions of the

system are as follows:

(1) Drying of material: Vaporization of liquid in the solid through the effects of;
   a. Heat transfer from high temperature gas (direct heating).
   b. Shock waves, which promote movement of liquid in the solids.
   c. Separation of hydrocarbons from the solid in combustion gas (inert gas).

(2) Pulverization:
   a. Collision of solid particles with inner surface of the chamber, and inter-collision with solids, by high turbulence generated by jet stream in the chamber.
   b. Decline of strength of solid due to high temperature.

EXPERIMENTAL PROCEDURES

Testing Operation

A set of Jet Re-cycle System pilot plant was installed at the Petroleum Research and Study Center (PRSC) of KISR, where the testing operation was conducted with actual sludge and oily contaminated soil collected in the oil fields in Kuwait.

The facility provided for the testing operation, testing procedure and the results are described in the succeeding sections.

Testing Items

The items related to functions and performances of the system to be confirmed and/or verified (through the testing operation) were established. The items are described as follows:

(1) Performance

The targeted minimum residual oil content in the treated solid was set at less than 1 (wt) %. The testing operations conducted have shown the capability and performance of the system

(2) Recovery of Hydrocarbons

Recovery of valuable hydrocarbons, in various types and components of material

Sludge, were measured. Furthermore, possible recycle/reuse of the recovered hydrocarbons was discussed.

(3) Secondary Waste Discharge

Gases exhausted from the system as secondary waste have been sampled and analyzed at each testing operation, in order to verify the conformance of the system with the environmental standard of Kuwait.

(4) Applicability and Operability

The properties and components of sludge vary in accordance with the source methods of discharging, storage, history of the sludge, and so on. Therefore, proper treatment of operational method suitable for the particular sludge should be selected.

Applicability, operability and performance of the system for such various kinds of sludge were verified and studied.

(5) Cost Effects

Actual operational cost for treatment of each kind of sludge, including utility consumption (such as fuels, electrical power, water, etc.) was calculated.

In addition, the optimum operational method(s) of the system was discussed considering cost

and effects expected.

Samples

Four kinds of sludge samples have been used for this testing operation, which were collected from the oil fields in Kuwait. The features of the sludge samples are shown in the above table 1.

RESULTS AND DISCUSSIONS

The testing operation of the system was carried out, using the above said four kinds of sludge samples. It was confirmed that the evaporation (separation) of hydrocarbons contained in the sludge is highly achievable at less than l wt% of residual oil content in the treated solid, by applying a proper treating temperature in the chamber according to the properties of the subject sludge. It was also verified that the expected carbonization of hydrocarbons contained in the sludge is possible to minimize, by adjusting the temperature and shortening the retention (processing) time in the chamber.

Different kinds of liquefied hydrocarbons were collected as samples from the condensing unit, at a temperature range of 95-110°C and 79-80°C. It is expected that the hydrocarbons evaporated (separated) from the sludge are recoverable separately according to the hydrocarbon components, by appropriate control of condensing temperature (depending on the requirements).
The proper functions of the control system, including fuel/air ratio control, temperature monitoring and control, material feed control, and safety devices along with emergency shutdown system were also confirmed.

(1) Performance of the Chamber (Separation of hydrocarbon from sludge)

The residual oil contents in the solid treated at various temperature ranges were measured by Total Extractable Matter (TEM) with toluene. The values of the residual oil contents are as follows:

According to the findings, the performance of oil separation tends to demonstrate as follows:

- Higher treating temperature contributes to a less residual oil content.
- Residual oil content varies, depending on the type of sludge treated even if the same treating temperature is applied.
- It is highly possible to decrease the residual oil content at less than l wt% by selection of proper treating temperature.

And it was confirmed from the results of the testing that the proper treating temperatures to assure residual oil content less than 1 wt% are as follows.

Sample A (Oily sludge):	350-400 deg.C
Sample B (Oily water sludge):	400-450 deg.C
Sample C (Oily soil):	300-350 deg.C

Recovery of Hydrocarbons

The hydrocarbons that evaporated at the treatment chamber were recovered by a simple scrubber-type condensing unit. Recovered oils were sampled at 2 sampling points, i.e. outlet of condenser (95-110°C); and at other collecting device (70-80^{0}C), in the downstream piping. The API gravity of recovered oils was measured and the readings are indicated in the above table.

According to the above findings, it was verified that the hydrocarbons in the sludge can be sufficiently recovered, using this system, and the qualities of the recovered oils are also selectable, within a limited range by the cooling temperature control of the condensing equipment.
The samples of the oil recovered by the system contain great amount of water and sediments as contaminants; due to the mixing of water sprayed in the condenser and the inclusion of pulverized treated solid particles in the chamber carried over to the gas/solid separation system. The quality of the recovered oil is usually specified by the user of the oil recovered; or client in accordance with the purpose of the product in general. Accordingly, it is necessary to consider the device/system to avoid such mixing/inclusion or elimination of the contaminants from the oil recovered for commercial facility.

Analysis for the component of recovered oil and treated solid

To evaluate this system performance, the analysis of hydrocarbon components (by gas chromatography) (OC) on the properties of the recovered oil, treated solid (sludge), and that of oil in the untreated sludge used as feed stock, were executed.
The CC analysis data are demonstrated in scanning figures as follows.
The figures indicate the chemical analysis value of recovered oil, and the oil in the solid, of the same sample (in different operating temperatures) at the treatment chamber.

Applicability and Operability for various sludges

Operation

In accordance with this feature, properties and oil, and water contents of the sludge to be treated, appropriate operating procedure and conditions suitable for each sludge, (such as processing time, temperature, combination with water spraying for adjustment of heat load, etc.) were successfully verified and confirmed through trial operations repeatedly carried out.
Also, the proper functions and effectiveness of the safety system, and the emergency shutdown system of the facility were also confirmed. Accordingly, the suitability of the basic operating procedure model newly developed consisting of startup, normal operation, shutdown and emergency shutdown, were verified.

Material feed system

The testing plant is designed and provided with 2-way feeding devices; a screw feeder for solid/non-fluid material, and a screw pump feeder for slurry and fluid material. The

feed rate (speed of feeder) is controlled automatically to maintain steady treatment temperature of the chamber by combination of the temperature control system and feeder controller.

The function of the screw feeder was tested using Sample A (Oily sludge), Sample B (Oily water sludge) and Sample C (Oily soil); and the screw pump feeder was tested with Sample D (Tank sludge: high viscous). It was confirmed that both feeding devices functioned satisfactorily in handling the various types of sludge. Especially, it was noted that an accurate feed control of the screw pump feeder could maintain less fluctuation in the operating temperature of the chamber.

Functions of treatment chamber

According to the analysis results of the residual oil contents in the treated solids, it was verified that the chamber is sufficiently applicable to the various type of sludge's (Sample A, B, C) evaporation (separation) of almost all hydrocarbons contained.

In addition to above, through testing with Sample D (High viscous tank sludge: extremely low sediment), it was confirmed that the chamber can achieved good evaporation of hydrocarbons in the sludge material with dedicated temperature and feed controls. Accordingly, the chamber can be utilized for a direct heated distiller for the extreme heavy oil cases, as an alternative application, if improved further.

Cost effectiveness

Reliable data for utility cost was obtained (fuel, electric power, and cooling water, etc.) through the long-term testing operation for the treatment cost estimation. We calculated the treatment cost for practical use, based on this result. By assuming the processing capacity of the equipment at 20-40 tons per day, the treatment cost is estimated at 70-120 dollars/ton.

Following figure shows the result of the cost comparison study with rival technologies.

This System can treat the sludge and oil-polluted soil containing wide-ranging oil concentrations, compared with other rival technologies. Moreover the processing unit price is also comparatively low, so this technology is considered competitive ion the present situation.

CONCLUSIONS

(1) Adaptability to Waste Processing

In the testing operation, the following has been confirmed:

a. The adaptability of the system to processing (making harmless), the polluted soil and oily sludge with wide ranging contamination, from comparatively lower level of pollution, up to the higher viscous and heavily polluted sludge.

b. The possibility of recovery of effective oil component evaporated and separated in the process.

c. It has been verified that the system is fairly competitive in the field of the processing business of oil industrial waste by Jet Re-cycle System, against existing rival technologies (in respect to the

processing cost and the feed-stock with wide-ranging oil content).

(2) Possibility of Future Development of the System
For the large scale commercialization of the system, the following points should be taken into consideration:
1) Scale-up of the equipment capacity based on the business plan
2) Optimization of the recovery system for the improvement of the recovery efficiency of oil content.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial and technical support of Japan Oil Engineering Company (JOEC) and Kuwait Institute for Scientific Research (KISR) for the execution of this project.

REFERENCES

1. Al-Hashem, A., Al-Muttawa, A., Elmohameed, E., and Hameed, Z., In *Testing Operation of Jet Recycle System in Kuwait,* Kuwait Institute for Scientific Research final report No.2461, 2001.

Table 1. Type of samples tested in the Jet Recycle system.

Sample	Sample A		Sample B		Sample C		Sample D	
Type of sludge	Oily Sludge		Oily Water Sludge		Oily sail		Tank Sludge	
Feature	Medium oil content		Medium oil and water content		Medium oily contaminated		Extremely high viscous	
Contents (w%)	Mm.	Max.	Mm.	Max.	Mm.	Max.	Mm.	Max.
- Oil	6.6	9.7	9.2	13.4	10.6	11.6	82.7	93.4
- Water	16.8	23.0	12.2	33.0	10.0	15.9	5.0	12.8
- Solid	67.8	75.5	53.1	74.1	72.6	78.9	2.1	5.5
- Others			High salt					
Quantity	8 drums		10 drums		8 drums		5 dnjnis	
Sources	Oil Lake Al Rawdatayn		Oil Lake Sarbia Oil Field		Oil Lake Al Rawdatayn		Sludge pit Al Burgan	

Table 2. Residual oil contents in treated solids (wt%).

Sludge samples	Oil Content in Sludge		Treated Temp. (deg. C)				
	Mm.	Max.	250	300	350	400	500
Sample A (Oily sludge)	6.6	9.7	-	2.1	-	0.7	Trace
Sample B (Oily water sludge)	13.4	15.9	-	Trace	-	1.1	0.6
Sample C (Oily soil)	10.6	11.6	9.0	0.7	Trace	Trace	Trace

Table 3. API gravity of recovered oils

Samples	Treated Temp. ^{0}C	API gravity	
		Mm.	Max.
Sample A	300-400	9.5	24.0
Sample B	300-500	8.1	15.7
Sample C	250-350	13.9	26.6
Sample D	300 - 400	22.4	26.3

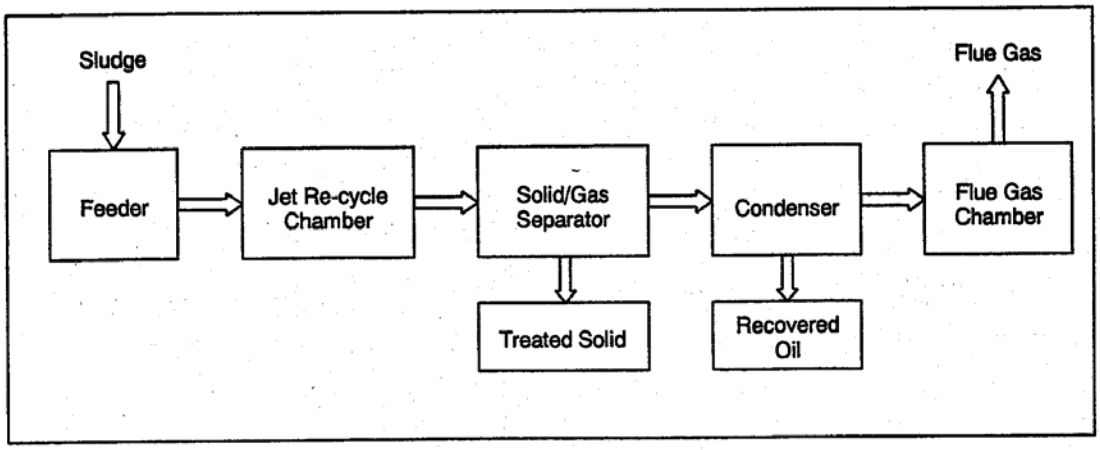


Figure 1.Process flow diagram and system configuration.

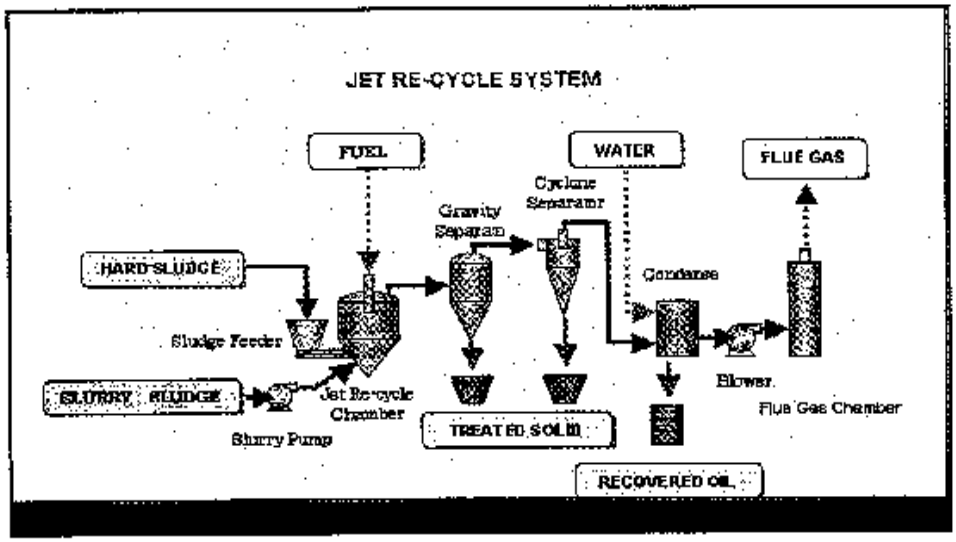


Figure 2.Schematic diagram of the jet re-cycle system.

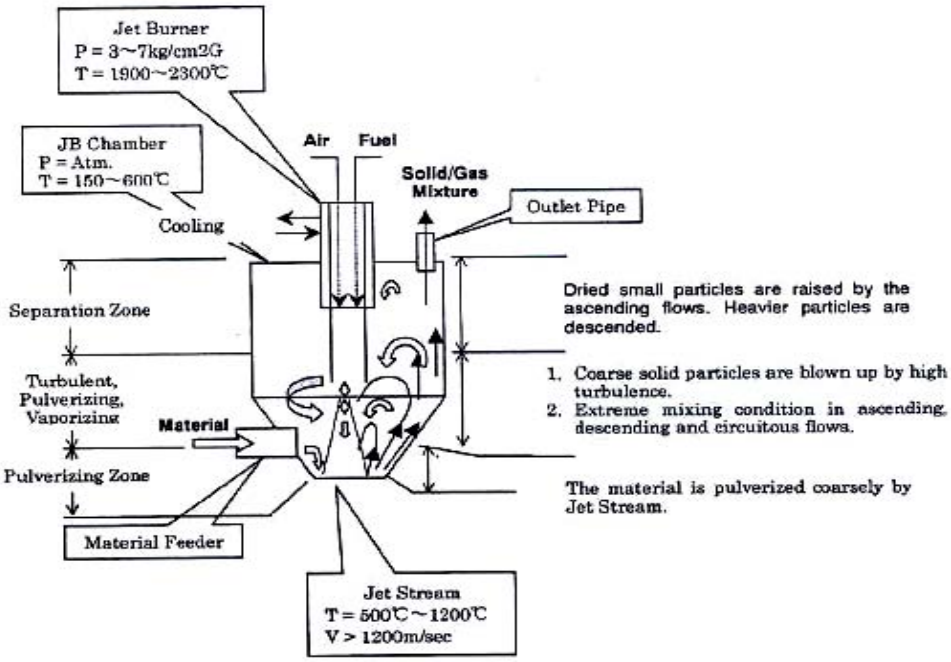


Figure 3.Behaviors of gas and solid in the chamber of the Jet Recycle System.

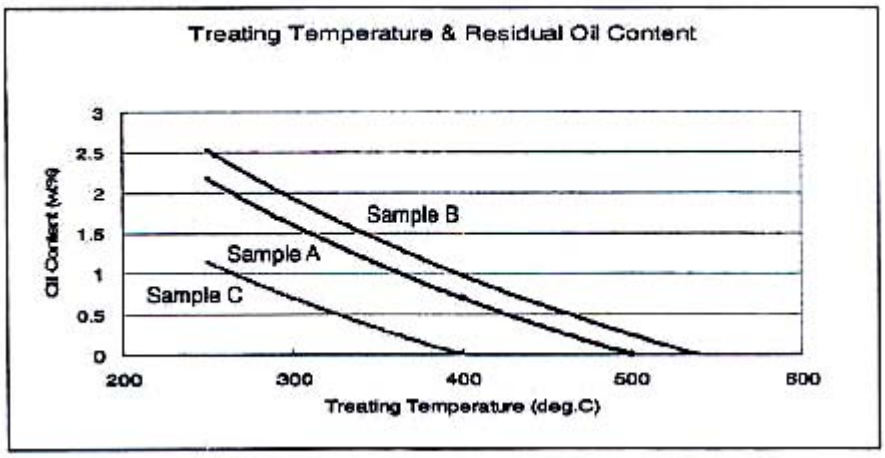


Figure 4.Treating temperature and residual oil contents of three samples.

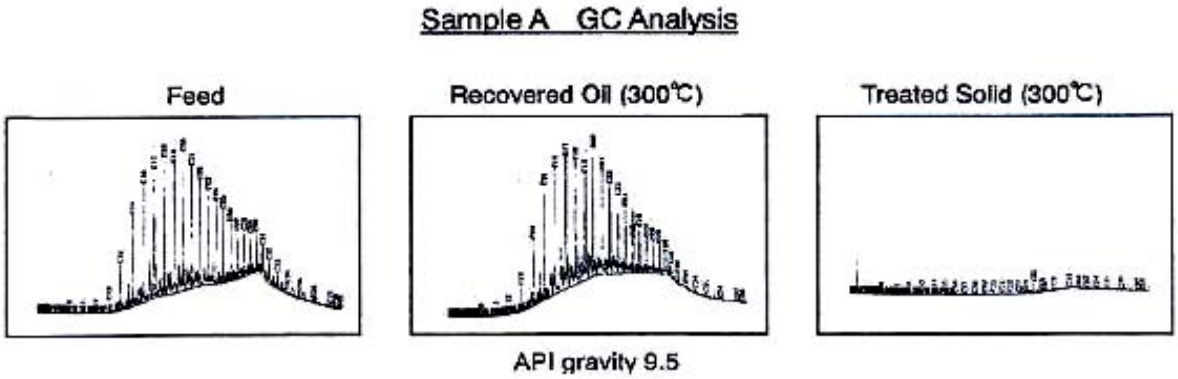


Figure 5.Analysis of sample A by gas chromatography.

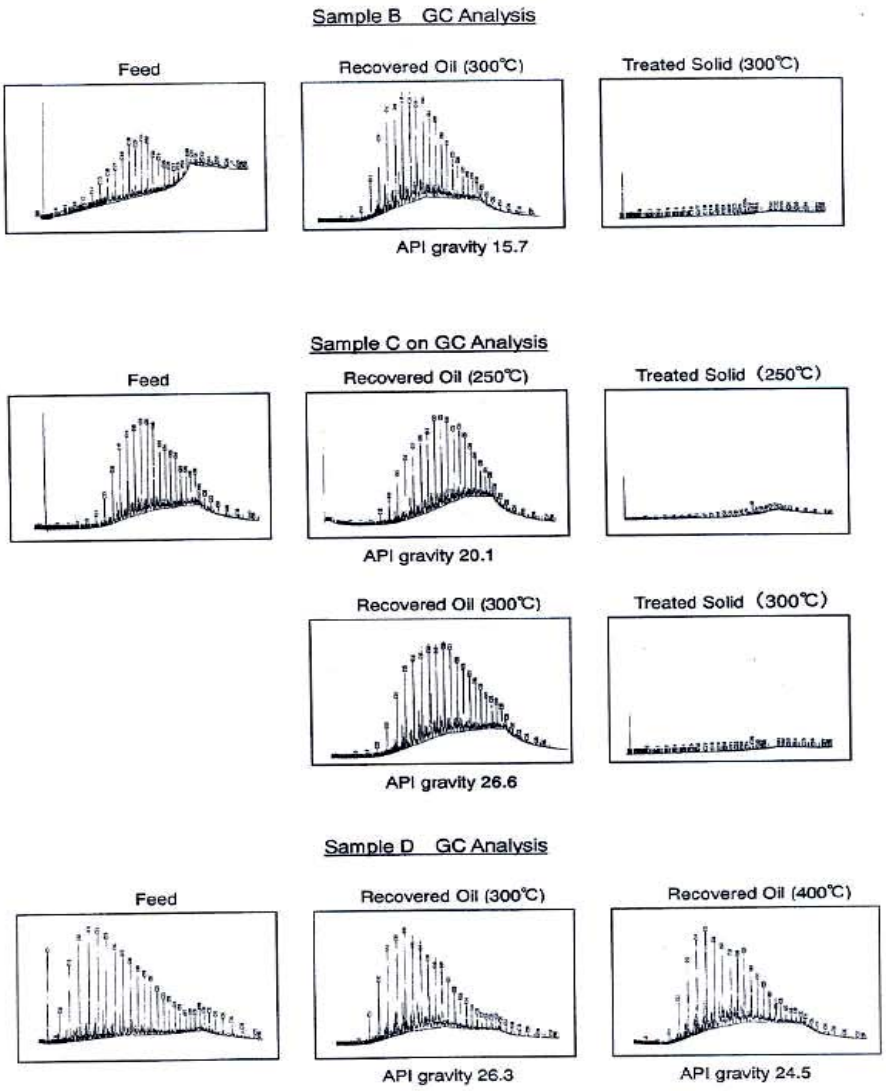


Figure 6.Analysis of samples B,C,and D by gas chromatography.

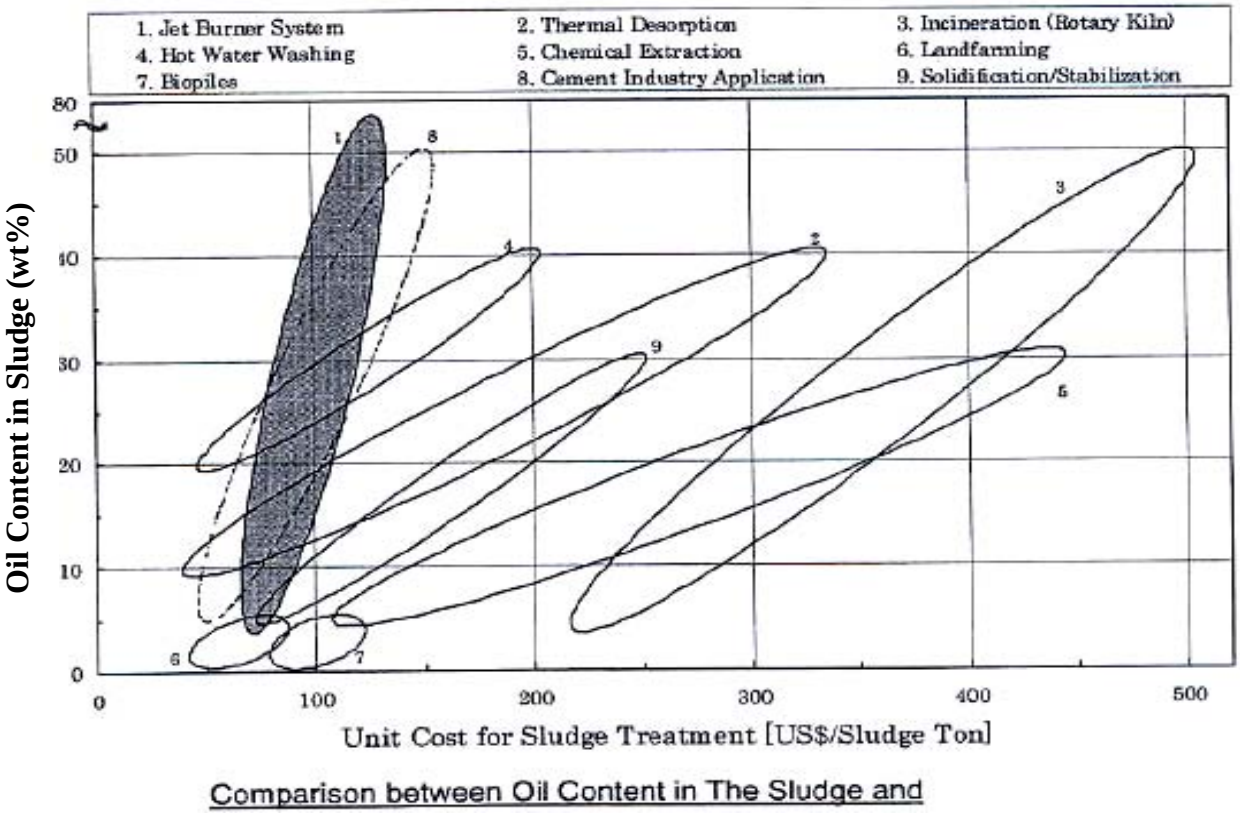


Figure 7.Comparison between oil content in the sludge and treatment costs for several applied technologies.

Restoration of Brine and Oil Contaminated Marshlands by Cationic Exchange and Chemical-Biological Stabilization

Randy H. Adams, J. Abisenas Alvarez R., Conrado Tinal O., and Francisco J. Guzman O.
Juarez Autonomous University of Tabasco (UJAT), Academic Division of Biological Sciences
Km 0.5 Carretera Villahermosa – Cárdenas, Villahermosa, Tabasco, México CP 86104
Tel.: (52-993) 391-6538, Fax: (52-993) 354-4308
e-mail: drrandocan@hotmail.com

ABSTRACT

Organic rich soil, containing 21 % and 56 % organic matter, was collected from a marshy area in southeastern Mexico from a tropical environment. The marsh had been contaminated by brine and oily water over several decades. The soil was treated serially by cationic exchange and chemical-biological stabilization. Cationic exchange resulted in a 60 % reduction in electrical conductivity (EC) , ~ 65 % reduction in de sodium adsorption ratio (SAR), and ~ 70 % reduction in the sodium ion concentration [Na^+]. Treatment by chemical-biological stabilization resulted not only in the remediation of of hydrocarbon-caused impacts to the soil, but also mitigated brine caused impacts, reducing the EC roughly 30 % more, reducing the SAR 20 – 30 %, and the [Na^+] ~ 25 %. Final values were EC = 1.8 dS/m, a SAR of 0.5 – 0.6, a [Na^+] of 3.5 – 3.7 cmol(+)/Kg, and a pH of 8.3. The chemical-biological stabilization also resulted in the elimination of of hydrocarbon leachates (< 1 mg/L TPH), and reduced toxicity to background levels. Comparison with data from other studies, indicated that the final values are appropriate for the type of salt marsh/mangrove vegetation native to this area. Subsequent planting with marsh fimbry resulted in establishment, vigorous growth and reproduction.

Adams, R. H., Alvarez R., J. A., Tinal O., C. and Guzman O., F. J. Restoration of Brine and Oil Contaminated Marshlands by Cationic Exchange and Chemical-Biological Stabilization. 12th International Environmental Petroleum Conference. International Environmental Petroleum Consortium (http://ipec.utulsa.edu) Houston, Texas 7 – 11 Nov. (2005).

INTRODUCTION

In southeastern mexico, there are many contaminated, marshy areas, the result of historical practices in production and refining involving very little environmental awareness or concern (1). One location typical of this kind of chronic contamination is a marsh downhill from a former gas and petroleum refining plant located in western Tabasco State, and consisting of approximantely three hectares of nearly barren marshlands covered with very weathered hydrocarbons and having salt concentrations in some places upto four times sea level. Toxicity in some places is also between four and nine times background levels as determined by Microtox bioassays (2). Possible treatment methods for these kinds of areas include bioremediation, chemical-biological stabilization, and cationic exchange. The purpose of this study is to evaluate a combination of techniques which mitigate the damaging affects caused by hydrocarbons and salts so that these kinds of areas can be restored and used according to their natural vocation and in agreement with Mexican environmental law. Prelimnary results are presented.

METHODOLOGY

Organic rich surface soil was collected near a former refining plant. The area is located in an ecotone between a white mangrove forest and a brackish marsh (3). This material was homogenized and placed in plastic pans (diameter: 55 cm, height: 40 cm, depth ~15 cm). After observing that the material obtained differed with respect to organic matter content and texture, it was seperated into different batches. Sufficient material was obtained for one kind of material to experiment in three replicates (Batch 2), but not of the other material (Batch 1), for which no replicates were possible. Subsequently, cation exchange leaches with calcium nitrate (equiv. 2.76 ton/Ha each) were realized followed by a freshwater rinse. Calcium nitrate was used instead of calcium sulfate due to lack of availability in southeastern Mexico. After the cation exchange, the material was treated by chemical-biological stabilization according to Adams, (2004, ref. 4) using two dosings of calcium hydroxide and an organic ammendment, to reduce toxicity and soil leachates. Finally, the soil was planted with a salt tolerant species native to the study area, marsh fimbry (*Fimbristylis spadicea*). TCLP leachates were determined (5,6) as well as residual toxicity (Microtox bioassay, 7).

RESULTS & DISCUSSION

In figures 1 – 3 results for [Na^+], EC, and SAR are presented. The initial pH was 7.0 and 6.5 in Batches 1 and 2, respectively, rising to 8.3 in both batches following treatment. Cation exchange treatment reduced the EC ~ 60 %. In the stabilization treatment, besides mitigating hydrocarbon caused impacts to the soil, an extra benefit was obtained consisting in a reduction of an additional ~ 30 % in EC in both batches. With respect to sodicity, similar results were obtained, with a reduction on the sodium ion concentration of ~ 70 % due to the cation exchange treatment, and a reduction of ~ 25 % due to the stabilization treatment. This tendency was also repeated for the Sodium Adsorption Ratio (SAR), being reduced by ~ 65 % in the cation exchange treatment, and 20 – 30% by stabilization treatment, with final values of 0.5 – 0.55, see figures 1 – 3 (8).

In Table 1 initial and final values for EC, SAR and pH are presented and compared with results obtained in other studies. The background levels shown are from a previous study in a mangrove forest about 200 m from the site. As shown in this table the values obtained in the treated soil are very similar to background and within the range of tolerance of native plant species. With respect to salinity parameters (EC, SAR) the treatment reduced these values much more than was necesary for this kind of vegetation and soil use. Considering that the chemical-biological stabilization alone was able to reduce these values aproximately 70 - 90 % (with reference to those values after cation exchange and before stabilization treatment), it is probable that this treatment alone (without previous treatment by cationic exchange) could have reduced the EC to 4 – 13 dS/m, and the SAR to roughly 1 - 4. This treatment in and of itself would probably of been sufficient to remediate salt caused impacts to the soil so that it could be used for a salt marsh or mangrove forest.

The chemcial-biological stabilization also resulted in a reduction in the toxicty to background levels in both batches (9). TCLP leachates were < 1mg/L in all treatments (non detect – 0.9 mg/L). Furthermore, this treatment resulted in an improved texture (less clayey) and soil structure (see figure 4). These improvements in soil fertility allowed the marsh firmbry to become established, grow vigorously, and reproduce, both vegatatively and sexually (figures 6 and 7).

CONCLUSION

Chemical-biological stabilization improved soil structure, reduced toxicity to below background and also reduced TCLP leachates to acceptable levels. Furthermore, this kind of stabilization not only was effective in overcoming hydrocarbon caused impacts to the soil, but also in restoring brine caused impacts: it resulted in an additional reduction of 30 % in the EC, and a 20 – 30 % reduction in the SAR, with final SAR values of 0.5 – 0.6. Predictions based on these results suggest reductions in EC and SAR values of roughly 70 – 90 % if only the chemical-biological stabilization had been employed without a pre-treatment by cation exchange. Chemical – biological stabilization is an ecnomically viable complement in tropical and semitropicial environments to other, mostly chemical, treatments for brine impacted sites, and it is especially useful to treat areas that are contaminated by both brine and hydrocarbons. Furthermore, it is very probable that chemical-biological stabilization can be used as a stand alone technology for treating areas moderately impacted by brine, without the need for other preliminary chemical treatments.

ACKNOWLEDGEMENT

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Table 1. Comparison of Conditions in Treated Soil to Background and Appropriateness for Use in Salt Marsh/Mangrove Forest.

Treatment or Reference	**EC (dS/m)**	**SAR**	**pH**
Batch 1 initial conditions	16.5	6.3	7.0
Batch 2 initial conditions	43.3	14.4	6.5
Batch 1 after treatment	1.8	0.50	8.3
Batch 2 after treatment	1.8	0.55	8.3
Batches 1- 2 predicted results if only chemical – biological stabilization had been employed (without cation exchange treatment)	4 - 13	1 - 4	8.3
Background (Mangrove, Zavala *et al.*,1999)			
Range	19.9 – 52.5	6.7-12.1	6.6 – 7.8
Average	32.4	9.5	7.2
Superficial Horizons	36.2	9.4	6.8
Salt Marsh – Marsh Fimbry (*Fimbristylis spadicea*) (Hmieleski,1994)			8.1
White Mangrove Forest (*Laguncularia racemosa*) (Little, 1983)			6.0 – 8.5

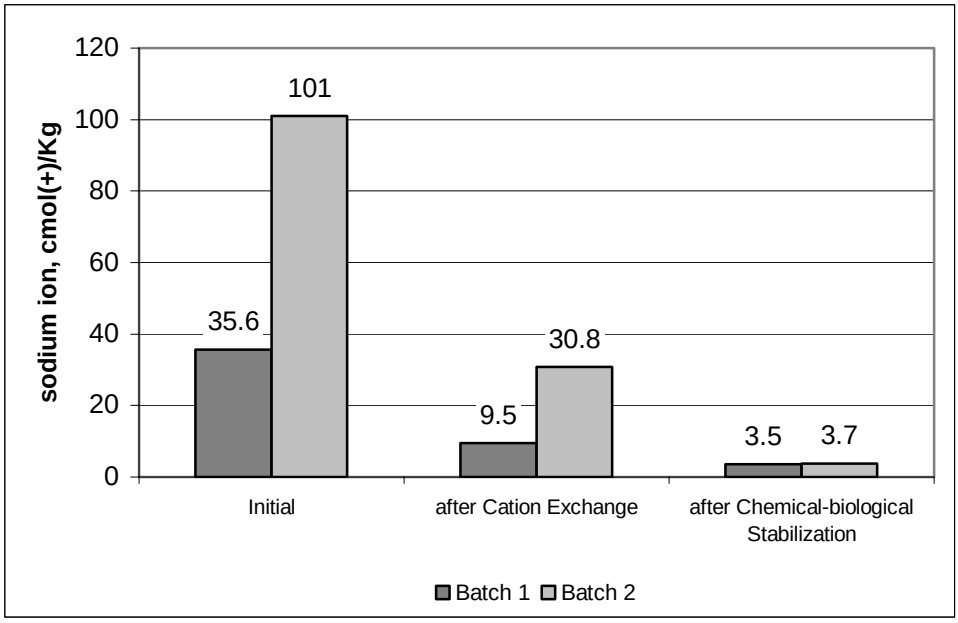

Figure 1. Reduction in sodium ion concentration with serial treatment.

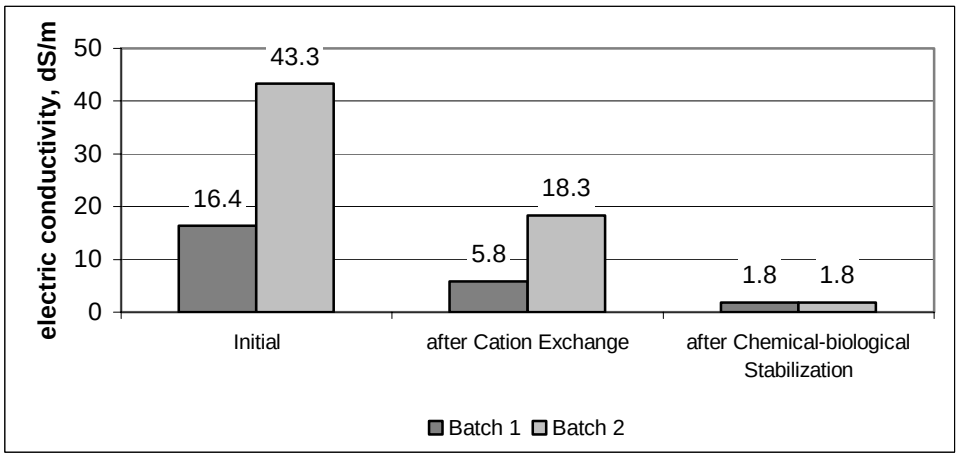

Figure 2. Reduction in electrical conductivity with serial treatment.

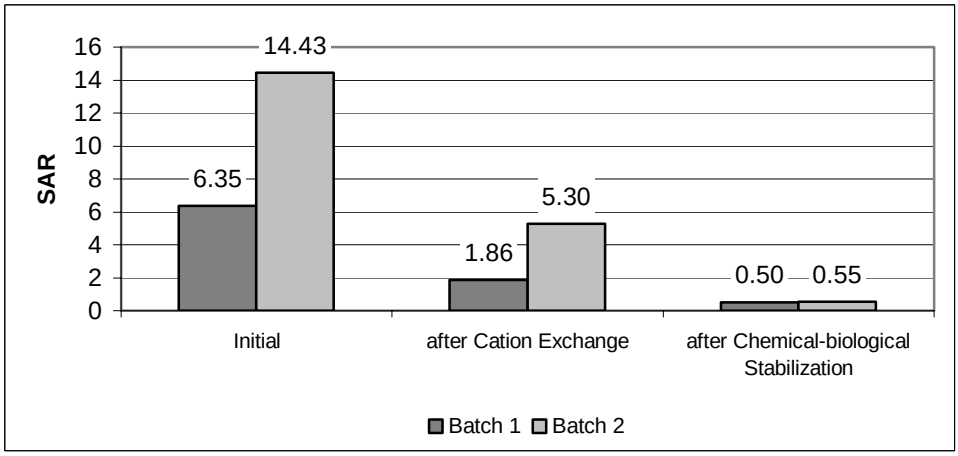

Figure 3. Reduction in the sodium adsorption ratio (SAR) with serial treatment.

Figure 4. Changes in consistency with stabilization treatment.

Figure 5. Cation exchange treatments.

Figure 6. Initial establishment and vegetative reproduction of marsh fimbry.

Figure 7. Vigorous growth of marsh fimbry in treated soil after first cutting.

Environmental Concerns in Real Estate Transactions

by Ann R. Barker
Baker Petrolite Corporation

Real Estate Transactions and Issues

Background

Since the early 1980s, federal and state legislation has been enacted that has made environmental liability issues a matter of significant concern in many commercial and industrial real estate transactions. During this time, the cost to clean up often presented multi-million dollar liabilities, and the legal theories used to collect on those liabilities involved multiple parties and years of legal and consulting fees, in addition to cleanup costs and possible penalties or fines. Because of the heavy potential liability costs, the demand for information about sites emerged in a number of ways and to some degree before standards of practice had been developed. Variations in practice and procedure to gain the desired information also fueled some of the real estate litigation during this period. Because various parties to a transaction, (i.e., purchasers, sellers, lenders, attorneys investors, real estate brokers, landlords, tenants), often had competing or unique interests, the need to develop a recognized and accepted standard of practice became obvious. The need for a more uniform and reliable standard of practice for environmental assessments was also driven by the various types of transactions (i.e., corporate acquisitions and divestitures, bankruptcy, estate management, and investment)(1).

Due Diligence

"Due Diligence" is the term used to describe the general process by which parties involved in a commercial or industrial real estate transaction obtain information on the environmental condition of the property and inform themselves on whether the property is environmentally sound or presents a risk of future liability. The scope of due diligence has varied greatly over the past twenty years. Even after the advent of recognized and accepted standards for conduct of due diligence, those standards vary depending upon the transaction type and/or level of known risk associated with the property (i.e., Transaction Screen, Phase I Environmental Assessment (ESA), and Phase II Site Assessment). These standards will be discussed in more detail below.

In general, due diligence incorporates some form of preliminary evaluation and/or Phase I ESA so that a purchaser or lender may quickly determine whether they have no further interest in the property because of high potential risk of liability. Today most transactions begin with a Phase I ESA because very few lenders will participate in a transaction without one. If a Phase I ESA shows evidence of "recognized environmental conditions"(2), the parties may move to the next step, a Phase II Site Investigation (SI), which will include intrusive site investigation (i.e., soil or groundwater sampling and testing). If the Phase II confirms that the site is contaminated then the parties may cancel the transaction, or proceed with negotiations to account for the environmental liabilities.

Due diligence is essential to allow prospective purchasers to reduce the probability that they may purchase contaminated property and be subject to expensive cleanup and to have the necessary evidence to satisfy the "*all appropriate inquiry*" standard. Satisfying this standard is necessary to qualify for the various defenses to liability available under federal Superfund and most state cleanup liability laws(3).

Site Assessment

Responsible parties to corporate transactions and real estate acquisitions, leasing of property, lending of money, creating of security interests, among other things, now require that some form of environmental audit or site assessment be conducted to identify and quantify environmental liabilities, to the extent possible. These steps are necessary to properly value the assets and determine whether to go forward with the transaction, and/or negotiate reasonable terms and conditions. A site assessment can establish an environmental baseline as protection against future cleanup costs or enforcement action. Sometimes lenders and lessors may negotiate to conduct assessments or audits periodically during the term of the loan or lease to ensure that on-going operations are not creating environmental liabilities(4).

Transaction Screen Process

The ASTM Transaction Screen Process is a general site assessment that typically includes the following (1) asking questions contained within the transaction screen questionnaire of owners and occupants of the property, (2) observing the site conditions of the property with direction from the questionnaire, and (3) ducting a limited research and review of governmental agency records, databases and standard historical sources. This process may be conducted by an environmental professional, purchaser, or lessee. The analysis is based on reasonable business judgment and the totality of the answers provided to the questionnaire and any unresolved or unknown issues. If questions in the questionnaire are answered in the affirmative or the answer is unknown, then additional information must be obtained or the rationale for determining that no further inquiry is warranted must be documented. If additional inquiry is warranted, then it may be limited to the open questions or proceed to a full ASTM Phase I ESA conducted by an environmental professional(5).

Phase I Environmental Site Assessment

In the early 1990s, the American Society for Testing and Materials ("ASTM") organized a group with representatives from industry, real estate, banking, engineering, consulting, and environmental protection to work on better defining "the good commercial or customary practice." The effort produced the E 1527-93: Standard Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process. This standard was originally published and almost immediately accepted as the "due diligence" standard for commercial and industrial real estate transactions. The standard has been revised twice, with the last revision in 2000 and continues to be the standard for conduct of "all appropriate inquiry" until EPA publishes its final regulations(6). It is expected that ASTM will revise the standard to be in accord with the regulations following final promulgation.

A Phase I ESA includes four major elements:

- records review
- site reconnaissance
- interviews with owners or occupants and with government officials
- written report to the client.

The information must only be "reasonably ascertainable", which is interpreted to mean that it must be:

- publicly available,
- obtainable from its source with reasonable time and cost constraints,
- practically reviewable.

Thus, difficulty in obtaining information and the time allocated to complete the work will frequently drive the amount of detail contained in the final report. Regardless, the level of effort must be sufficient to identify recognized environmental conditions and to determine whether contamination is likely(7).

Phase II Site Investigation

If the Transaction Screen or Phase I ESA identifies a recognized environmental condition, such as staining, the presence of underground storage tanks, or historical evidence of contamination on adjacent property, additional investigation is warranted. A Phase II Site Investigation (SI) is typically performed to gain sufficient information to determine the nature and extent of contamination, if any, to make an informed business decision about the property. The ASTM E 1903-97 (2002)(8) is generally accepted as "good commercial and customary practice" in this step in due diligence for real property transactions.

The parties to a transaction usually negotiate the level and extent of the investigations. Nevertheless, the typical Phase II SI has four main components:

- developing a scope of work,
- conducting assessment activities,
- evaluating and presenting the data, and
- presenting the finding and conclusions.

In some cases the SI may be conducted in stages, with each stage being more detailed and/or intrusive, with the option to cease if parties have obtained sufficient information to make an informed business decision concerning purchase, lease, or lending for the real property. The report should be clear, concise, unambiguous and legally defensible to support decisions concerning the property(9).

Environmental Liability

Purchasers of real estate acquire the property subject to applicable environmental regulations that restrict use of the land and subject the owner to liabilities imposed by applicable environmental programs. Generally, the regulatory authority will look to the owner of the property or the operator of enterprise that involves hazardous substances if issues of contamination surface. That is not to say that the parties to a real estate transaction may not find various contractual mechanisms to shift those responsibilities or liabilities(10), but the government will look first to the land owner. Both federal and state Superfund statutes create liability and withdraw protective defenses for owners and operators who know of hazardous substance contamination and fail to disclose that to purchasers(11).

Federal Laws

Pollution prevention programs and chemical regulatory programs may affect real property transactions because they frequently give rise to substantial liabilities for prior activities conducted in violation of the requirements. Liabilities associated with current or historical on-site conditions may arise out of the following federal programs and statutes:

- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C. §§ 9601-9675, commonly known as Superfund, was enacted in the 1980 to address the unregulated historic disposal of hazardous substances. The liability structure is set very wide to capture numerous parties, including the current owner, even if the owner was not involved in the disposal

of contaminants. CERCLA created the concept of strict, joint and several, and retroactive liability. Defenses to Superfund liability are discussed below.

- Resource Conservation and Recovery Act, enacted in 1976, was amended in 1984 to require cleanup of contamination from improper waste management practices that occurred at RCRA-permitted facilities, providing for corrective action for releases migrating beyond the property boundary and to abate imminent and substantial hazards caused by releases of solid or hazardous waste(12).
- Underground Storage Tank Program was an amendment to RCRA that regulates underground and above ground storage tanks containing petroleum or hazardous substances and provides a cleanup liability scheme(13).
- Toxic Substances Control Act establishes the programs for regulation of Polychlorinated biphenyls; ("PCBs"), asbestos, and lead paint abatement(14);
- Occupational Safety & Hazard Administration imposes requirements on building owners and operators relating to building demolition or renovation because of the presence of asbestos(15); and

State Laws

Many contaminated sites in the United States do not meet the strict requirements for listing under Superfund or fit into the RCRA corrective action program; however, these sites are frequently covered under state remedial action programs. There are a variety of state-specific remediation programs, but typically include the following:

- State "Mini-Superfund" Statutes – many states have cost recovery statutes similar to Superfund(16);
- Risk Reduction or Corrective Action Programs – programs of risk-based corrective action for remediation of releases of toxic and hazardous substances(17);
- Brownfields Redevelopment / Voluntary Cleanup Programs – incentives for clean up of contaminated land, and frequently provides liability defenses for voluntary state-law mandated cleanup(18); and
- Contaminated Land Transfer – liens authorized to secure cleanup costs incurred by regulatory agency(19).

Limited Liability Defenses

Federal Superfund provided certain limited defenses to its strict liability scheme: (1) the act of a third party, (2) act of god, or (3) act of war. The last two defenses were pretty unlikely to be invoked, and it was not particularly easy to succeed in claiming the Third Party Defense:

1. release was caused by third party;
2. owner did not have contractual relationship with third party;
3. owner took reasonable actions against the acts or omissions of the third party; and
4. owner exercised due care regarding hazardous substances at the property.

To reduce the harsh effects of the strict liability provisions of federal Superfund liability, the innocent owner defense was added as part of the first set of amendments to Superfund (Superfund Amendments and Reauthorization Act, "SARA")(20). This defense allows that even with a contractual relationship the purchaser could gain innocent landowner status if after conducting a due diligence inquiry, he had no reason to know that any hazardous substances were disposed on the facility. This language became a primary driver for performance of due diligence to meet the "*all appropriate inquiry*" standard before completing a real estate transaction. Although the innocent owner defense provided some limited protection for those purchasers who,

after performing *all appropriate inquiry* did not detect contamination at the site, this defense did not solve problems of liability attaching at those sites with known contamination or where due diligence had not been adequate. Thus, environmental liability remained as a significant obstacle to development of existing commercial and industrial property with evidence of contamination.

CERCLA Amendments and "*all appropriate inquiry*"

The Brownfields Act(21), which became law in January 2002, modifies CERCLA to encourage development of properties that are contaminated or are perceived as contaminated(22) and to recognize liability exemptions for certain parties who might be liable for the cost of cleaning up site contamination at Superfund sites. The law recognized the previous "innocent landowner" defense and added two additional new defenses:

- bona fide prospective purchaser; and
- contiguous property owner.

The innocent landowner defense, as describe above, allows a purchaser of property to qualify for the third party defense notwithstanding a contractual relationship with the party responsible for the contamination, provided the person undertook *all appropriate inquiry* into the previous ownership and uses of the property consistent with good commercial or customary practice in an effort to reduce liability and did not know or have reason to know of the existence of hazardous substances.

To qualify as a bona fide prospective purchaser, a person must not be affiliated with the party responsible for the contamination and be able to establish the following:

- Disposal occurred prior to acquisition;
- Made *all appropriate inquiry* into the previous ownership and uses of the facility under good commercial and customary standards and practice;
- Provided all legally required notices;
- Exercised appropriate care with respect to hazardous substances to stop any continuing release and preventing future releases and human, environmental and natural damage exposures;
- Fully cooperated with party authorized to conduct response or natural resource restoration action;
- Complying with land use restriction and is not impeding institutional controls; and
- Responds to requests for information.

The Act also creates a landowner defense for persons who own real property that is contiguous to land that is or may be contaminated by hazardous substances by a release from real property not owned by that person; However, the owner must take reasonable steps to stop the release and observes the other continuing obligations that are set out below.

All Appropriate Inquiry (AAI) – Redefined

In the past, the "good commercial or customary practice" was sometimes open to debate, but generally regarded as contained in the ASTM Phase I ESA Standard. However, the Act now defines the standards for *all appropriate inquiry* and set a two-year deadline by which EPA must promulgate regulations for implementation of the standard, which must include the following:

- Inquiry conducted by an environmental professional;
- Interviews with past and present owners, operators, and occupants;
- Review of historical sources;
- Searches for recorded environmental cleanup liens;
- Review of governmental and other records

- Visual inspection of the facility and adjoining properties;
- Specialized knowledge or experience on the part of the defendant;
- Relationship of purchase price to value of property if property was not contaminated;
- Commonly known or reasonably ascertainable information about the property and
- Degree of obviousness of presence or likely presence of contamination of property, and ability to detect contamination by appropriate investigation(23).

The EPA published the new AAI definition and standards in August of 2004(24). The regulations were the product of a stakeholder rulemaking committee with many of the same commercial and industrial interests that were involved in development of the ASTM standard. The regulation has received so many comments that EPA is now estimating that the response to comments and final will rule will not be published until sometime in early 2006.

The new AAI regulations seem to require a more involved assessment than is currently conducted under ASTM. The AAI is more performance-based allowing discretion on the part of the environmental professional, as long as the investigation is successful in detecting any existing or threatened releases of hazardous substances. The new AAI seems to ratchet up the level of due diligence and is likely to have significant short-term effects on commercial / industrial real estate transactions. The breadth of investigation, time necessary for investigation, and cost of due diligence under the AAI standard are very likely to increase.

The following elements of the new AAI standard depart from the ASTM standard and broaden the scope of inquiry(25):

- Interviews – requires interviews with a wider range of individuals with knowledge of the property, including past and present owners and operators, employees of current and past occupants, current and past facility managers with relevant knowledge, and (if abandoned property) owners and operators of nearby property;
- Visual Inspection – requires a more comprehensive visual inspection of adjoining properties
- Review of Government Records – goes further that the ASTM required government databases, listing categories of federal and state records that must be reviewed (i.e., records of public risks & public health threats; registries of engineering controls, institutional controls, and land use restrictions, etc.);
- Data Gaps – requires a final report that acknowledges areas of uncertainty (data gaps) that impact conclusions;
- Environmental Cleanup Liens – requires search for environmental cleanup liens under federal, state, tribal, or local laws;
- Timing of AAI – requires that certain inquiries must be conducted six (6) months prior to the date of purchase of the property: interviews with past and present owners, searches of recorded liens, reviews of governmental records, visual inspections, and the environmental professional's declaration (if a transaction is delayed, then certain elements may have to be updated); and
- Environmental Professional(26) - AAI must be conducted by an "environmental professional" who meets certain elevated educational, training and experience requirements (this may limit the number of consultants authorized to perform ESAs and increase the cost)(27).

Table I – ASTM – AAI Element Comparison(28)

ASTM	Issue	AAI
Users identified back to "1st developed use or back to 1940	Research	Review back as far as "it can be shown that the property contained structures or from the time property was 1st used for residential, agricultural, commercial, industrial, or governmental purpose
Identifies 8 standard historical sources: aerial photos, fire insurance maps, property tax files, recorded land title records, topographic maps, local street directories, building dept. records, and zoning/land use records	Historical Sources	Environmental Professional judgment determines which specific historical sources are reviewed
Environmental professional explain the reason for any gaps in history of the property use	Data Gaps	Environmental professional must identify data gaps, document all sources of information consulted to resolve data gaps, comment upon significance of gaps.
No specific requirement for research	Abandoned Site	Interviews with 1 or more of owners/occupants of near by properties from which one could observe abandoned properties are mandatory
No specific requirement to interview person who know about prior operations	Interview Past Occupants	Environmental professional should interview current and past facility managers, past owners, occupants or operators, or employees of current and past occupants

Continuing Obligations

Under the new Act, a person must not only conduct a due diligence inquiry under the AAI criteria established under the Act, but must also take "reasonable steps" to stop any continuing release, prevent any threatened future release, and prevent or limit any human, environmental, or natural resource exposure to any previously released hazardous substances. The additional obligations that are necessary for a purchaser to preserve its status as an innocent owner include:

- cooperate with response actions and natural resource restoration;
- comply with and not undermine the effectiveness or integrity any land-use restrictions or institutional controls; and
- provide access to persons authorized to conduct response actions at the facility to operate, maintain, or otherwise ensure the integrity of land-use controls that may be a part of a response action.

Thus, a purchaser can qualify for the innocent landowner defense up-front, but still be compelled to perform certain acts to remain qualified for the protections of the defense.

Conclusion

With every commercial / industrial transaction comes the need for due diligence and a clear understanding of actual and probable environmental liabilities for every purchaser. While the prior ASTM standard and statutory defenses have provided some level of assurance in the past, the various stakeholders have been working together to seek greater clarity and a greater degree of assurance that purchasers could avoid environmental liability. Unfortunately, the most recent changes to the *all appropriate inquiry* standard under the Brownfields Act do not seem destined to provide that greater clarity or appear adequate to ensure that the purchaser will qualify for key environmental liability defenses. In real estate transactions, all parties must be fully

informed on the new AAI standard, the new continuing obligations, and the potential for increased costs associated with both. A purchaser's focus must be the same as before changes to the law, i.e., taking reasonable and appropriate steps to assess the environmental risks associated with a specific site and taking appropriate action to minimize the risk of future liability.

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2. "Recognized environmental condition" is defined as the presence or likely presence of any hazardous substances or petroleum product under conditions that indicate an existing release, a past release, or a material threat of release of any hazardous substance or petroleum products into structures on the property or into the ground, groundwater, or surface water of the property.

3. *Texas Practice: Environmental Law*, Vol. 46, § 32.9, 2005 ed.

4. Geltman, Elizabeth, *Environmental Issues In Business Transactions*, Vol. 1, § 2.1, 1995ed.

5. *Id*. at § 2.1.4.1.

6. Federal Register, Vol. 68, No. 90, pg. 24888, May 9, 2003.

7. *Id*. at § 2.1.4.2; see also *Site Auditing* § 3A-1.

8. ASTM standards are reviewed or updated every five years to ensure continued reliability and credibility. This standard was re-approved "as is" in 2002.

9. *Site Auditing*, § 4A-1.

10. Typical liability shifting mechanisms include the following: price adjustment, cleanup prior to closing, risk allocation, liability sharing agreements, indemnification and support mechanisms (bond, letters of credit, escrow accounts, etc), insurance, carve out of contaminated property, and limitations on damages. Geltman, Elizabeth, *Environmental Issues In Business Transaction*s, Vol 2. Ch. 26, 1995 ed.

11. *Texas Practice: Environmental Law*, Vol 46 § 32.9.

12. 42 U.S.C §§ 6901 – 6992k; see also RCRA § 7003, 42 U.S.C § 6973.

13. 42 U.S.C §§6991 – 6991i.

14. 15 U.S.C §§ 2601 – 2692.

15. 29 C.F.R. § 1910.1001 and § 1926.58 (construction standards).

16. Tex. Health & Safety Code Ann. § 361.197; La. Rev. Stat. Ann. § 30:2171; Ark. Code Ann. § 8-7-401.

17. See Texas Risk Reduction Program, 30 T.A.C. ch. 350.

18. Tex. Health & safety Code Ann. §§ 361.601 - .613. In addition, Oklahoma Voluntary Cleanup Program contains special provisions that include sites regulated under RCRA, and EPA may suspend response actions for sites being cleanup under the VCP.

19. See La. Rev. Stat. Ann § 30.2225(F), Ark. Code Ann. § 8-7-516, and Ill. Rev. Stat. ch.415 § 5/21.3.

20. Pub. L. No. 99-499, Oct. 17, 1986.

21. The Small Business Liability Relief and Brownfields Revitalization Act [Pub. L. No. 107-118; 42 U.S.C. Sec 19601, et. Seq.].

22. The Brownfields Act provides funding to state brownfields programs and local governments who seek to return contaminated properties to productive use.

23. For property purchased before May 31, 1997, courts must follow a prescribed set of factors, for property purchased after that date but before the EPA promulgates rules, ASTM standards satisfy the requirements for all appropriate inquiry, and for residential property a site inspection and title search that reveal no need for further investigation are adequate.

24. Federal Register, Vol. 69, No. 165, August 26, 2004.

25. Nasi and Abazari, "The Reshaping of CERCLA Liability – Are Landowners Really Better Off?", Seventeenth Annual Environmental Superconference, August, 2005.

26. See 40 C.F.R. § 312.10, "Environmental Professional:, Federal Register 26, 2004, Vol. 69, No. 165.

27. The EPA requirements are in accord with the general movement toward professionalizing of environmental auditors (e.g. the Board of Environmental Auditor Certifications and ISO 14015 for site assessment other audit services).

28. All Appropriate Inquiry/Due Diligence, Consultant's Perspective, Chapin, Bob, Weston Solutions, Inc., Seventeenth Annual Texas Environmental Superconference, August 2005.

Natural Attenuation of PAHs and Heterocyclic Organics in Groundwater: 10 Years of Experience with a Controlled Field Experiment

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Jim Barker, Michelle Fraser, Fred Blaine, Department of Earth Sciences, University of Waterloo, Waterloo, ON CANADA N2L 3G1. Caitlin Cooke, Golder Associates Ltd., 32 Steacie Drive, Kanata, ON CANADA K2K 2A9

ABSTRACT

In 1991 74 kg of coal tar creosote was emplaced below the water table within the sandy Borden Research Aquifer. The lateral groundwater flow at 9 cm/day produced plumes of dissolved chemicals. A detailed network of multilevel monitoring wells provided four major and four minor "snapshot" samplings of > 500 points each time. Nine organics were followed for ten years. Phenolic compounds were essentially completely dissolved from the source within 278 days and vanished from the plume within about 626 days. Xylenes were also strongly attenuated by day 1357. By day 1357 the plume of dissolved naphthalene was most extensive, almost 60m long, but then began to shrink. Quantitative analysis of the dissolved plumes through numerical modeling including consideration of sorptive retardation and biotransformation has proved problematic. After 10 years, dissolved plumes of acenaphthene, anthracene, carbazole, dibenzofuran and phenanthrene continued to slowly expand, but did not extend 50 m. Natural biotransformation has played a leading role in limiting the extent of dissolved chemicals leached from this small coal tar creosote source.

INTRODUCTION

Coal tar creosote is a complex mixture of aromatic, heteroaromatic and phenolic compounds. Similar tars are common waste products in the petroleum, coal and wood preserving industries (1). When creosote enters the subsurface, different solubility and sorptive properties of the compounds generate a number of overlapping individual compound plumes. Natural attenuation processes such as sorptive retardation and biodegradation may restrict the extent of these plumes.

In 1991, 74 kg of coal tar creosote liquid (Non-Aqueous Phase Liquid or NAPL) was mixed with 5800 kg coarse sand and emplaced in the University of Waterloo research sand aquifer at Canadian Forces Base (CFB) Borden (2). CFB Borden is approximately 80 km northwest of Toronto, Ontario, Canada. Two sources were emplaced, each 1.5 m deep, 2 m wide (perpendicular to the horizontal groundwater flow) with about 1 m between and 0.5 m thick. The top was 2 m below ground surface and about 0.5 to 1.5 m below the water table. The coal tar creosote NAPL was emplaced at below residual concentrations in the sand so the NAPL should not have been mobile. This aquifer is probably the most highly characterized aquifer in the world. It consists of relatively uniform medium to fine grained unconsolidated sand. Groundwater flow is essentially horizontal at about 9 cm/day. Organic carbon-dominated sorptive retardation is small as the fraction of organic carbon in the aquifer is only about 0.0002. King and Barker (2) summarize the aquifer properties. In situ oxidation was undertaken in 2001 and so this paper reports the extent of natural attenuation in this experiment over the 10 year period from 1991 to 2001.

PLUME MONITORING AND DATA ANALYSIS

The dissolved chemical plumes migrated through an existing network of over 280 multi-level samplers (2). The typical sampler has 14 vertical ports at 20 or 30 cm intervals over the depth interval of 1.5 to 5 m below ground surface. The spacing between multi-levels is 1 meter or less near the source and increases to 4 meters at the downgradient end of the network.

The plume has been sampled for organic chemicals and electron acceptors. The sampling dates or snapshots of interest for this study occur on days 278, 626, 1357, 2900, and 3619 after source installation. Up to 25 days was required to complete some of the latter sampling. On day 2110 a funnel and gate system was installed about 25 m downgradient from the source and so the behaviour of the plume beyond this distance was affected both physically and chemically. Minimal organic removal was noted and so this remediation research experiment has not significantly impacted the findings reported here (3). From 450 to 1630 points were analysed at each snapshot for: phenol, m-xylene, 2,6-dimethylpnenol, naphthalene, 1-methyl naphthalene, acenaphthene, biphenyl, phenanthrene, anthracene, dibenzofuran, carbazole and pyrene. In addition, select points were analyzed for electron acceptors (oxygen, nitrate, sulphate) and reduction products (Fe^{2+}, methane) and some anaerobic metabolites were also sought (4).

A number of data manipulations were undertaken to evaluate the migration and attenuation (mass loss) of chemicals from this source. Data were plotted to illustrate the lateral distribution of chemicals at the 5 snapshot times (Techplot version 8.0; Amtech Engineering Inc., 1999). These contour plots use the maximum concentration detected at each multi-level well for a particular sampling event. Contours start at the fence approximately 3.7 meters down gradient from the source.

Second, input of dissolved chemicals from the source to the dissolved plume was estimated by monitoring 8 to 15 multilevel wells (112 or 210 points) near the downgradient end of the source zone (3.7 m from the emplaced source). A program called Average Flux written by Robert McLaren at the University of Waterloo was used to calculate the flux across the fence by interpolating the known concentration at each sampled point to a dense grid. There is a significant and poorly-understood uncertainty associated with this estimate of flux from the source zone into the plume. This uncertainty is under review and so results are not presented here.

The mass leached from the coal tar creosote NAPL and input to groundwater as it flowed through the source was also estimated by calculating the expected rate of dissolution from the NAPL using Raoult's law. Raoult's law has been found to be a reasonable (factor of 2) prediction of NAPL source dissolution in this (2) and other experiments in the Borden aquifer (5). The mass of chemical present in the plume is both dissolved (M_D) and sorbed onto aquifer solids (M_S). The estimation of dissolved mass was made by 3 dimensional interpolation of the dense sampling data for each snapshot (2). The sorbed mass was estimated using the organic carbon sorption theory assuming a linear relationship between dissolved and sorbed concentrations. The distribution coefficient, K_d, describing this relationship, was measured or estimated from batch sorption experiments and/or by empirical correlation of organic carbon keyed K_D with K_{OW} by (4). The total mass in the plume at any snapshot day (M_T) was then the sum of the dissolved and sorbed masses.

The source leachate evolution over time was also estimated using Raoult's Law as:

$$C_1^i = x_1^i S_L^i = ((M_0^i - q\,A\,\Delta t\,C_0^i) / M_0^T)\,S_L^i \qquad (1)$$

where subscripts 0 and 1 indicated t=0 and t=1. M^i is moles of *i* in the NAPL phase, q is Darcy flux through the source (0.03 m/d), A is the cross sectional area of the source perpendicular to groundwater flow (6 m^2) and M^T is the total moles of all the compounds in the NAPL phase (498 moles initially). It is assumed that all groundwater entering the source for a given Δt (25 days) equilibrated with the creosote.

A fourth manipulation was to divide the mass of an individual compound into 32 slices perpendicular to groundwater flow at increasing distance from the source. These approximately 1 meter slices each had a mass value which was then plotted versus distance from the source (3). The total mass of each chemical in the plume at each snapshot was done by summing the dissolved mass in all 32 slices and adding the sorbed mass.

FINDINGS

Figure 1 illustrates the estimated changing concentration, C, over 5,000 days, relative to the initial concentration, C_o, as predicted with equation (1). Note that the very water soluble chemicals (phenol and 2,6-dimethylpnenol) are expected to be quickly depleted in the source. This was confirmed in the field. Phenol and 2,6-dimethylphenol were not found in the plume after day 626. No significant xylene was detected in the plume after day 1357. The source zone quickly became anaerobic, so anaerobic biotransformation of phenolics and xylene isomers is likely.

Figures 2 and 3 illustrate the evolution of the naphthalene and carbazole plumes. By day 3619 the naphthalene plume was receding while the carbazole plume was still growing. Table 1 summarizes the trends for the selected chemicals. By day 3619 there was no phenol or 2,6-dimethylphenol and only about 5 g of xylenes in the plume (Table 2). The naphthalene and biphenyl

plumes were less extensive by day 3619 than at previous sampling times. Two factors may be involved when plumes shrink. The first is that there is a decline in the mass flux from the source. Figure 1 suggests this is a possible factor for naphthalene as the expected concentration of naphthalene leaching from the source is declining as the mole fraction of naphthalene in the NAPL is depleted. The shrinking of the biphenyl plume might to thought to reflect a similar source behaviour over time. However, a compound with solubility similar to biphenyl, namely anthracene, should have increased flux into the plume over time because its concentration in the source is expected to increase as the mole fraction of anthracene (and by analogy, biphenyl) increases. So the evolution of the NAPL is not the cause of the shrinking biphenyl plume. The second factor which may contribute to shrinkage of plumes such as biphenyl is an increase in the mass loss rate within the plume. There is really no simple, direct method to evaluate the rates of biotransformation from the field data.

Figures 4 and 5 show the distribution of total mass of naphthalene and carbazole in the plume at the different sampling times. For naphthalene, the mass expanded downgradient until day 1357 and then dramatically declined by day 2900. In contrast, the carbazole mass moved out, in a complex manner, until the last sampling on day 3619. The "pull back" of naphthalene after day 1357 is striking. The mass everywhere in the plume has declined precipitously. This suggests the major factor in naphthalene plume shrinkage is a decline in the flux into the plume and that little additional attenuation is occurring within the plume, save at the downgradient margin. Figure 1 suggests this decreased flux into the plume is not likely due to decreased release from the source. Rather, it would appear to be an increased mass removal, via biotransformation, before the 3.7 m monitoring fence. For carbazole, the input flux has increased on day 3619 and the carbazole mass has penetrated further downgradient. This suggests some combination of increased flux into the plume and decreased biodegradation within the plume may be responsible for the growth of the carbazole plume. Figure 1 suggest that carbazole dissolution should be decreasing, not increasing, and so the enhanced input of carbazole into the plume suggests a decline in the rate of biotransformation upgradient of the 3.7 m monitoring fence used to define the input to the plume.

Table 2 (column 2) presents the total (dissolved + sorbed) mass found in the plume on day 3619 for all chemicals. Phenol, 2,6-dimethylphenol and all xylenes isomers have essentially disappeared. Naphthalene and biphenyl masses in the plume were declining and the extent of these plumes had decreased. Acenaphthene, phenanthrene, anthracene, dibenzofuran and carbazole were still growing (extending further with increasing total plume mass). For all these chemicals the plume appears to hold much less mass at day 3619 than was likely leached from the NAPL source. This probably reflects biotransformation in the source zone and in the plume.

EXTENT OF NATURAL ATTENUATION

Figures 2 and 3 illustrate the restricted advance of the organic plumes. Naphthalene was the most extensive plume. Retardation is not a dominant control. For example, naphthalene should migrate at about 45% of the groundwater velocity (4). By day 3619 the naphthalene plume front should have been about 150 m from the source. However, naphthalene have only reached about 50 m downgradient of the source. For highly retarded chemicals the plume extent may have been controlled in part by retardation. Phenanthrene, which was expected to migrate at only 9% of the groundwater velocity (4), should have reached 30 m. It has reached 40 m (7). However, even when the sorbed mass is taken into account, 87% of the phenanthrene mass was apparently lost.

After about 10 years the mass loss due to biotransformation was impressive. Table 2 indicates the mass of selected chemicals initially present in the coal tar creosote NAPL, the mass likely leached

from the NAPL, the mass remaining in the plume (sorbed included) on day 3619 and, by difference, the mass likely leached into the plume that had been biotransformed. Note that the calculations are really approximations and not quantitative. Clearly, however, more mass was estimated to have been dissolved than was subsequently found in the plume. Even considering only the organics selected here, over 9 kg have been removed by biotransformation. This mass removal likely occurs under both anaerobic and aerobic conditions. As further confirmation of anaerobic processes, King et al. (4) note that organic acids typically produced during fermentation of aromatics were found in the plume.

The electron acceptors that appear to be most significant in organic transformation in this plume are oxygen, sulphate and Fe^{3+} (4). However, if the available electron acceptors in the background groundwater are expressed as equivalent oxygen values, only about 5 mg/L as O_2 is available. A bounding calculation can be done to estimate the significance of mineralization of organics via redox reactions. The mass of O_2 entering the source and plume by advection over the 3619 days is estimated as 6500 g. This assumes a cross section to flow of 12 m^2, Darcy flux of 0.03 m/d, and 5 mg/L O_2. A simplistic reaction assuming phenanthrene represents the degraded organics indicates that mineralization of 180 g phenanthrene would consume 540 g O_2. The 6500 g of electron acceptors (as O_2) apparently available over 3619 days would only cause 2200 g of organics to be mineralized. This is insignificant compared to the 9000 g of organic chemicals apparently biotransformed. It appears likely that fermentation reactions must account for the bulk of the biotransformation.

While the extent of mass removal in this small and well-defined coal tar creosote NAPL source and plume is impressive, we are not yet able to define the microbial mechanisms and controls. Substrate interactions are likely spatially and temporally heterogeneous and certainly modeling efforts assuming no spatial and temporal variation in biodegradation rates have had only limited success in matching even the naphthalene plume evolution (3). Further sampling to determine electron acceptors, anaerobic metabolites and redox reaction products is underway as are additional laboratory microcosm experiments under anaerobic conditions.

In this study, monitored natural attenuation has restricted the organic contaminant plume lengths to < 60 m. However, some more retarded organic plumes were still expanding. Mass loss via biotransformation was clearly a dominant control of plume length and strength, but a comprehensive understanding of the biotransformation processes has not yet been gained. Given uncertainty about the longer-term mass removal processes, more active remediation seemed warranted. In 2001, Lamarche (6) flushed an oxidant, permanganate, through the residual coal tar creosote and the long-term success in reducing the flux of organics into the plume is still being assessed.

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Table 1. Description of the behaviour of selected chemical dissolved plumes by day 3619.

Chemical	Formula	Solubility (liquid), mg/L	Plume Status
Phenol	C_6H_6O	160,000	Gone
2,6-Dimethylphenol	$C_8H_{10}O$	13,700	Gone
Carbazole	$C_{12}H_9N$	240	Growing
m, p-Xylene	C_8H_{10}	196	Gone
Naphthalene	$C_{10}H_8$	151	Shrinking
Dibenzofuran	$C_{12}H_8O$	53	Growing
1-Methylnaphthalene	$C_{11}H_{10}$	29	Growing
Phenanthrene	$C_{14}H_{10}$	9.9	Growing
Anthracene	$C_{14}H_{10}$	8.6	Growing
Biphenyl	$C_{12}H_{10}$	7.5	Shrinking
Acenaphthene	$C_{12}H_{10}$	3.5	Growing

Table 2. Mass of selected chemicals input, remaining in the plume, and lost after 3619 days.

Chemical	1 Initial Mass g	2 Mass Leached g	3 Mass in Plume g	4 Mass Lost Overall g	5 Mass Lost Overall %
Phenol	1040	1040	0	1040	100
Xylenes	2890	2320	5	2310	99.6
Naphthalene	7100	4690	347	4340	92
1-Methyl naphthalene	1410	240	106	130	54
Anthracene	890	40	23	17	42
Carbazole	244	180	95	85	47
Dibenzofuran	3260	835	143	690	83
Phenanthrene	8880	460	60	400	87

1: estimated from replicate analysis of coal tar creosote (4)
2: estimated via equation 1
3: estimated from sampling of the plume at day 3619
4, 5: calculated as column 2 minus column 3 with % expressed relative to column 2

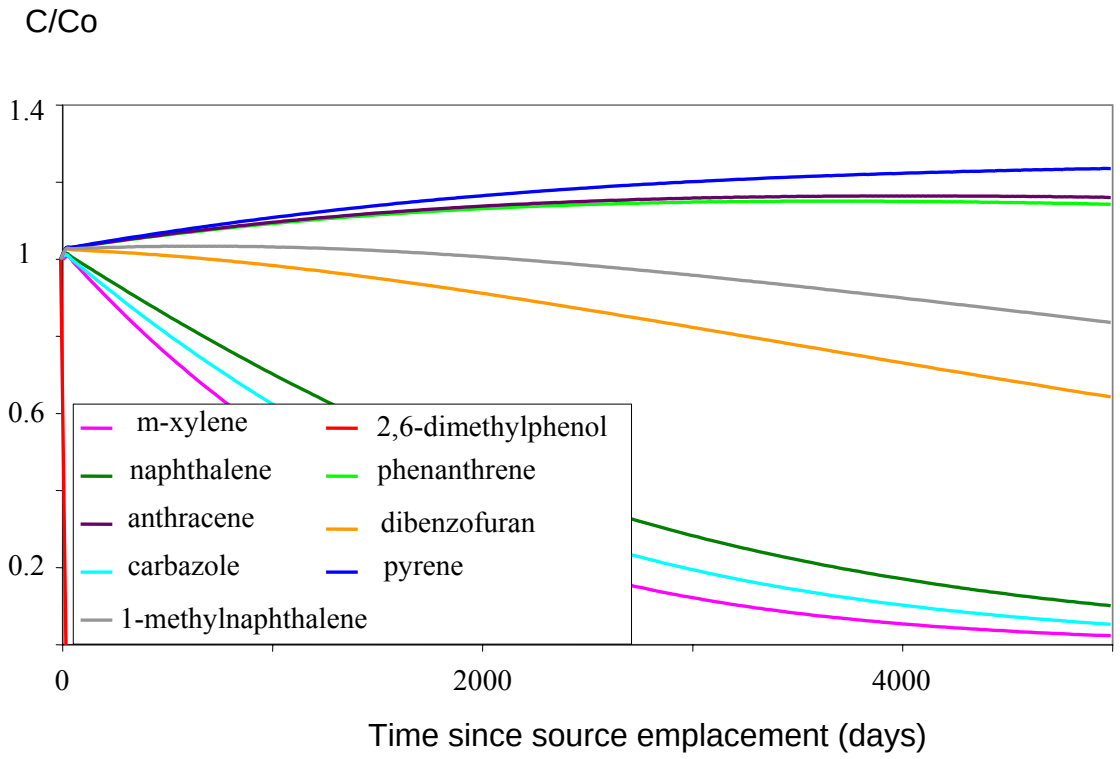

Figure 1. Change in the concentration of groundwater emanating from the coal tar creosote NAPL. Concentration is relative to the initial concentration (C/C_0).

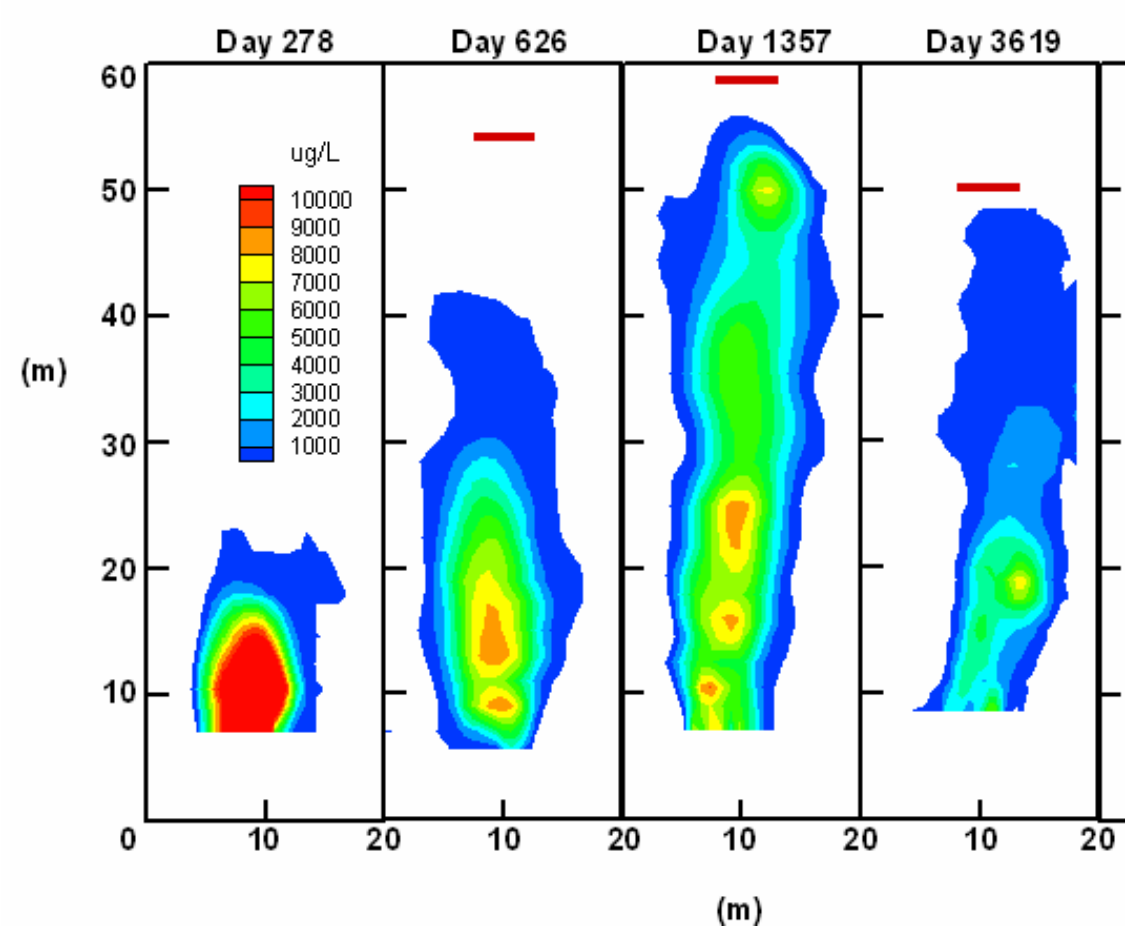

Figure 2. Extent of the dissolved naphthalene plume at various snapshot sampling days. The source is near the bottom and groundwater flow is upwards. Contours of maximum naphthalene concentration at each multilevel well are contoured. Red lines indicate the downgradient extent of groundwater sampling for that day.

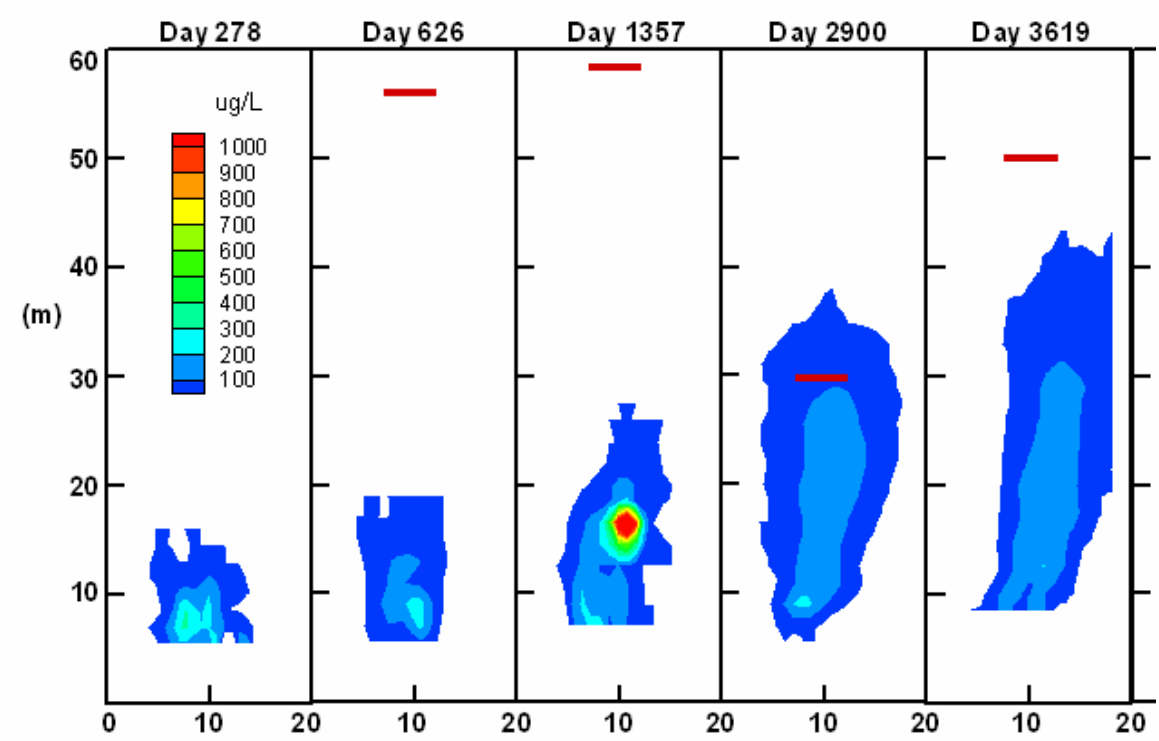

Figure 3. Extent of the dissolved carbazole plume at various snapshot sampling days. The source is near the bottom and groundwater flow is upwards. Contours of maximum carbazole concentration at each multilevel well are contoured. Red lines indicate the downgradient extent of groundwater sampling for that day. Note that for day 2900 the carbazole plume extends beyond the sampling for that day. Note that sampling on day 2900 did not cover the entire carbazole plume.

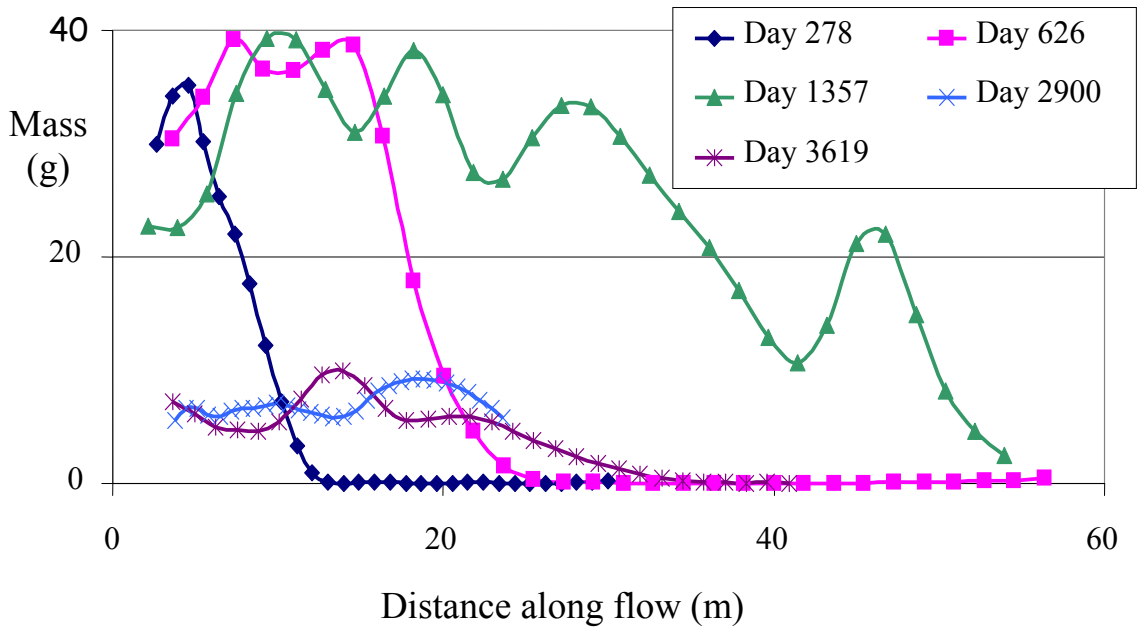

Figure 4. The distribution of the mass of naphthalene along the dissolved plume for five snapshots. The distribution begins 3m downgradient of the emplaced source at the end of the source zone. Note that the naphthalene plume was not fully covered by sampling at day 2900.

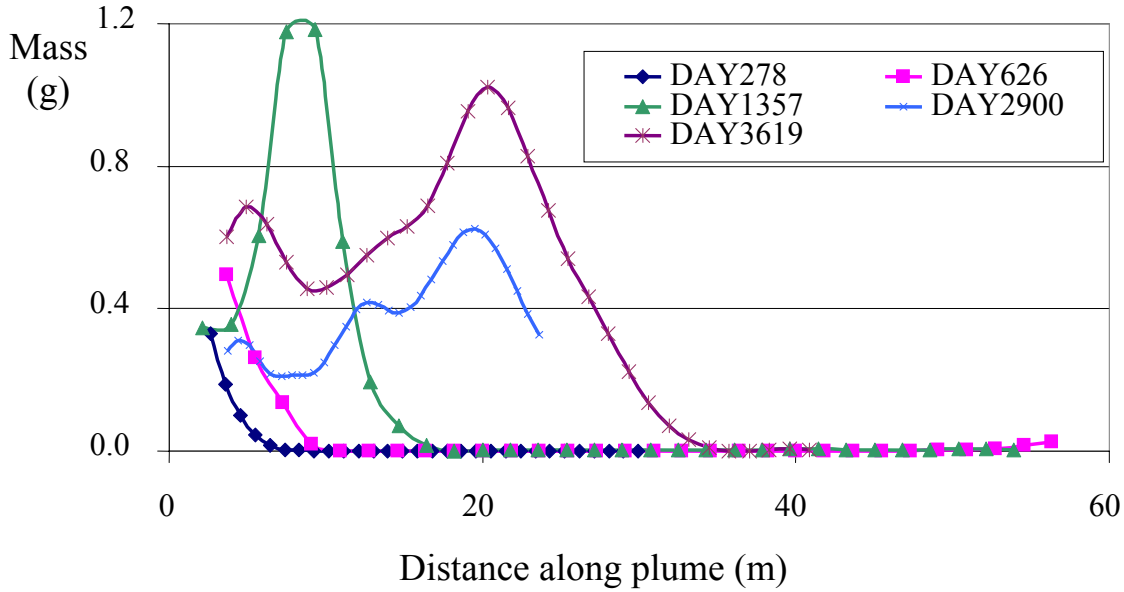

Figure 5. The distribution of the mass of carbazole along the dissolved plume for five snapshots. The distribution begins 3m downgradient of the emplaced source at the end of the source zone. Note that the carbazole plume was not fully covered by sampling at day 2900.

New STRONGER Guidance for State Stormwater/Erosion Control Measures at Oil and Gas Sites

By Patricia Billingsley

STRONGER[1]

STRONGER is a non-profit corporation established to:

- educate regulators and the public on state oil and gas environmental regulatory programs;
- administer the State Review Process; and
- Recommend improvements for state E&P environmental regulations and processes.

1 State Review of Oil & Natural Gas Environmental Regulations

STRONGER

- STRONGER representatives and Board members come from state O&G agencies, EPA, DOE, industry, consultants, and public interest groups
- http://www.strongerinc.org/

STRONGER History

- STRONGER grew out of the Interstate Oil and Gas Compact Commission (IOGCC) and EPA-supported state review process, which began in 1988 as a way to evaluate state oil and gas exploration and production waste control regulatory programs.
- STRONGER took over this review process in 1999, and has since issued many state guidelines.

Why Issue This Guidance?

This STRONGER Stormwater/erosion control guidance originated because:

- Several states have included stormwater/erosion control guidance or rules in their O&G regulatory programs;
- EPA proposed an NPDES Phase II one acre stormwater permitting process for oil and gas construction sites, and
- STRONGER wanted to outline a set of uniform best practices for the industry.

STRONGER Stormwater/Erosion Control General Guidelines

Stormwater in E&P areas can become contaminated from contact with:

- spilled or stored materials;
- E&P waste, or from
- eroding soils.

This guidance is mostly for #3.

General Guidelines, Continued

Stormwater management requirements differ from region to region of the country based on geographical differences in:

- topography;
- rainfall (annual average, episodic and seasonal);
- major soil types;
- proximity to surface waters, floodplains, seasonal and permanent swamps, wetlands & marshes; and
- natural vegetative cover.

General Guidelines, Continued

- STRONGER recommends that states implement programs to minimize potential contamination of surface water from sediment and other E&P stormwater contaminants <u>unless field monitoring data and other</u>

scientific information shows that stormwater runoff in the state does not pose a significant risk to human health and/or the environment.

General Guidelines, Continued

State management programs should:

- Include compliance evaluation and enforcement capabilities;
- be applicable to spills and release responses;
- contain data management capabilities; and
- provide for outreach and training on stormwater management requirements and practices for operators, landowners and the public.

General Guidelines, Continued

Stormwater requirements should include:

- a description of the action(s) the operator will take to meet state program goals for the geographic location;
- specific state requirements, or outline operator- specific plan(s);
- specific time frames when stormwater control measurements are to be in place; and
- specify when any state notifications are to occur.

General Guidelines, Continued

- Oil and gas agency staff should be trained so that they can, as time and staffing allow, provide information and referrals to operators, even if they are not the state's stormwater compliance agency.

General Guidelines, Continued

- State stormwater management programs should be evaluated periodically, including an analysis of all aspects of the program and procedures for making necessary program changes.

Specific Criteria - Planning

Well site, roadway, pipeline considerations:

- the area to be disturbed (minimize this);
- current land uses;
- site gradient;
- type of facility to be constructed;
- springs and seeps, floodways, stream crossings; and
- facilitating the management of E&P wastes.

Specific Criteria - Planning

Other factors:

- well density, and the distance between wells;
- the size needed for each site & its equipment;
- existing roads – new, temporary or permanent;
- the availability of vegetative filter strips; and
- disposal of trees and stumps to be removed during construction.

Specific Criteria - Construction

- State agencies should develop practices appropriate for the construction of well sites, access roads, pipelines, and crossings of streams, wetland, swamps and marshes to prevent contamination of stormwater and/or adjacent surface waters.
- Standards or management practices should be appropriate for the region in which the construction activity will occur.

Specific Criteria - Construction

Considerations at each site include:

- the construction of upgrade diversion channels;
- collection of construction site runoff;
- the use of brush, rock, and other barriers;

- the stockpiling of topsoil and subsoil during clearing and grubbing;

Specific Criteria - Construction

5. road alignment, slope, grade and length;

- the grading of cut and fill slopes, road embankments, road surfaces (crowned, in-sloping or out-sloping) and roadside ditches; and
- The temporary and final covers that will be used, from compacted soil or gravel to paving or re-vegetating.

Specific Criteria - Construction

Requirements should be developed for both temporary and long term stream/swamp crossings, including

- bridges and culverts;
- causeways;
- cofferdams;
- fords; and
- bank stabilization.

Specific Criteria - Construction

Stormwater controls needed during construction can include:

- drainage ditches;
- basins and sediment traps;
- berms and sediment barriers;
- vegetative filter strips, broad-based swales;
- turnouts, culverts, cross-drains and waterbars;
- rock filters, straw bale barriers and fabric filter fence.

Specific Criteria - Construction

Pipelines construction may include:

- ditchline barriers;

- varying the timing of backfilling;
- varying the materials used for trench backfill;
- stream diversions;
- planning the location of staging areas; and
- the use of trench plugs.

Specific Criteria - Construction

- If crossing fragile soil, wetland or marshy areas is necessary, laying construction mats, board roads or geotextiles should be considered.

Specific Criteria - Construction

Temporary stabilization practices may be necessary at sites where quick permanent closure is not possible, including:

- mulching;
- seeding with annual grasses;
- compacting soil to reduce erosion or installing a temporary gravel cover; or
- seed/filter fabric combinations.

Specific Criteria - Construction

Permanent stabilization can include:

- the application of sufficient rock and/or gravel to well sites and roads;
- paving; and/or
- achieving adequate growth of (or sodding with) permanent vegetation.

Specific Criteria - Construction

Factors considered during revegetation include:

- calculation of acreage;

- soil types and distribution;
- seed bed preparation, seed mixtures;
- soil amendments; and
- mulching and anchoring.

Criteria - Operation and Maintenance

- Stormwater control measures have to be operated and maintained in a manner that will assure their effectiveness.
- This includes preventing E&P waste and spills as well as controlling sediment.
- The frequency and type of inspection(s) needed, preventative maintenance, and repairs should be considered.

Criteria – Site Remediation

Sites may have to be repaired or remediated following a spill. This can include:

- removing damaged equipment;
- digging up damaged pipelines;
- removing or soil farming contaminated soil, and
- installing monitoring wells and remediation equipment.

Criteria – Site Restoration

Restoration is necessary when a site is shut down or plugged and abandoned. Activities include:

- removal of equipment;
- restoration of pits;
- disconnection & abandonment of pipelines;
- backfilling and grading; and
- access road reclamation.

Criteria – Site Restoration

- Erosion prevention and stormwater management similar to that during construction has to be incorporated into planning for these site restoration activities.

Summary

- Considerations for stormwater management and erosion prevention practices are necessary at every stage of oil and gas field exploration and production activities, from initial site preparation to final closure.
- State and other regulatory agencies need to have well understood rules and/or standard operating procedures in place to ensure proper procedures are followed.

MANAGED IRRIGATION FOR THE BENEFICIAL USE OF COALBED NATURAL GAS PRODUCED WATER IN THE POWDER RIVER BASIN

Kevin C. Harvey, Dina E. Brown, and Aaron J. DeJoia
Certified Professional Soil Scientists
KC Harvey, LLC
233 Edelweiss Drive, Unit 11, Bozeman, Montana 59718
Voice: 406-585-7402, Fax: 406-585-7428
Email: kevin@kcharvey.com

ABSTRACT

Managed irrigation with groundwater produced during CBNG operations is defined as: the application of soil science, water chemistry, agricultural engineering and agronomic principles to utilize CBNG produced water in a beneficial manner to produce forage for livestock and wildlife while protecting soil physical and chemical properties. Managed irrigation is one tool that is being used by several CBNG producers in the Powder River Basin to handle the co-generated groundwater. The purpose of this paper is to provide information about using produced water in a beneficial manner to produce forage for livestock and wildlife in the Powder River Basin of Wyoming and Montana. Case studies of laboratory-scale pilot tests and full scale-operations conducted over the last four years in Wyoming's Powder River Basin are discussed.

INTRODUCTION

The methods for managing and using the groundwater produced by coalbed natural gas (CBNG) operations have become an important issue that is being debated by the public, Federal and State agencies, special interest groups, and energy companies. The purpose of this paper is to provide information about using produced water in a beneficial manner to produce forage for livestock and wildlife in the Powder River Basin of Wyoming and Montana. The information, data, and processes described in this paper are based on the research and development and the actual full-scale managed irrigation operations performed by Fidelity Exploration & Production Company (Fidelity) of Sheridan, Wyoming, and Williams Production RMT Company (Williams) of Gillette, Wyoming.

BACKGROUND

In 2000, at the beginning of the CBNG expansion in Wyoming, Fidelity and Williams realized that a larger volume of produced water would be generated than could be discharged through the National Pollutant Discharge Elimination System (NPDES) process. These companies began seeking options for managing the produced groundwater in a beneficial manner. One such possibility was using the produced water to irrigate a forage crop that local ranchers could use in their cattle operations.

However, irrigation with produced water had never been done. Produced water is unaltered groundwater that is naturally enriched with sodium and bicarbonate minerals. Sodium in irrigation water can be a hazard to soils because it can cause the clay particles in the soil to swell and disperse, resulting in damage to the soil structure and decreased water infiltration and permeability. If, however, enough calcium is present in the soil, the clay particles will stay aggregated. Therefore, adding calcium to the soil-water system should negate the impacts of the sodium. This relationship of sodium to calcium, in water or soil, is known as the sodium adsorption ratio (SAR). Water or soil with relatively more dissolved sodium than calcium has a high SAR and is considered sodic. Often, CBNG produced water is referred to as saline, or having a high salt content. But in reality it is the sodicity, not the salinity that is the primary concern. Salinity levels in CBNG produced waters from the Powder River Basin are actually quite moderate.

In addition to high SAR levels, the CBNG water from the Powder River Basin is naturally enriched with bicarbonate alkalinity. In alkaline waters such as coalbed groundwater, any added calcium will react with bicarbonate and drop out of solution as calcium carbonate. The calcium in calcium carbonate then becomes unavailable to keep the clay particles in the soil aggregated. So, to irrigate with CBNG produced water, the bicarbonate alkalinity needs to be neutralized so that calcium can be added to negate the effects of the sodium. The practice of neutralizing bicarbonate alkalinity and adding calcium is based on established soil and water chemistry principles.

To test the possibility of irrigating with the CBNG produced water, Fidelity and Barrett Resources Company (now Williams) embarked on a series of scientific tests. First, geochemical models were consulted and results indicated that by using standard agricultural soil and/or water amendments, the produced water could potentially be used for irrigating a forage crop. The modeling results were then validated in the laboratory using “jar tests.” The jar tests involved blending differing ratios of produced water with appropriate amounts of an acidifying agent (sulfuric acid) and calcium (gypsum). The promising jar test results led to a laboratory pilot-scale test using actual columns of soil and CBNG produced water from the Powder River Basin of Wyoming. In the laboratory pilot tests, soils were amended with standard agricultural chemicals and irrigated with the produced water for several weeks.

The laboratory pilot tests demonstrated the success of using the agricultural amendments elemental sulfur and gypsum, in combination with the produced water to safely irrigate the soils. The success of the laboratory pilot tests led to several full-scale pilot tests where the sulfur and gypsum amendments were applied to the soil and the produced water was applied using center-pivot irrigation equipment. The pilot-scale tests successfully demonstrated that the elemental sulfur effectively consumed the bicarbonate in the produced water and allowed the added calcium in the gypsum to counter-balance the sodium in the produced water.

With careful addition of elemental sulfur and gypsum amendments to the soil surface, irrigation with CBNG produced water is yielding 2 to 4 tons per acre of alfalfa and forage grasses annually for local ranchers during a period of severe drought. To protect the soil resource, the CBNG producers employ an intensive soil and water-monitoring program. Since the successful field-scale pilot tests, several CBNG producers in the Powder River Basin have embraced managed irrigation as a key method for handling and using CBNG produced water in a beneficial manner.

DEFINITION OF MANAGED IRRIGATION

For the purposes of this paper, managed irrigation with groundwater produced during CBNG operations is defined as: *the application of soil science, water chemistry, agricultural engineering and agronomic principles to utilize CBNG produced water in a beneficial manner to produce forage for livestock and wildlife while protecting soil physical and chemical properties*. Managed irrigation practices include, among other things:

- selection of appropriate irrigation sites with suitable topography, soils, and hydrology,
- close cooperation with the landowner to ensure that the beneficial objectives of irrigation and the production of a crop are achieved,
- water balance analyses to support irrigation system sizing and design,
- water treatment or soil amendments to mitigate the risks associated with the sodium bicarbonate chemistry of produced water,
- irrigation scheduling and maintenance of a suitable leaching fraction to prevent the accumulation of salts in the root zone,
- selection and maintenance of a crop that is tolerant of expected soil moisture and salt levels,
- prevention and control of irrigation water runoff,
- systematic monitoring of water, soil, and vegetation during the life of the project, and
- implementation of site closure actions in accordance with landowner objectives.

Managed irrigation is one alternative out of several available for managing CBNG produced water. Its suitability as a water management alternative depends on many factors, including produced water chemistry, site and soil characteristics, landowner objectives, and project economics. As such, its suitability can only be evaluated on a project- and site-specific basis.

SOIL AND WATER CHEMISTRY ASSOCIATED WITH CBNG PRODUCED WATER IRRIGATION

The water that is generated during the production of CBNG in the Powder River Basin is commonly referred to as "produced water." CBNG produced water is naturally occurring groundwater. CBNG can be recovered from wells when groundwater contained in the coal seams is pumped to the surface to reduce pressure. The CBNG production process does not change the chemical nature of the water within the coalbed aquifer. All groundwater contain a mixture of naturally occurring chemicals. The chemicals dissolved in coalbed water result from natural processes that occur as rainfall and snowmelt percolate through the soils and deeper geologic formations during recharge of the groundwater system. These natural processes result in groundwater that is rich in sodium and bicarbonate minerals.

CBNG produced water is often of higher quality than other available water sources in the Powder River Basin and is commonly used for domestic purposes, including drinking. Because of its low to moderate level of salinity, it is a very good source of water for livestock and wildlife use. However, because of the naturally elevated levels of sodium and bicarbonate ions dissolved in the water, it can be a concern if used to irrigate soils to grow crops without proper management.

The suitability of water used for irrigation depends on a number of factors including the type of crops grown, the soil type, irrigation methods, and the types and quantity of salts dissolved in the water. Water quality guidelines for assessing irrigation water suitability generally consist of four components: salinity, sodicity, alkalinity, and specific ion toxicity. The most comprehensive and widely used guidelines were formulated for the Food and Agriculture Organization (FAO) of the United Nations by Ayers and Westcot (1) and the University of California by Hansen and others (2).

Salinity

All irrigation waters contain a mixture of naturally occurring salts. Soils irrigated with water will contain a similar mix of salts but usually at a higher concentration than in the applied water. Salts can be defined as minerals that dissolve in water, e.g., table salt, which is sodium chloride. Typical salt components in water and soil in the western U.S. include calcium, magnesium, sodium, potassium, sulfate, chloride, carbonate, and bicarbonate. The concentration of salts in water is measured two ways: total dissolved solids (TDS) or electrical conductivity (EC). The EC is the most commonly used measure of water and soil salinity because it is a rapid and inexpensive test. As the dissolved salt content of a water sample increases, its ability to conduct electricity also increases. Therefore, the EC, measured in deci-Siemens per meter (dS/m), provides a reliable and widely used index of salinity.

The salinity of irrigation water does not directly impact soil physical properties. Instead, salts make it more difficult for plants to extract water from the soil and are a concern if the salt level is high enough to affect crop yield. Plant species vary with respect to salt tolerance. Generally, most forage and field crops grown in northeastern Wyoming and southeastern Montana are moderately to strongly salt tolerant. For example, based on research conducted by the USDA Natural Resource Conservation Service (NRCS) at the Bridger Plant Materials Center in Bridger, Montana, the soil salinity threshold where alfalfa begins to exhibit yield declines is 4.0 dS/m (3). With careful management and suitable crops, irrigation waters with EC ranging from 4.0 to 7.5 dS/m have been used successfully for irrigation (4). CBNG water from the Powder River Basin has an average salinity of around 2.0 dS/m, which is suitable for irrigation.

Sodicity

For CBNG produced water, the key issue with respect to irrigation suitability is the naturally elevated sodium levels and its potential affect on soil infiltration and permeability. The infiltration and permeability of clayey soils can decrease if an abundance of sodium ions are adsorbed by the clay minerals in soil. Excessive adsorbed or exchangeable sodium can result from sustained use of irrigation water that is high in sodium and low in calcium and magnesium. Consequently, the ratio of sodium to calcium and magnesium ions in irrigation water is an important property affecting the infiltration and permeability hazard. The index used to measure the hazard related to sodium abundance or sodicity in irrigation water is the sodium adsorption ratio or SAR.

The SAR can be calculated from the sodium, calcium, and magnesium concentrations via the formula:

$$SAR = [Na^{+}] \div \sqrt{\frac{[Ca^{++}] + [Mg^{++}]}{2}}$$

where the concentrations are in milliequivelents per liter (meq/L).

Clay minerals in soils are negatively charged and consequently attract ions with a positive charge such as sodium, calcium, and magnesium. When sodium comprises more than about 15% of the exchangeable ions, the clay particles can begin to repel one another causing the soil structure to degrade. The percentage of exchangeable sodium ions relative to the total exchangeable ions in soil is termed the exchangeable sodium percentage or ESP. The continued swelling and dispersion of clay minerals and subsequent degradation of soil structure can reduce the rate of water infiltrating the soil and the permeability of water through the soil. In general, soils with moderately high, to high, clay contents are at higher risk.

What is not apparent from the SAR formula is the fact that the higher the salinity of the water, the higher the SAR can be without impacting soil structure and impairing soil infiltration and permeability. Put another way, for a given SAR, infiltration rates generally increase as salinity (measured by the EC) increases. The changes in soil infiltration and permeability occur at varying SAR levels. Ayers and Westcot (1) and Hansen et al. (2) describe the relationship between salinity and sodicity in irrigation water and the effect on soil infiltration and permeability.

Most CBNG water produced in the Powder River Basin of Montana and Wyoming exhibit SAR values at a level that make them potentially unsuitable for irrigation on most soils. Therefore, to be used beneficially to produce forage, some type of water treatment (e.g., sodium removal) or soil/water conditioning (e.g., calcium addition using gypsum) is required to mitigate the effects of the elevated SAR.

An important soil parameter was introduced above -- the exchangeable sodium percentage or ESP. The ESP, in conjunction with soil pH and EC, are used to judge the level of soil sodicity and are therefore very useful measurements in managed irrigation. The ESP is defined as the “percentage of the cation exchange capacity of a soil occupied by sodium ions” (5).

Every soil has a definite capacity to adsorb the positively charged constituents of dissolved salts, such as calcium, magnesium, potassium, sodium, etc. This is termed the cation exchange capacity (CEC). The various adsorbed cations (such as calcium and sodium) can be exchanged one for another and the extent of exchange depends upon their relative concentrations in the soil solution (dissolved), the ionic

charge (valence), the nature and amount of other cations, etc. ESP is accordingly the amount of adsorbed sodium on the soil exchange complex expressed in percent of the cation exchange capacity in milliequivalents per 100 grams of soil (meq/100 g). Thus,

ESP = (exchangeable sodium / cation exchange capacity) x 100

Sodic soils are "nonsaline soils containing sufficient exchangeable sodium to adversely affect crop production and soil structure" (5). As stated above, high levels of exchangeable sodium tend to disperse soil particles thereby sealing the soil. The result can produce hard surface crusts, reduced infiltration rates, and reduced oxygen diffusion rates, all of which interfere with or prevent plant growth. By definition, sodic soils are those that have an ESP of more than 15%, an EC less than 4 dS/m, and a pH between 8.5 and 10 (6).

Bicarbonate Alkalinity

Alkalinity is a measure of the buffer capacity of water or the ability to neutralize an acid. The major form of alkalinity in CBNG produced water is bicarbonate. High bicarbonate levels in irrigation water will react with the available calcium and magnesium and form insoluble calcium carbonate (lime) or magnesium carbonate precipitates. As can be seen by the SAR formula above, the reduction of available calcium and magnesium thus raises the effective SAR of the water. High levels of bicarbonate can also result in elevated pH values due to degassing of carbon dioxide. The equilibration of carbon dioxide in the produced water with atmospheric carbon dioxide results in an increased pH in produced water. This is analogous to a can of carbonated soft drink, which is carbonated under pressure during the manufacturing process. The carbonation process results in a lowered pH in the soft drink. When the soft drink is depressurized upon opening, the carbonation (carbon dioxide) degasses causing the drink to become "flat" and the pH to increase. In the case of CBNG produced water, the subsequent increase in soil-water pH hastens the transformation of bicarbonate to carbonate, which readily reacts with calcium and magnesium forming a relatively insoluble compound. The net result is less dissolved calcium and magnesium relative to sodium and higher effective SAR values.

Bicarbonate concentrations in CBNG produced water from the Powder River Basin typically range from 750 mg/L to 3,000 mg/L. These are relatively high values for irrigation water and can cause pH increases in water and soil, and subsequent increases in water and soil SAR. To prevent the reduction in available (or added) calcium, the bicarbonate alkalinity must be neutralized with an acidifying agent (for example, sulfur soil amendments which oxidize to produce sulfuric acid).

Specific Ion Toxicity

While generally not a concern with respect to CBNG water from the Powder River Basin, sodium, chloride, and boron ions can be toxic to certain crops if their concentrations are too high in any irrigation water. Damage from sodium and chloride toxicity usually occurs only in woody plants such as tree and vine crops where soil salinity is extremely high or when saline water is used for sprinkler irrigation (1, 2). Chloride concentrations in CBNG produced water from the Powder River Basin are typically very low. Since tree and vine crop types are not usually grown on managed irrigation sites, or by local farmers and ranchers in the Powder River Basin, sodium and chloride toxicity is not an issue. Boron concentrations in produced water from the Powder River Basin are typically below detectable levels to very low levels and should not be a potential toxicity problem.

DESIGN, OPERATION AND CLOSURE OF CBNG MANAGED IRRIGATION SYSTEMS

The research and development program discussed above, along with four years of full-scale operational experience has led to the development of a process for evaluating, designing, operating, monitoring, and closing CBNG managed irrigation systems in an environmentally sound manner. This process has been successfully employed by the authors of this document and their clients on managed irrigation projects totaling over 2000 acres in the Powder River Basin of Wyoming. The primary components of the managed irrigation process are as follows:

- Irrigation Water Quality Suitability Assessment
- Soil Amendment Prescriptions
- Project Water Balance Estimates
- Site Selection
- Site Characterization
- Crop Selection
- Selection and Design of Irrigation Systems
- Soil Water Balance Modeling and Irrigation Scheduling
- Water, Soil, Crop and Meteorological Monitoring
- Annual Irrigation Management Plans
- Site Closure Planning

Each of these components is discussed below.

Irrigation Water Quality Suitability Assessment

As discussed above, to assess the suitability of produced water for irrigation, four specific areas are addressed: salinity, sodicity, alkalinity, and specific ion toxicity using the criteria specified in Ayers and Westcot (1) and Hanson et al. (2). This is the first step in any managed irrigation project to determine overall project feasibility. Soil and/or water conditioning prescriptions are then developed (if necessary) based on water chemistry to allow long-term irrigation with CBNG produced water.

Soil Amendment Prescriptions

Based on the chemistry of CBNG produced water, it is apparent that the natural sodicity of CBNG produced water is the primary issue to be addressed before the water can be used for irrigation and forage production. The SAR formula presented above indicates that two general treatment methods would result in a reduction in SAR prior to irrigation: (1) removal of sodium, or (2) addition of calcium and/or magnesium (the scientific literature suggests that calcium is more effective than magnesium in lowering the effect of sodium in soils, therefore, magnesium addition will not be discussed further).

Salt removal systems (e.g., reverse osmosis, ion exchange, etc.) are technically feasible, however, due to operational and economic limitations and issues associated with concentrated reject waters, they are not usually used in conditioning water for managed irrigation projects. The process of calcium addition, however, is a common practice used today in the Powder River Basin.

The level of bicarbonate alkalinity and the solubility limits of gypsum and calcite minerals limit the maximum amount of calcium that can be dissolved in produced water. Minimum SAR will be achieved by maximizing dissolved calcium concentrations in the soil-water system. This requires the

addition of an acid to neutralize the bicarbonate alkalinity, control pH, and maintain the solubility of the added calcium. The approach most commonly selected for managed irrigation in the Powder River Basin involves the application of conventional agricultural amendments such as elemental sulfur and gypsum (calcium sulfate dihydrate) to the soil.

The elemental sulfur product oxidizes in the presence of air, water, and soil microbial activity to form sulfuric acid, which in turn dissociates to sulfate and hydrogen ions (protons) as follows:

Oxidation of sulfur (S): $S + 1.5O_2 + H_2O = H_2SO_4$

Dissociation of sulfuric acid (H_2SO_4): $H_2SO_4 = 2H^+ + SO_4^{2-}$

Sulfuric acid neutralizes the bicarbonate alkalinity and controls soil pH as follows:

Neutralization of bicarbonate (HCO_3^{2-}): $H^+ + HCO_3^{2-} = H_2O + CO_2$

Gypsum provides dissolved calcium to the soil or water as follows:

Dissolution of gypsum ($CaSO_4.2H_2O$): $CaSO_4.2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$

The added calcium effectively competes against sodium for the negatively charged exchange sites on soil clay particles. The positively charged divalent calcium ions (two positive charges) are more strongly attracted to clay particles in soil than are monovalent sodium ions (one positive charge), resulting in a stronger bond between the clay particles. Clay particles that are strongly bound by calcium ions are less likely to swell and disperse.

Geochemical equilibrium models such as PHREEQC and MINTEQA are used to calculate the amount of sulfur and gypsum amendments necessary to reduce the SAR of the water to a target level. Calcite and gypsum minerals are then allowed to precipitate (reach their solubility limits) and the solution is equilibrated with atmospheric carbon dioxide (CO_2 gas). This equilibration step is very important because the high bicarbonate (HCO_3^-) concentrations in the produced water indicate that this water is in equilibrium with considerably higher CO_2 levels, which results in a lower solution pH value. As the carbon dioxide exsolves (degasses) and equilibrates with atmospheric carbon dioxide, the pH increases.

Soil amendment rates derived by geochemical equilibrium modeling depend on the chemistry of the water and the expected volume of water to be applied to the soil. Gypsum and sulfur amendment rates for irrigation sites within the Powder River Basin typically range between 3 and 6 tons per acre per year, and 0.5 and 1.5 tons per acre per year, respectively. It must be noted that the soil amendments in equilibrium with the water will result in an increase in the overall salinity of the soil-water system. The increase in salinity is estimated during the geochemical modeling process to ensure that soil EC values will be less than the established salt tolerance limits for the selected crops grown.

Soil amendment scheduling is site-specific. Typically, soil amendments are applied proactively in the spring prior to the initiation of irrigation for the season. Calculated soil amendment rates are adjusted for product purity and a 1.25 multiplier is applied to the gypsum rate to account for imperfect field application and irrigation variability. If necessary, gypsum alone can be applied in the fall at calculated rates to lower the exchangeable sodium percentage (ESP) of the soil over the winter. This technique takes advantage of winter and early spring moisture to dissolve the gypsum and allow calcium to exchange with sodium on the clay minerals. Not only does this reduce the sodicity of the soil, it also increases the salinity of the soil to safer levels at a time when excess leaching may be occurring.

Project Water Balance Estimates

Development of irrigation plans for CBNG produced water requires a detailed understanding of water inventory at project startup and throughout the projected operational life. In other words, how much water will be available from CBNG operations and when will it be available? Estimates of the project water balance are made using spreadsheet-based water balance models. These simulations facilitate initial irrigation planning, design, and operations. During each phase of project planning and development the water balance may be considered one of the most important decision making tools.

The baseline water balance for a new project provides the foundation for planning by estimating the magnitude of produced water that will need to be managed. The feasibility of water management alternatives such as storage and seasonal irrigation, injection, discharge to surface water, treatment, or any other alternatives may be evaluated using the water balance as a screening tool. Feasibility costs for these management alternatives may then be evaluated considering net present value for capital and operating costs. Once the operation/management strategy is defined, design optimization can be evaluated using the water balance. Design assumptions may be updated and verified as pumping rates and other information become available. The operational water balance is used to monitor and manage operations.

The water balance model includes deterministic functions to reflect project specific operations such as annual drawdown rates for wells and development schedules, and probabilistic functions to predict water balance uncertainty and variability associated with climate and pumping rates.

Site Selection

Screening the soils in the general area of the CBNG project using geographical information system (GIS) technology and published USDA-NRCS soil survey data is conducted to rapidly and inexpensively identify candidate irrigation sites. The GIS-based screening examines topography, soil texture, soil permeability, and soil depth to categorize the soils on maps as very likely suitable, possibly suitable, and not likely suitable for managed irrigation. Other site selection factors include vegetation presently growing on the site, surface hydrology and depth to groundwater, current land use, landowner preferences, and the overall potential (e.g., can the site be improved as in the case of overgrazed upland areas). If the screening demonstrates that there is a high likelihood of suitable soils in the area, a more thorough site and soil investigation would be required (see below).

Site Characterization

An on-site evaluation of the candidate irrigation site is necessary to determine the exact soil types present, current soil chemical and physical properties, and overall suitability of the site. The on-site evaluation is also necessary to collect soil data to assist in design of the irrigation system, establish baseline (pre-irrigation) soil conditions, and to meet Bureau of Land Management and or State requirements for water management planning.

An Order 1 soil survey (as defined by the USDA-NRCS) is completed for all managed irrigation sites. This equates to approximately one soil profile description test pit per five to ten acres of area investigated (more for highly variable soils, less for more homogeneous soils). Test pits are excavated with a backhoe to a depth of 60 inches. At each test pit a soil profile description is performed in accordance with USDA-NRCS protocols (7). Bulk samples from each natural soil horizon are collected and submitted to a contract laboratory for analysis of pH, electrical conductivity (EC), sodium adsorption ratio (SAR), saturation percentage, exchangeable sodium percentage (ESP), percent lime, percent organic matter (surface horizon only), fertilizer requirements, bulk density, and soil texture (percent sand, silt and

clay). In addition, baseline soil infiltration rates are measured near several of the test pit locations representing each soil-mapping unit.

Crop Selection

Crops typically grown under managed irrigation systems in the Powder River Basin are alfalfa and native forage grass mixes. Crop selection is based primarily on landowner preference, soil type, available equipment for harvesting, and the projected root zone salinity level resulting from the CBNG produced water in equilibrium with the soil amendments. For alfalfa, the average root zone EC at which alfalfa is expected to begin to decline is 4.0 dS/m (3). Alfalfa can tolerate much higher average root zone EC levels (i.e., up to 8.0 dS/m) before significant yield reductions or mortality occurs. Native forage grass species can typically tolerate much higher average root zone salinity levels than alfalfa.

Most managed irrigation projects are constructed on private land for a landowner who wants and can use the extra forage for livestock. Most of the sites utilized for managed irrigation in the recent past have been overgrazed, upland range areas that support little in the way of native plants. Typically, these sites are vegetated with sagebrush, introduced grass species, prickly pear cactus and weedy species such as cheat grass. Managed irrigation projects have been shown to rehabilitate these small areas into productive forage sources for both livestock and wildlife.

Selection and Design of Irrigation Systems

Several mechanized and non-mechanized irrigation systems are used in the Powder River Basin for applying CBNG water to managed irrigation sites, including center pivot sprinklers, side roll/wheel line sprinklers, hand moved or fixed solid set sprinklers, big gun sprinklers, surface drip, subsurface drip, gated pipe flood, and ditch flood. The preferred system is the center pivot because of the significant advantages in automation, overall control, runoff control, distribution of water, operation costs, reduced labor costs, and reliability. The selection of a particular system is based on topography, soil conditions, landowner preferences, size of the site, crop type, post-irrigation land use, available labor, and project economics.

Soil Water Balance Modeling and Irrigation Scheduling

A spreadsheet-based soil-water balance model is used to determine the amount and timing of irrigation required to produce a healthy forage crop and to ensure that sound agronomic leaching practices are followed. With a soil-water balance assessment, all water inputs to and outputs from the soil are identified and balanced according to the following equation (8):

Total Irrigation Water Applied = Crop Requirement + Leaching Fraction + Irrigation Losses – Precipitation – Change in Soil-Water Content.

For sprinkler irrigation systems, several assumptions, actual data, and calculations are used in developing the soil-water budget and resulting irrigation schedule. Typically, 25 to 30 inches of CBNG produced water are applied per season to grow crops such as alfalfa and forage grasses in the Powder River Basin.

As discussed in the water quality suitability assessment above, salt removal through leaching with excess water is required to minimize the concentration of salts in the root zone. This is termed the "leaching requirement." With irrigation, the EC of the produced water by itself should not cause any serious increases in soil salinity; however, amendments applied to the soil to negate the possible impacts

caused by the sodicity (SAR) of the produced water will cause an increase in soil EC, requiring leaching with excess water. In most cases, a leaching fraction of 10 to 20 percent will result in a soil EC approximately equivalent to the EC resulting from the equilibration of the produced water with the soil amendments. At the end of each irrigation season, actual (as opposed to projected) soil-water balances are prepared for each irrigation site with site-specific climatic data and total irrigation amounts. This is necessary, among other things, to ensure that the required leaching fraction is achieved.

Discussion of the soil water balance and the amount of water applied to support crop growth and a suitable leaching requirement brings up an important point regarding potential groundwater interaction. In order for groundwater to be significantly influenced by managed irrigation systems, or any source of water applied to the surface, there must be saturated flow through the soil/unsaturated zone and into the groundwater. As defined above, managed irrigation is not a process whereby water is applied to the ground on a continual basis throughout the year. It is applied in an agronomic manner in accordance with crop needs, soil water holding capacities, climatic characteristics, soil infiltration rates, and leaching requirements. It is not desirable or practical to irrigate crops in a way that results in saturating the soil to the point where water is moving in a continuous wetting front under gravity to the water table. With a continuous wetting front flowing under gravity, water is moving in accordance with what is termed "saturated flow." When the soil water content is less than saturation, the water moves in accordance with what is termed "unsaturated flow." Simply put, water moving through the soil under unsaturated flow conditions moves from areas of higher water content to lower water content in accordance with capillary forces, which means it can move diffusely in almost any direction.

Under managed irrigation conditions and in accordance with the soil water balance approach to irrigation scheduling, water is applied in amounts that will be evaporated from the soil and transpired through the roots and out the plant leaves during crop growth. Under these conditions, there is no net movement of water beneath the root zone. As discussed above, additional water is applied over the course of the irrigation season to ensure that salts do not accumulate within the root zone. This leaching requirement typically equates to approximately 5 to 10 inches of additional water spread out over the entire year. The additional 5 to 10 inches of additional water includes natural snowmelt and rainfall. Therefore, a volume of water of this magnitude spread out over an entire year is not expected to induce saturated flow conditions beneath the root zone and connect with groundwater. This is especially true in project areas that are located on upland range sites that have relatively deep water tables.

Irrigation scheduling also brings to mind the issues associated with runoff and erosion, and potential runoff/discharge into streams. This is certainly possible if irrigation systems were allowed to run continuously resulting in an exceedance of the soil infiltration rate. Managed irrigation systems are designed and operated in a way that supplies enough water to meet the demands of the crop, provides for an adequate leaching requirement, and apply water at or below the infiltration rate of the soil.

Water, Soil, Crop and Meteorological Monitoring

The purpose of soil, water, crop, and meteorological monitoring is to ensure that the managed irrigation site is operated in a manner that (1) promotes the beneficial use of CBNG water to produce forage, (2) maintains soil productivity and sustainability, and (3) minimizes the possible impacts associated with saline and sodic water irrigation. The data collected from soil, water, crop and meteorological monitoring are used to determine the overall performance of the managed irrigation system as well as to make adjustments to irrigation scheduling and soil amendment application rates. Site monitoring documents how the managed irrigation system is performing and data collected during monitoring are utilized in the creation of annual operations and monitoring reports.

Site specific monitoring plans are developed that include soil sampling and analysis, soil infiltration testing, surface and subsurface observations made by a qualified soil scientist, measurements of vegetation performance and health, water sampling and analysis, depth of water applied, evapotranspiration rates, air temperature and precipitation. Soil samples are typically collected to a depth of 8 feet from each irrigation area to monitor the depth of solute movement and to confirm that adequate leaching is occurring. Soil monitoring begins with baseline sampling and analysis prior to the project startup and ends when the system is permanently closed. Seasonal soil monitoring begins prior to the startup of irrigation in the spring, continues through the irrigation season and ends with post irrigation season sampling in the early fall.

Annual Irrigation Management Plans

The annual irrigation management plan addresses seasonal landowner and land use goals, crop selection, site preparation, seeding, irrigation system operations, harvesting/grazing plans, soil amendment application rates and scheduling, irrigation scheduling, leaching requirements, and monitoring. This document serves as the overall planning, operations, and monitoring guide. The irrigation and crop management plan is revised each winter based on the monitoring results and other input from the previous irrigation season, and the operational requirements for the upcoming irrigation season.

Site Closure Planning

A critical component of the managed irrigation planning process is site closure. Issues to be addressed during site closure planning are:

- What are the post-irrigation land use goals and landowner preferences?
- Will the site continue to be cropped or will it be put back into native vegetation?
- Will the irrigation equipment be removed or will it be left in place to be used by the landowner?
- If the irrigation equipment is to remain, what are the water sources available for continued irrigation?
- What do we expect in the way of post-irrigation soil physical and chemical conditions?
- Will the chemistry of the soil require adjustment to meet post-irrigation land use and landowner goals?
- What level of post-irrigation monitoring will be required to meet post-irrigation land use and landowner goals?

Some of the answers to these questions can be anticipated at project startup, while others can only be answered towards the end of the project. In any event, the primary goal of site closure is to leave a physically and chemically stable site capable of moving towards a sustainable vegetative community that meets or exceeds landowner goals.

MANAGED IRRIGATION CASE STUDIES

Since 2001, the authors of this paper have been involved in the application of full-scale operational managed irrigation of CBNG produced water totaling approximately 2000 acres in the Powder River Basin of Wyoming. These projects include those operated by Fidelity and Williams, and several other CBNG producers in the basin. Summarized below are three case studies of managed irrigation projects, including (1) laboratory pilot tests conducted on behalf of Fidelity, (2) full-scale operations at four managed irrigation sites managed by Fidelity, and (3) full-scale operations at five managed irrigation sites managed by Williams.

Laboratory Pilot Testing: Fidelity

Prior to the start of full-scale managed irrigation operations in 2001, a bench-scale laboratory test was conducted to determine the best method for controlling the high levels of sodium and bicarbonate in the CBNG produced water. Once the sodium and bicarbonate are controlled, the SAR is reduced and the chances of forming sodic soil conditions are decreased. The bench-scale test was conducted using intact soil columns and CBNG produced water from the Tongue River Basin. The soil, with textures of loam to clay loam, and clay contents ranging from 24 to 38%, came from a candidate irrigation area within Fidelity Exploration & Production Company's, Sheridan, Wyoming, Tongue River production area. The produced water was collected from a nearby Fidelity CBNG well and exhibited an EC of 2.5 dS/m and an SAR of 60.

To implement the bench-scale test, 18-inch long intact columns of soil, in eight-inch diameter plastic (PVC) pipes, were brought into the laboratory. Three basic treatment strategies were tested; (1) amendments applied directly to the soil, (2) amendments added to the produced water, and (3) blending the produced water with irrigation water from a local water source. Soil and water amendment rates were based on the chemistry of the water and the results of geochemical equilibrium modeling. The amendment rates were designed to reduce the SAR of the soil-water system to approximately 8. Experimental controls consisting of (1) irrigation with straight produced water with no treatment, and (2) irrigation with water from the Tongue River, were also incorporated into the study. In all, seven different treatment scenarios were applied and the columns were irrigated for 84 days to simulate several years of irrigation in the field.

To determine the effects of the treatments, soil samples from the columns were measured for pH, EC, and SAR. Results from four of the treatments and from a control column that was not irrigated or treated at all are shown in Table 1. Average soil pH values were within the typical range for most undisturbed range soils of 6.5 to 8.4. As expected, soil EC increased in all treatments when compared to baseline conditions. Also as expected, the largest increase in soil EC was seen in the soil applied amendment treatment. However, soil samples from all treatments exhibited average EC values of less than 4 dS/m, and were below the 4 to 12 dS/m soil salinity thresholds for western rangeland and forage plant species (Bridger Plant Materials Center, 1996).

Except for the produced water control treatment, all of the soil SAR values stayed well below the established sodic soil threshold value of 13 (9). As expected, irrigation with straight CBNG produced water (no soil amendments) resulted in an average soil SAR of 20. The soil within this column was clearly dispersed, reducing infiltration and permeability to near zero. In contrast, irrigation with CBNG produced water on soil amended with elemental sulfur and gypsum resulted in an average soil SAR of 7.5. Soil structure and permeability for the soils amended with calculated amounts of sulfur and gypsum were not visibly impacted. The laboratory column test successfully demonstrated the concept of using the

agricultural soil amendments, elemental sulfur and gypsum, in combination with the produced water to safely irrigate the soils.

Full-Scale Operations: Fidelity

Fidelity Exploration & Production Company, Sheridan, Wyoming, currently implements managed irrigation of CBNG produced water on approximately 840 acres. Water is applied to ten different irrigation areas using center pivot, side-roll, and solid-set irrigation systems. Fidelity's CBNG produced water has a pH of 8.2 to 8.4, an EC of 1.8 to 2.6 dS/m, an SAR of 21 to 60, and bicarbonate levels of 1120 to 1430 mg/L. Irrigating, on average, 25 inches of produced water per irrigation season, requires roughly 1.5 tons per acre of sulfur and 3.5 tons per acre of gypsum amendments. The resultant expected soil EC and SAR, in equilibrium with the amendments and produced water, is 5 dS/m and 7.5, respectively. The typical irrigation season is May through October, depending on climate variability. Alfalfa and alfalfa/forage grass mixes are grown on most Fidelity areas.

To protect the soil resource, Fidelity employs an intensive soil-monitoring program. The monitoring program includes soil sampling at the beginning, middle, and end of every irrigation season to track the soil chemical and physical condition. Soil sampling and analysis results from four of Fidelity's managed irrigation areas that have been irrigated as long as four years are shown in Figure 1. Each of the four project areas shown in Figure 1 is irrigated using center pivot irrigation equipment and each receives between 20 and 25 inches of CBNG produced water annually.

Soil samples were collected from each irrigation area prior to the initiation of operations to document baseline conditions. The samples were analyzed in a laboratory for pH, EC, SAR, and ESP, among other things. Baseline soil pH levels generally ranged between 6.0 and 8.5 (Figure 1). Pre-irrigation EC levels generally ranged between less than 1 and 5 dS/m, while the ESP usually ranged between less than 1 and 5 percent. The baseline pH, EC, and ESP ranges represent samples collected to a depth of 24 inches.

Over time soil pH levels in surface (0 to 6 inch) samples collected from Fidelity's four managed irrigation areas have generally remained between 7.0 and 8.0 and have not greatly changed from pre-irrigation values (Figure 1). Soil EC levels have increased to predicted levels over time in the samples collected from the managed irrigation areas and have generally stabilized between 4.0 and 6.0 dS/m. Soil EC levels were expected to increase with the addition of sulfur and gypsum soil amendments in equilibrium with the CBNG produced water. As can be seen in the fluctuating EC levels in Figure 1, winter and spring precipitation results in a decrease in EC due to natural leaching of the salts down through the soil profile.

ESP values are shown in Figure 1 and are used to monitor the sodicity of the soil. In the soil samples collected from the Fidelity managed irrigation areas, ESP values increased initially, at the start of operations, and then generally stabilized over time. This was expected and indicates that the added calcium has reached equilibrium with the sodium being added by the produced water during irrigation. For reference, sodic soils are defined as having ESP levels greater than 15% (6). All of the Fidelity managed irrigation areas have ESP levels that are well below 15%, and are generally below 10% (the soil management goal for ESP in these areas is less than or equal to 10%).

Full-Scale Operations: Williams

Williams Production RMT Company, Gillette, Wyoming, currently uses over 700 acres of managed irrigation to handle much of its CBNG produced water. Water is applied to 19 different

irrigation areas using center pivot irrigation systems. The produced water used for irrigation exhibits a pH of 7.3 to 8.3, an EC of 2.8 to 3.5 dS/m, an SAR of 21 to 36, and bicarbonate levels of 2600 to 3000 mg/L. Irrigating, on average, 28 inches of produced water per irrigation season, requires roughly 2.1 tons per acre of sulfur and 5.0 tons per acre of gypsum amendments. The expected soil EC and SAR, in equilibrium with the amendments and produced water, is 8.0 dS/m and 10, respectively. The typical irrigation season is April through September, depending on weather. A native range forage grass seed mix is grown on most Williams' areas.

Williams conducts soil sampling at the beginning, middle, and end of every irrigation season to track the soil chemical and physical condition within each irrigation site. Soil sampling results from five Williams managed irrigation areas that have been irrigated for two years, are shown in Figure 2. Each of the four project areas shown in Figure 2 receives between 18 and 29 inches of CBNG produced water annually.

Soil samples were collected from each irrigation area prior to the initiation of operations to document baseline conditions. The samples were analyzed in the laboratory for pH, EC, and ESP, among other things. Pre-irrigation surface (0 to 6 inches) soil sample pH levels generally ranged between 7.3 and 7.8 (Figure 2). Pre-irrigation surface EC levels were generally less than 1 dS/m, while surface ESP usually ranged between 2.0 and 3.3 percent.

Over time soil pH levels in samples collected from Williams five managed irrigation areas have generally remained between 7.0 and 8.0 and have not greatly changed from pre-irrigation values (Figure 2). Soil EC levels have increased to predicted levels over time in the samples collected from the managed irrigation areas and have generally stabilized between 3.7 and 6.5 dS/m (Figure 2). Soil EC levels were expected to increase with the addition of sulfur and gypsum soil amendments in equilibrium with the CBNG produced water. As can be seen in the fluctuating EC levels in Figure 2, winter and spring precipitation results in a decrease in EC due to natural leaching of the salts down through the soil profile.

ESP values are shown in Figure 2 and are used to monitor the sodicity of the soil. In the soil samples collected in the Williams managed irrigation areas, ESP values increased initially, at the start of operations, and then generally stabilized over time. This was expected and indicates that the added calcium has reached equilibrium with the sodium being added by the produced water during irrigation. For reference, sodic soils are defined as having ESP levels greater than 15% (6). All of the Williams managed irrigation areas have ESP levels that are well below 15%, and are generally below 12% (the established soil management goal for ESP in these areas is less than or equal to 12%).

CONCLUSIONS

The production of natural gas in the Powder River Basin of Montana and Wyoming and the concurrent production of unaltered groundwater are occurring in a region that is naturally arid during a time of severe drought. Research and development programs and full-scale irrigation projects have demonstrated that CBNG water can be beneficially used to grow forage where there was none, while protecting the soil resource. Since Fidelity and Williams first embarked on developing this process for beneficially using produced water, several other CBNG producers in the Powder River Basin have added "managed irrigation" to their water management "tool kit." Upwards of two to four tons per acre of alfalfa are routinely produced with CBNG irrigation water in the Powder River Basin of Wyoming. Managed irrigation has evolved into a practice that is based on established soil science, water chemistry, and agronomic principles, and should be evaluated as a water management and beneficial use alternative on a project- and site-specific basis.

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Table 1. Results of soil sampling and analysis from the Fidelity bench-scale managed irrigation tests.

Treatments	Average pH	Average Electrical Conductivity (dS/m)	Average Sodium Adsorption Ratio
Gypsum and sulfur applied to the soil and irrigated with CBNG produced water	7.8	2.9	7.5
Gypsum and sulfuric acid added to the CBNG produced water and irrigated on the soil	7.5	2.8	8.9
Untreated CBNG produced water irrigated on the soil	8.3	1.6	20
Untreated Tongue River water irrigated on the soil	7.7	0.69	0.69
Non-irrigated control where no water or treatments were applied to the soil	7.9	0.41	0.44

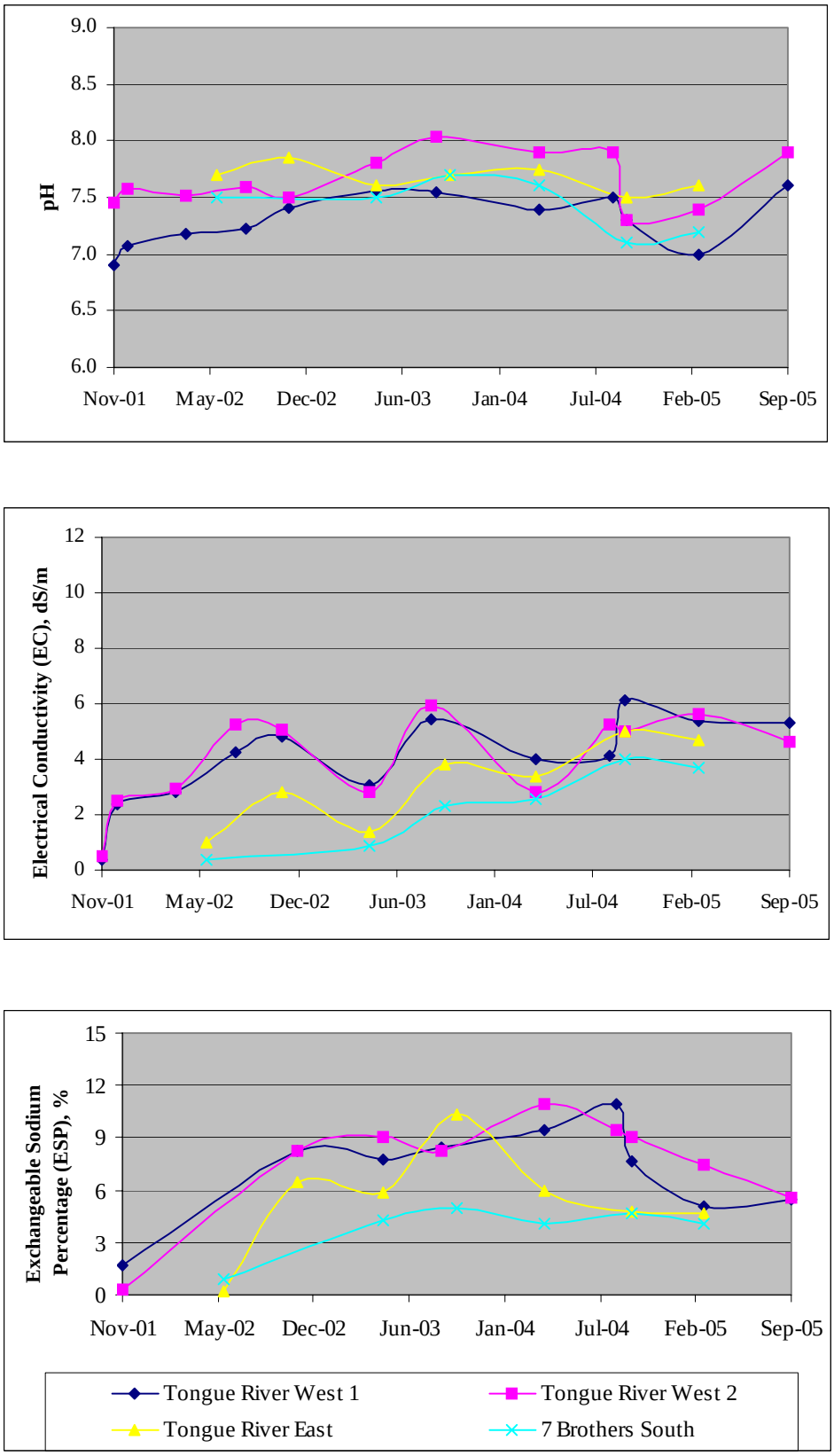


Figure 1. Median pH, average electrical conductivity, and average exchangeable sodium percentage in surface soil (0 to 6 inches) samples from four Fidelity managed irrigation areas in the Powder River Basin of Wyoming.

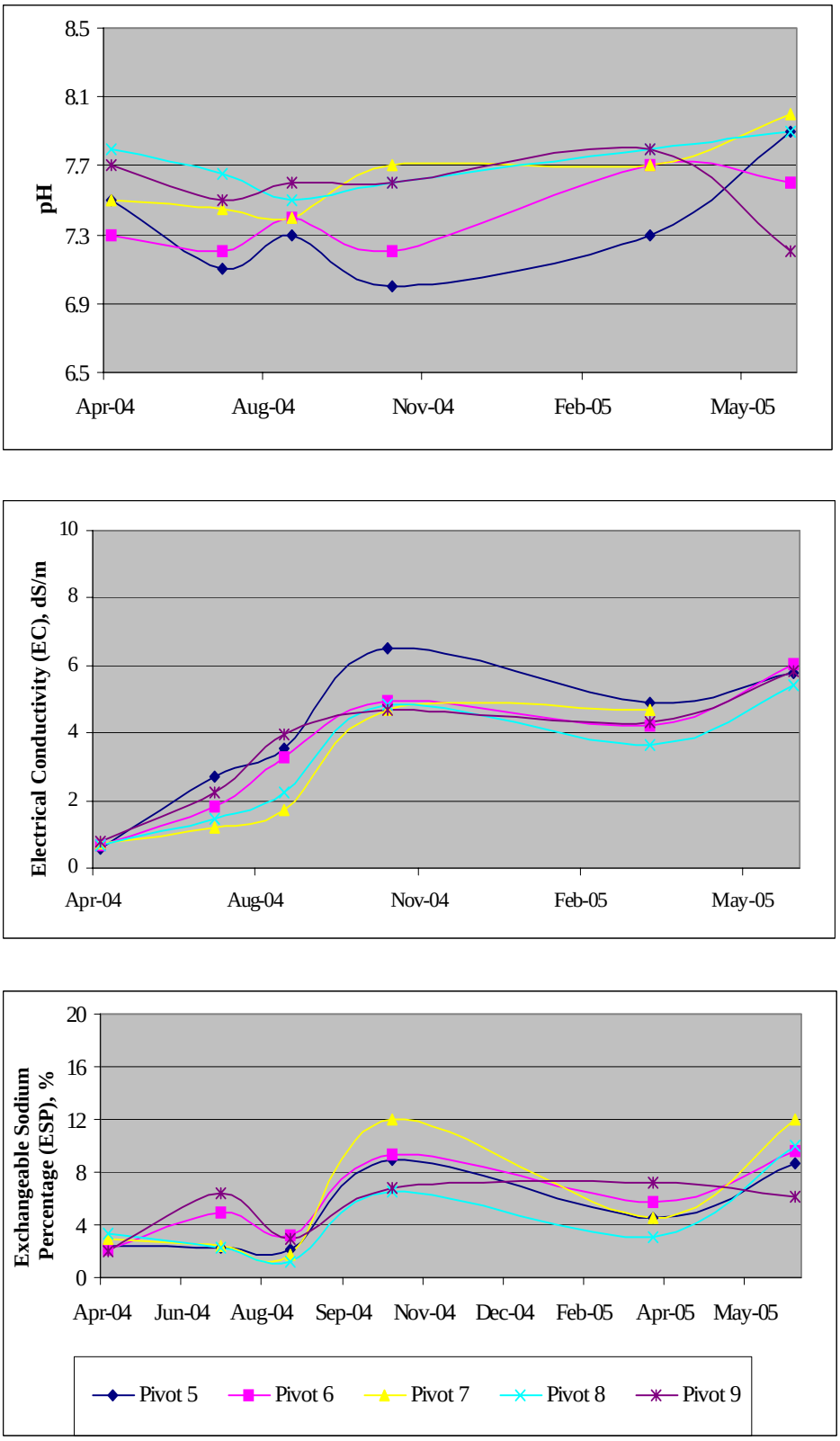


Figure 2. Trends in pH, electrical conductivity, and exchangeable sodium percentage in composite surface soil (0 to 6 inches) samples from five Williams managed irrigation areas in the Powder River Basin of Wyoming.

Assimilative Capacity in the Powder River for Discharge of Coal Bed Natural Gas Produced Water

Jeff Cline, Anadarko, Anadarko Petroleum Corporation
Arthur O'Hayre, Applied Hydrology International
Glen Maynard, Devon Oil Company

ABSTRACT The purpose of this study was to determine the quantity of produced water from coal bed natural gas (CBNG) production that can be discharged on a monthly basis into the Powder River in Wyoming and be assimilated without causing exceedances of the surface water quality standards established by Montana for the Powder River as it flows across the state line.

In the Powder River Basin of Wyoming, the DOE estimates there is 27 TCF of recoverable natural gas from coal. Producing CBNG requires production of ground water to reduce the pressure, allowing the gas to be released from the coal. The quality of the produced water is sufficient for many beneficial uses, but typically the sodium adsorption ratio (SAR) is too high for direct application to land. Operators have sought NPDES permits for direct discharge to the Powder River, where other water management options are not economically feasible (e.g. onsite injection and treatment to remove sodium) or may cause adverse impacts. The Wyoming Department of Environmental Quality (WDEQ) recently issued a template for watershed-based NPDES permitting for the Powder River drainage. The WDEQ seeks to equitably allocate the finite amount of assimilative capacity in the Powder River under the NPDES program. The amount of assimilative capacity available in the Powder River is determined in part by the water quality standards prescribed by the Montana Department of Environmental Quality (MDEQ) for the Powder River at the state line.

On July 15, 2005 the WDEQ issued a draft policy for "Assimilative Capacity Allocation and Control" for the Powder River. Assimilative capacity is the mass load of a constituent of concern that can be discharged to the river without exceeding the greater of the applicable Montana water quality standards or the baseline concentrations. By assessing historical water quality data and applying the BSNMODY model, industry has determined that TDS and sodium are the only constituents with sufficient potential to cause an exceedance of the water quality standards at the state line. Data shows that the Powder River has the capability to assimilate significant volumes of CBNG produced water, even at low flows, and therefore continuous discharges can be allowed without increasing the risk that flows at the state line will exceed the Montana water quality standards.

This presentation will set forth this unique, developing regulatory scheme, identify the economic burdens associated with watershed-based NPDES permitting, and demonstrate that the BSNMODY model determines assimilative capacity in the Powder River in a manner that is scientifically defensible, enforceable in NPDES Permits, and practicable with respect to CBNG water management.

1.0 INTRODUCTION

The purpose of this study was to determine the quantity of produced water from coal bed natural gas (CBNG) production that can be discharged on a monthly basis into the Powder River

in Wyoming and be assimilated without jeopardizing the surface water quality standards established by the State of Montana for the Powder River at the Wyoming/Montana state line.

In the Powder River Basin of Wyoming, the DOE estimates there is 27 TCF of recoverable natural gas from coal. Producing CBNG requires production of ground water to reduce the pressure, allowing the gas to be released from the coal. Produced water removed from coal to produce gas is classified as beneficial use by the Wyoming State Engineer. Most of the produced water is discharged into drainages, ponds, reservoirs or stock tanks. Some of the water is also used directly for irrigation. The produced water from dewatering the coal have been beneficially used for irrigation, domestic or stock water for decades. But recently the expansion of coal bed natural gas (CBNG) production in the Wyoming portion of the Powder River Basin (PRB) has been slowed due to regulatory concerns. The potential impact of discharge of produced water to the Powder River in Wyoming may affect the levels of total dissolved solids, as measured by specific conductance (SC,) and the magnitude of the sodium adsorption ratio (SAR), in the Powder River in Montana.

SAR is the proportion of sodium (Na) to calcium (Ca) plus magnesium (Mg) in the water and is defined as:

$$SAR = Na\ (meq/l) \ / \ [\{Ca\ (meq/l) + Mg\ (meq/l)\}/2]^{1/2} \qquad (1)$$

The SAR indicates the potential for water to impact soil structure. Water that has a high SAR, is poor for irrigation. However, the magnitude of SAR that is acceptable for irrigation varies with the characteristics of both the irrigation water and the soil. Despite the complexities of determining acceptable SAR criteria for irrigation water, the State of Montana has numeric standards for the Powder River SC and SAR as follows:

March 2 Through October 31

- SC Monthly Mean 2000 umhos/cm
- SC Instantaneous Max 2500 uhmos/cm
- SAR Monthly Mean 5
- SAR Instantaneous Max 7.5

November 1 Through March 1

- SC Monthly Mean 2500 umhos/cm
- SC Instantaneous Max 2500 uhmos/cm
- SAR Monthly Mean 6.5
- SAR Instantaneous Max 9.75

The ambient levels of SC and SAR in the Powder River at the Wyoming/Montana state line frequently exceed the Montana standards and the levels increase as the Powder River flows through Montana to its confluence with the Yellowstone River.

Operators have sought NPDES permits for direct discharge to the Powder River, where other water management options are not economically feasible, not appropriate for the site conditions, or cannot accommodate the total volume of produced water. Other water management options include:

- Injection
- Impoundments with infiltration & evaporation

- Irrigation with treatment of the soil or the water to manage SAR
- Beneficial use for livestock and wildlife watering or road dust suppression

Most of the produced water within the basin meets all aquatic based discharge criteria after passive treatment (aeration) to remove iron and manganese. However, treatment to reduce sodium and TDS levels to meet Montana stream standards typically costs a prohibitive $0.30 – 0.50/bbl of produced water. This can increase operating costs to $0.50 to $2.50 per thousand cubic feet (MCF) of produced gas.

The Wyoming Department of Environmental Quality (WDEQ) recently issued a Policy to establish a mechanism, within the existing Wyoming Pollutant Discharge Elimination System (WYPDES) regulatory framework, to allocate the magnitude of allowable discharge of CBNG produced water to the Powder River mainstem which will protect the Montana standards for SC and SAR. A critical factor for implementation of this Policy, is the identification of the magnitude of CBNG produced water that the Powder River can assimilate through the year without exceeding the greater of; the applicable Montana water quality standards at the State Line or the baseline concentrations.

This paper describes an approach to determining the assimilative capacity of the Powder River that is scientifically defensible, enforceable in NPDES Permits, and practicable with respect to CBNG water management. It is critical for operations planning, that the assimilative capacity allocated to each operator be well defined on a seasonal basis and not tied to ambient flow levels in the River. Although operators can manage water to reduce discharge levels during low flow months, zero discharge may not be attainable, especially when wells are being tested for design parameters and economic viability before the water management infrastructure can be developed. Additionally, operators may not have another water management option economically available during the low flow months, so constant allowable discharge is preferred.

Publicly available water quality data from the Powder River, and its tributaries (including CBNG inflows) is used to statistically and historically evaluate assimilative capacity. A model is then applied to the data to find if the assimilative capacity can be predicted from the historical data, in order to allocate discharge quantities to the operators.

2.0 METHODS

Water Quality Data

Operators have monitored, on a monthly basis, the flow and water quality of the tributaries to the Powder River that receive CBNG discharge, and also the water quality on the mainstem of the Powder River upstream and downstream of the tributaries in accordance with WDEQ NPDES permit monitoring plans. A conceptual representation of the required water quality monitoring is depicted in Figure 1. The initial water quality monitoring stations (WQMS) were established and first monitored starting in March 2001. The USGS has also monitored flow and water quality at several locations on the mainstem of the Powder River and on major tributaries in Wyoming, including Clear Creek and Crazy Woman Creek. The locations and frequency of the USGS monitoring has varied over time. The USGS monitoring program and the WQMS programs that were active through years 2003 and 2004 are shown in Figure 2.

The flow and water quality data from both of these monitoring programs from March 2001 through December 2004 was assembled and evaluated as part of this study. The evaluations included tributaries, and, up and down stream Powder River monitoring from operators and the USGS for years 2003 and/or 2004. These were used to assess the changes in Powder River water quality both locally and at the State Line.

These data were also used to conduct mass balance analyses to determine the appropriateness of the mass balance assumptions for SAR prediction. The mass balance method is being considered by the WDEQ to estimate assimilative capacity, and is developed below.

This study also used all available data from August 1969 through December 2004 to determine whether there have been any changes in the levels of SC and SAR at the USGS monitoring location on the Powder River at Moorhead, Montana (near State line) that have occurred as a result of the start of CBNG produced water discharge in year 2000. Time series plots of Flow, SC and SAR at this location are provided in Figures 3, 4 and 5, respectively. It is apparent from these plots that there is considerable variation in baseline levels for these parameters. Three time periods are identified on these plots:

1. The time period prior to 1990 when relatively large quantities of higher salinity water were released into Salt Creek, which is tributary to the Powder River upstream of the Sussex monitoring station.

2. The time period from 1990 through 1999 after reduction in the salinity of the water discharges to Salt Creek.

3. The time period from 2000 to 2004 when CBNG produced water was discharged to the Powder River and tributaries within the reach from the Sussex monitoring station to the to the Moorhead monitoring station at the state line.

The Powder River flows and measured water quality varies by time period. Examination of the flows in Figure 3 shows time period 2 to be a period of relatively (2001 to present) high flow in the Powder River and time period 3 to be a period of relatively low flow. Both high and low flow periods are present in time period 1. Also, during the time period from 1990 to May 2001 SC was measured at the Moorhead Station on the Powder River but chemical analysis of water samples was not conducted. Thus, there are no SAR data for time period 2 as indicated in Figure 5.

Modeling of Water Quality

Finally, evaluations were performed on the two approaches for estimating the assimilative capacity of the Powder River, identified in the WDEQ Policy:

1. "Spreadsheet Model" - The spreadsheet model is an EXCEL monthly mass balance calculation method developed by the United States Environmental Protection Agency (EPA) for the Powder River Oil and Gas EIA and adapted by the WDEQ.

2. "BSNMODY" – The BSNMODY model is an adaptation of a USGS regression based monthly average TDS simulation model of the Powder River that was

modified to predict SAR and to adjust for overestimation of SC during lower flow conditions.

To select the appropriate method, the WDEQ will give greater weight to the model demonstrating the highest confidence level in predicting assimilative capacity, taking into consideration the stream flow data for each month. The BSNMODY was based on a previous salinity and sodium modeling study conducted on the Powder River Drainage Basin by the USGS (Linder-Linsford et al 1992) (1). This approach was selected by a committee comprised of representatives from the USGS, the CBNG Industry in Wyoming, the WDEQ and hydrologic consultants. The committee sought to develop a relatively simple predictive tool that could be used by WDEQ in an adaptive mode for evaluating assimilative capacity of the Powder River.

3.0 RESULTS AND DISCUSSION

3.1 Water Quality and Flow Evaluations for Powder River at Wyoming/Montana State Line

The natural SC and SAR levels at the State line vary widely depending upon the proportion of flow derived from the various tributaries entering upstream of the monitoring station. For instance, the SC and SAR levels in streams draining from the Big Horn Mountains, such as Clear Creek and Crazy Woman Creek, are much lower than the levels in streams draining the plains, such as Salt Creek and Dead Horse Creek (1). The levels of SC in these tributary streams varies with flow, seasonally and with storm events. Normally, the SC levels decline with increase in flow.

Comparison of water quality conditions between these time periods 2 and 3 (Figure 3) must take into account the water quality dependency on flows. Figure 6 shows the significant relationship between flow and SC on the Powder River at the Moorhead Station located near the state line. On the other hand, SAR at this station is not dependent upon flow as shown in Figure 7. The SC dependency upon flow was removed from data by establishing the “best fit” power curve relationship between SC and Flow using all of the data from all three time periods. An evaluation of the residuals or deviations of the actual data points from the “best fit” relationship was performed to determine if the change in Specific Conductance levels in the Powder River at this station may be related to conditions other than flow, such as CBNG discharges, which differs among the three time periods.

The plots and table of SC residuals in Figure 8 show that the specific conductance (when adjusted for flow dependency) does not increase after the introduction of CBNG produced water in 2000. As mentioned, the SC residuals are the deviations above and below the “best fit” power curve relationship between SC and Flow as shown in Figure 6. A time period in which conditions other than flow may have caused an increase in SC in the Powder River at the Moorhead Station would have a SC residual mean that is greater than zero. A time period in which conditions other than flow may have resulted in decreases in SC levels in the Powder River at the Moorhead Station would have a SC residual mean that is less than zero. Time periods 2 and 3 both show SC residual means of less than zero, indicating that the SC levels in these two time periods were less in comparison with time period 1, when flow variations are taken into account. The similar mean for SC residuals between the time periods 2 and 3 indicates no apparent influence on SC levels other than flow. Thus, CBNG produced water released during time period 3 has had no statistical

effect on SC at the State line in comparison with time period 2 and that SC levels in the river are significantly lower in comparison with time period 1.

The comparison between the SAR means in Figure 9 shows there has not been a significant change in SAR comparing time period 3 with time period 1. Since SAR at the Moorhead Station is not dependent upon flow as shown in Figure 7, the plots and table in Figure 9 provide a direct comparison of SAR between time periods 1 and 3. Time period 2 is not included in these results because there were no SAR data for the Moorhead Monitoring Station during this time period.

3.2 Powder River Reach Monitoring Evaluations

The flow and water quality monitoring performed by the USGS and CBNG operators on the Powder River and its tributaries for the period from March 2001 through December 2004 were analyzed to develop the understanding of the localized assimilative capacity near the tributary inflow points along the Powder River and to identify the primary factors controlling SAR levels in the Powder River at the state line monitoring station at Moorhead, Montana. The USGS and the WQMS monitoring locations are shown in Figure 2. Monthly reach monitoring plots were prepared for years 2003 and 2004 to present and interpret the SAR and flow data in tributaries and at Powder River monitoring locations.

The reach plot (Figure 10) for June 2004 shows that SAR levels in the Powder River are controlled by the high SAR level measured upstream at the Sussex monitoring station, and not by the CBNG produced water inflows. Relatively high SAR levels from CBNG water in tributary inflows does not appear to change SAR levels in the Powder River upstream and downstream of the tributaries. SAR levels in the Powder declines below the confluence with Clear Creek but the SAR levels remain above the Montana Standard at Moorhead due to the lack of flow in Clear Creek.

The Reach Plot for May 2004 (Figure 11) shows that the SAR level at Sussex was much lower than for the previous plot for June. The SAR levels in the Powder River remain at essentially the same level through the entire reach of the Powder River to Moorhead. The relatively high SAR levels from CBNG water in tributary inflows does not appear to change SAR levels in the Powder River upstream and downstream of the tributaries, even though the SAR levels in the Powder were much lower in comparison with June. SAR levels remain slightly above the Montana Standard at Moorhead due to the lack of flow in Clear Creek.

The Reach Plot for September 2004 (Figure 12) is a low flow scenario for SAR. SAR level at Sussex was much higher for September than for the previous plots for May and June. Again, the SAR levels in the Powder River remain at essentially the same level within the Powder until its confluence with Clear Creek. The relatively high SAR levels from CBNG water in tributary inflows does not appear to change SAR levels in the Powder River upstream and downstream of the tributaries despite the very low flow levels in the Powder River. The SAR levels were below the Montana Standard at Moorhead due to the inflow from Clear Creek.

The SAR levels in the Powder River significantly increased from upstream to downstream locations in only August 2003 in Years 2003 and 2004. Flow on the Powder River at the flowing tributary locations was essentially zero. A geochemical assessment of major ion concentrations along with SAR and SC for this month is presented in Figure 13.

The geochemical assessment shows the effects of in situ calcium and magnesium salts on the SAR of inflowing CBNG water. In figure 13, the SAR level in the Powder River increases below Burger Draw and below Dry Creek. Due to the absence of flow on the Powder River upstream of Burger Draw, the water in the Powder below these tributaries was comprised of CBNG water. Nevertheless, SAR levels are significantly attenuated in the river immediately downstream of these locations. For example, the SAR level in several miles of the reach of Powder River below Van Houton Draw declines from a value of 29.6 to a value of 7.4 upstream of Dry Creek. The decline is thought to be due to ion exchange of sodium for calcium and magnesium, in the sediments, as indicated by the decline in sodium concentrations. Sulfate and chloride concentrations increase, but bicarbonate concentrations show a substantial decline. TDS concentrations also decline, even though there were no surface water inflows within this reach. Some of the geochemical changes are thought to be due to surface water and groundwater interactions, although the information has not been obtained to confirm this hypothesis.

Also shown in Figure 13, the water chemistry in the Powder River changes markedly below Clear Creek to a mixed cation and sulfate water with SAR levels well below the Montana Standard at Moorhead, as a result of inflow from Clear Creek.

In summary, the reach monitoring plots demonstrate that the SAR level at Moorhead is controlled primarily by the SAR level at Sussex and the relative flows in Clear Creek and in the Powder River at Sussex. CBNG water from tributaries to the Powder does not appear to significantly influence SAR levels measured on the Powder River at the state line monitoring station at Moorhead, Montana. Geochemical influences, including ion exchange and surface and groundwater interaction, appear to increase SAR assimilative capacity of the Powder River at low flows, while the background SAR of the Powder River at high flows quickly assimilates all influent SAR. However, further study is needed to quantify the SAR assimilative capacity on the Powder River.

3.3 Powder River Assimilative Capacity Model Evaluations

The two approaches identified in the WDEQ draft Policy (July 15, 2005) for estimating the assimilative capacity of the Powder River were evaluated. A conceptual representation of the BSNMODY model is provided in Figure 14. The model uses estimates of monthly flows and monthly average TDS concentrations on the Powder River at Sussex and on Clear Creek and Crazy Woman Creek at their confluence with the Powder River to simulate water quality. The adaptation of a USGS regression based model includes estimates of incremental reach flow and loadings based on specified regression relationships. These incremental reach flows and loadings may be negative for some months especially during drought conditions. Monthly flows and monthly average TDS from CBNG water at tributary locations is also needed for the reach from Sussex to Arvada and for the reach from Arvada to Moorhead in order to predict TDS levels at Moorhead with CBNG discharges. The BSNMODY includes an empirical adjustment of TDS estimates during low flow conditions to compensate for the tendency for the mass balance calculations to over predict TDS levels during low flow conditions.

In contrast, the spreadsheet model mass balance calculation method developed by the United States Environmental Protection Agency (EPA) for the Powder River Oil and Gas EIA and adapted by the WDEQ provides a simple mass balance mixing of monthly flows and monthly average TDS from CBNG water with specified flows and TDS levels on the Powder River at Moorhead. The validity of the mass balance assumptions for SAR prediction were evaluated by predicting SAR levels at Moorhead using mass balance calculations and comparing predicted

SAR values with the SAR values measured on the Powder River at Moorhead. The mass balance calculations were performed for the monthly flow and monthly cation concentration analyses on the Powder River and Tributaries during the period from January 2003 through December 2004. The mass balance calculation procedure is shown in Figure 15.

Figure 16 is plot of the difference between the mass balance predicted and the measured SAR values versus the monthly flow at Powder River, Moorhead Station. These results clearly show that mass balance over predicts SAR when average monthly flows are less than 200 cfs and that the magnitude of the bias increases as flows decrease. The mass balance bias is significant as average monthly flows were less than 200 cfs for 67% of the months over the 2003-2004 monitoring period. On the other hand, BSNMODY, which includes an adjustment for mass balance low flow over prediction bias, was found to have good predictability for TDS as shown in Figure 17.

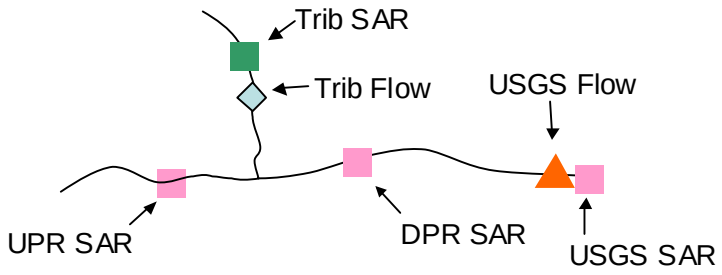
4.0 CONCLUSIONS AND RECOMMENDATIONS

The current SAR data on the Powder River and Tributaries show that SAR levels at Moorhead (Montana State line) are not influenced by current CBNG discharges at tributaries. The SAR value is primarily dependent upon the SAR level at Sussex and the relative flow in the Powder River at Sussex and in Clear Creek at its confluence with the Powder River. Geochemical influences appear to attenuate SAR levels in the Powder River, especially during low flow conditions.

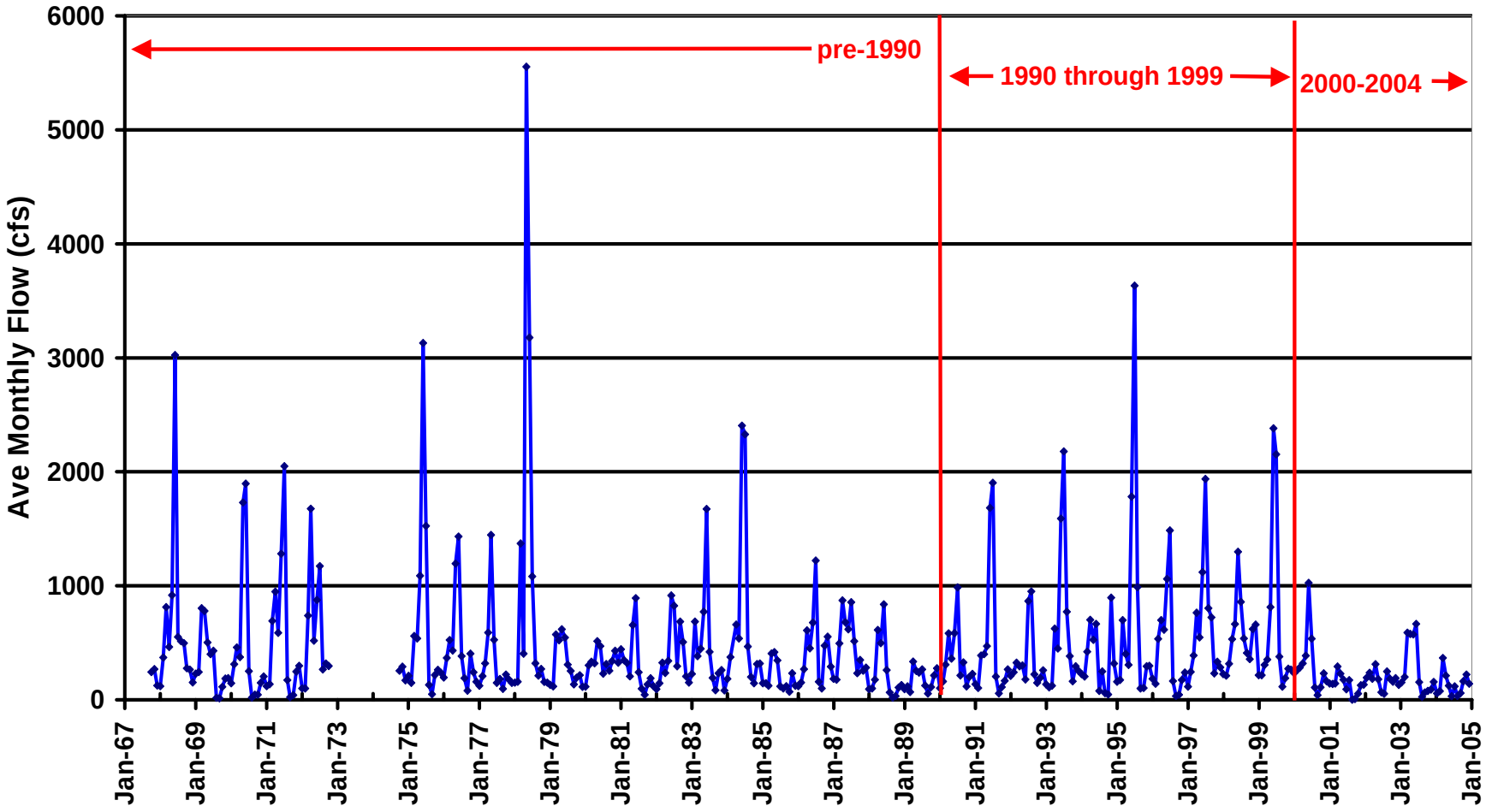
The WDEQ proposes to select the appropriate method which will give the highest confidence level in predicting assimilative capacity. Mass balance based methods do not accurately predict SAR values in the Powder River and significantly over estimate the SAR value during lower flows. The current data and models are too limited to adequately model SAR assimilative capacity and predict SAR values in the Powder River at the state line. The BSNMODY shows reasonably good predictability of assimilative capacity for average monthly TDS concentrations over a wide range of flow conditions and therefore is proposed as the preferred method to predict assimilative capacity for CBNG produced water entering the Powder River.

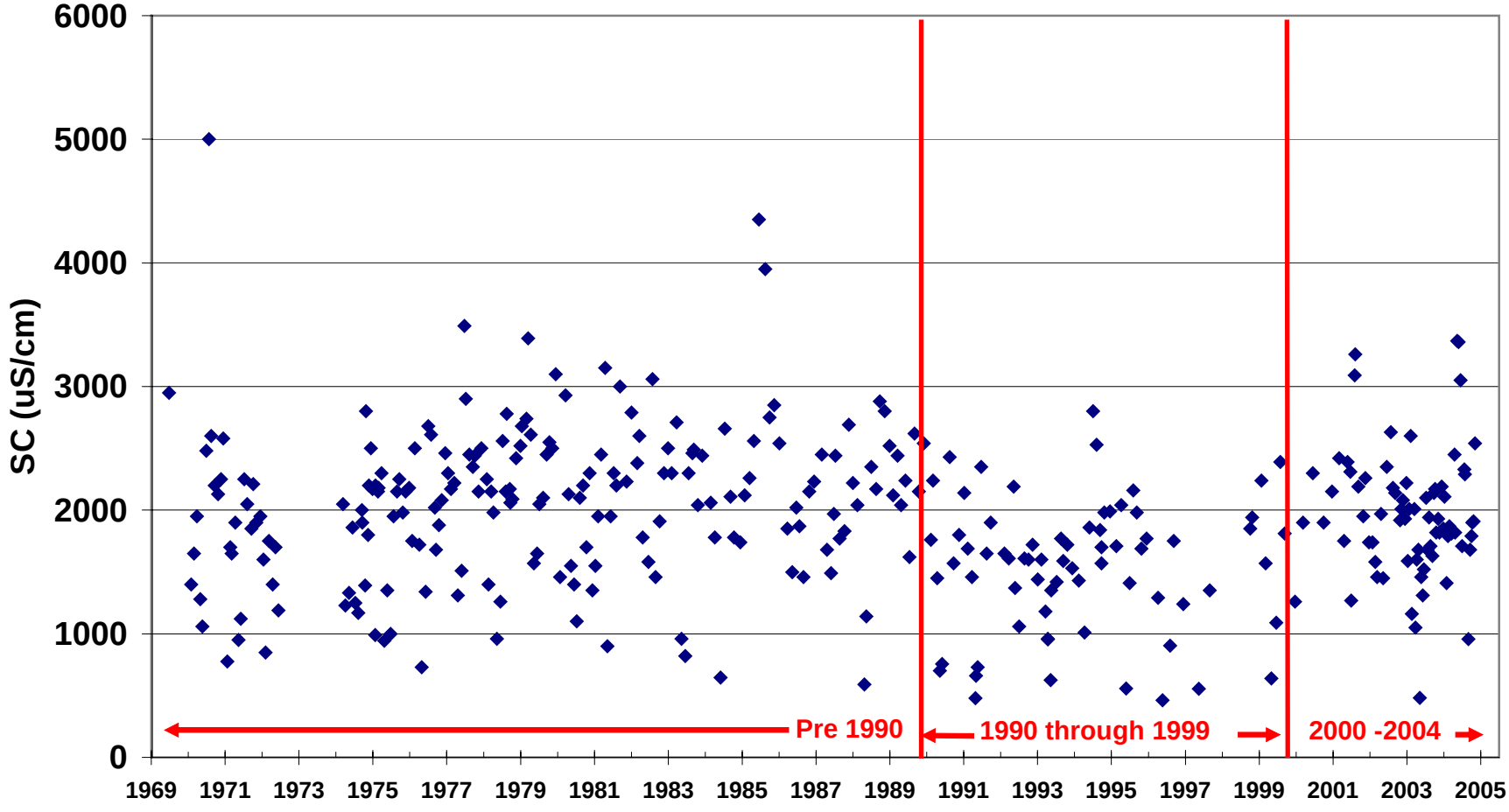
Based on the results of this study, it is recommended that the initial estimate of assimilative capacity be based on TDS using the BSNMODY model and approach. Specific conductance can be determined from TDS concentrations and the use of TDS provides the most reliable basis for predicting effects and estimating any water quality impacts due to CBNG discharges. The use of BSNMODY to determine assimilative capacity will cap total CBNG discharge to the Powder River. The BSNMODY approach calculates the allowable CBNG flow and TDS mass that can be discharged to the Powder River without increasing the frequency of exceeding Montana SC standard at the State Line, relative to the 1990 through 1999 baseline monitoring period.

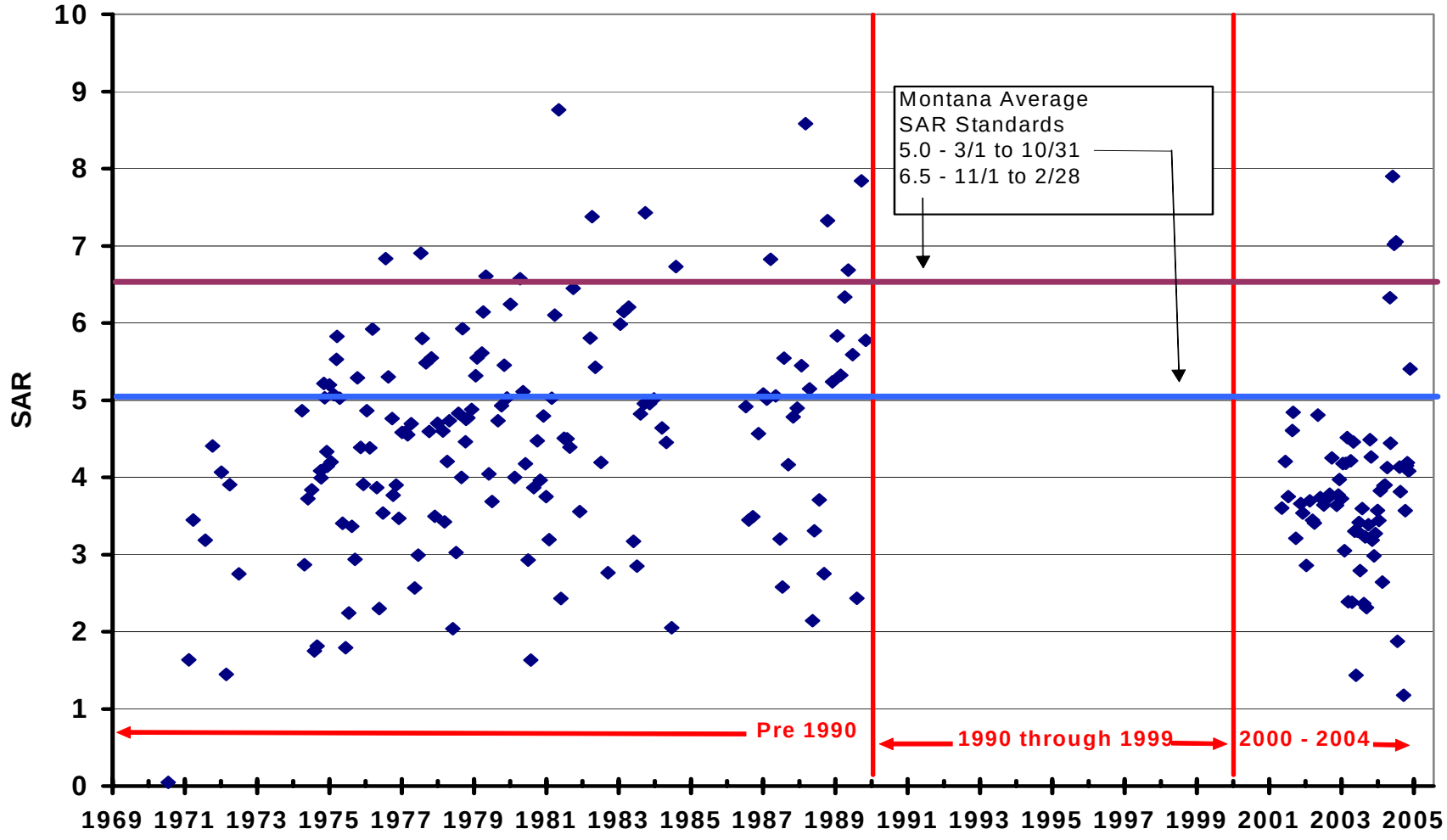
Generic Depiction of Powder River and Tributary SAR and Flow Monitoring

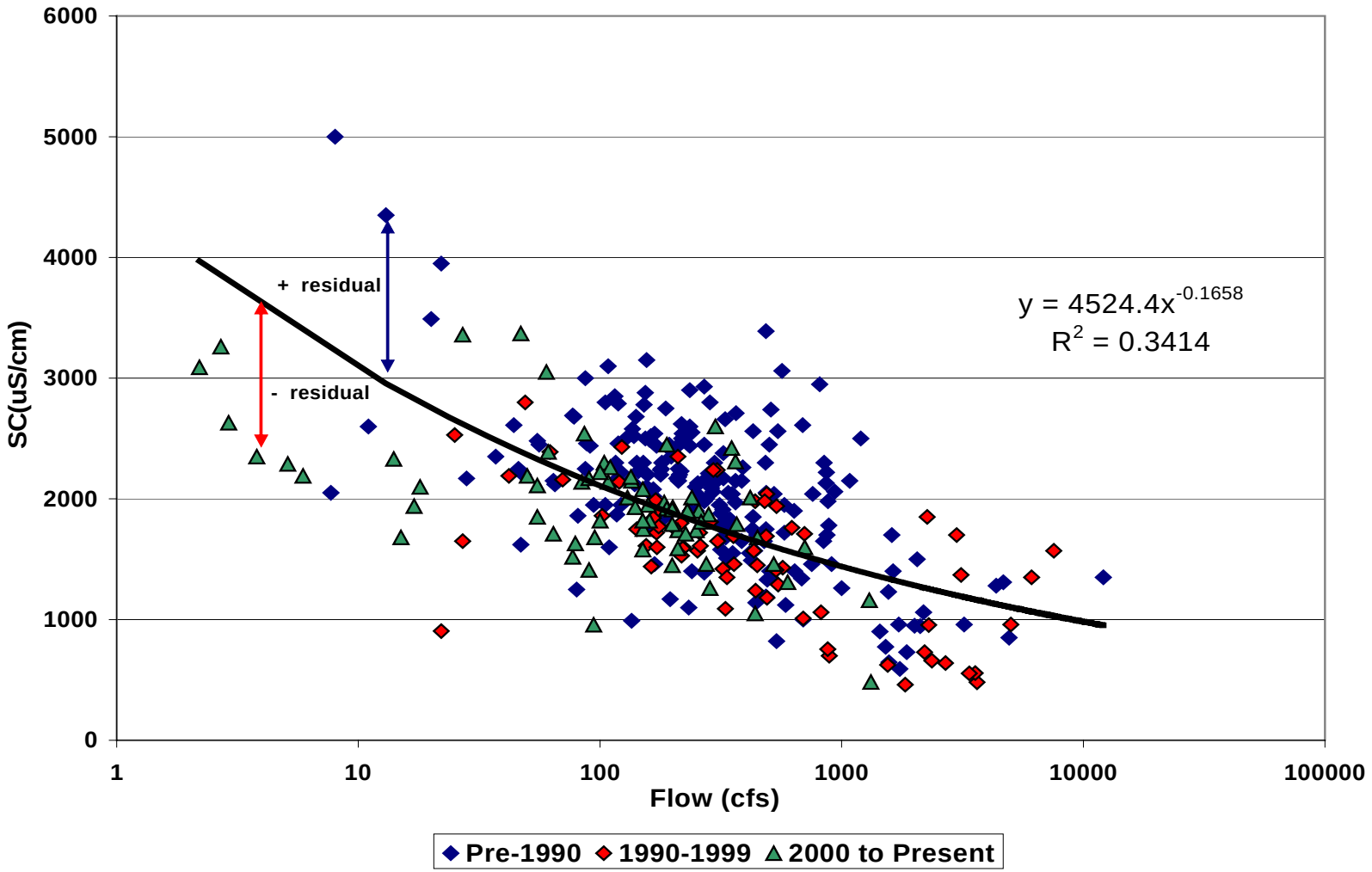


Tributaries are numbered 0 (Sussex) to 17 (Moorhead) per Powder WQMS

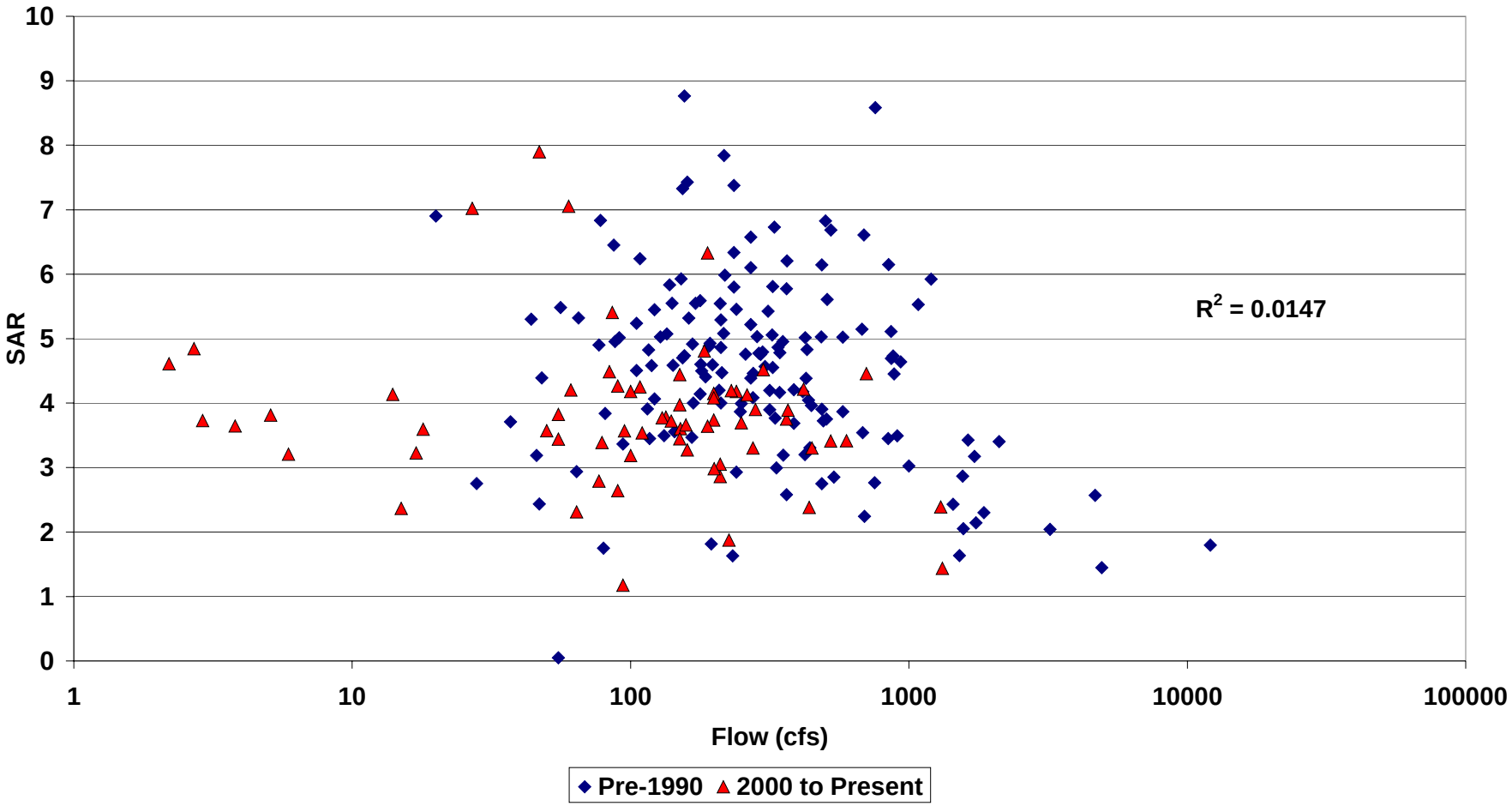

Ave Monthly Flow (cfs)
6000
5000
4000
3000
2000
1000
0
pre-1990
1990 through 1999
2000-2004
Jan-67
Jan-69
Jan-71
Jan-73
Jan-75
Jan-77
Jan-79
Jan-81
Jan-83
Jan-85
Jan-87
Jan-89
Jan-91
Jan-93
Jan-95
Jan-97
Jan-99
Jan-01
Jan-03
Jan-05


6000
5000
4000
3000
2000
1000
0
SC (uS/cm)
1969
1971
1973
1975
1977
1979
1981
1983
1985
1987
1989
1991
1993
1995
1997
1999
2001
2003
2005
Pre 1990
1990 through 1999
2000 -2004

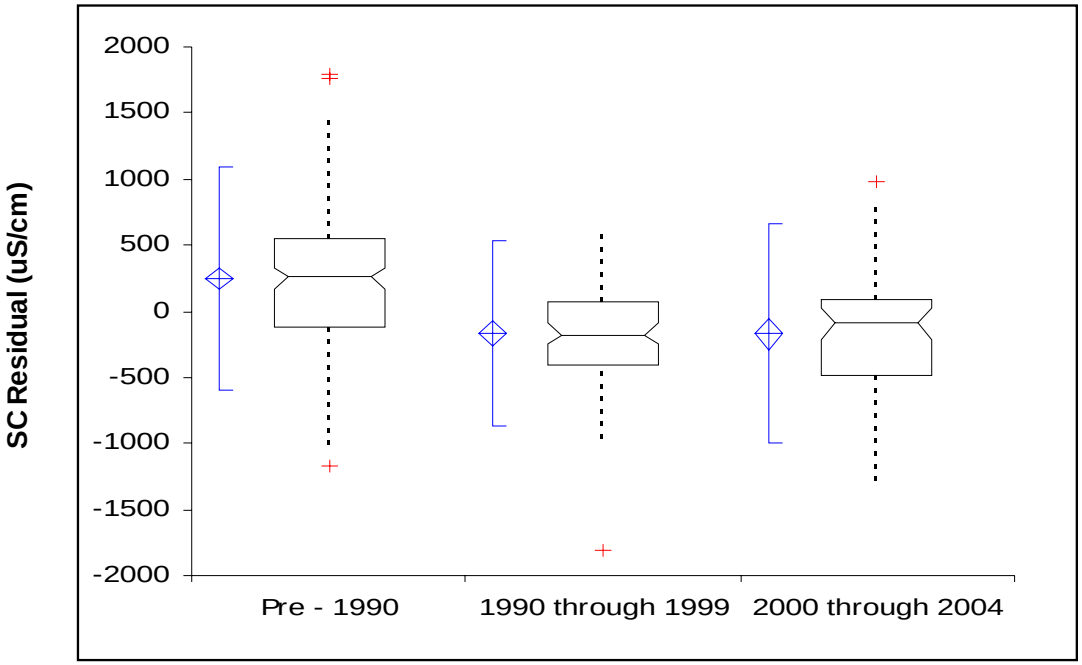

SAR
10
9
8
7
6
5
4
3
2
1
0
1969 1971 1973 1975 1977 1979 1981 1983 1985 1987 1989 1991 1993 1995 1997 1999 2001 2003 2005
Montana Average
SAR Standards
5.0 - 3/1 to 10/31
6.5 - 11/1 to 2/28
Pre 1990
1990 through 1999
2000 - 2004



Residual is difference between actual value and value predicted by relationship


10
9
8
7
6
5
4
3
2
1
0
SAR
1
10
100
1000
10000
100000
Flow (cfs)
R2 = 0.0147
Pre-1990
2000 to Present

SC Normalized For Flow Dependency

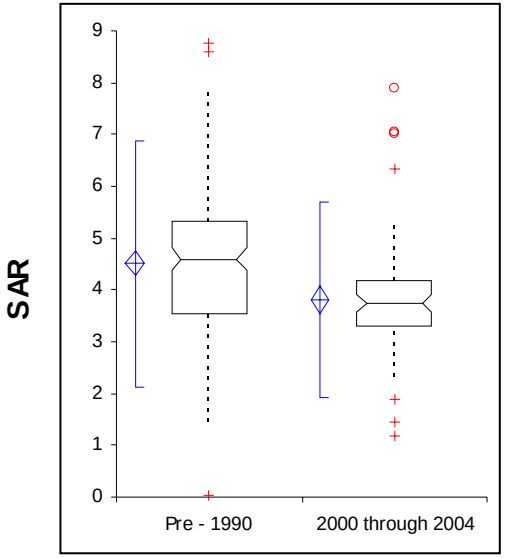


SC Residual by Interval	Mean	SD
Pre - 1990	246.6	513.50
1990 through 1999	-168.5	422.84
2000 through 2004	-168.1	505.92

p-value ~0.995 for t-Test comparing 1990-1999 to 2000-2004 residuals

SAR is Not Impacted by CBNG Discharges

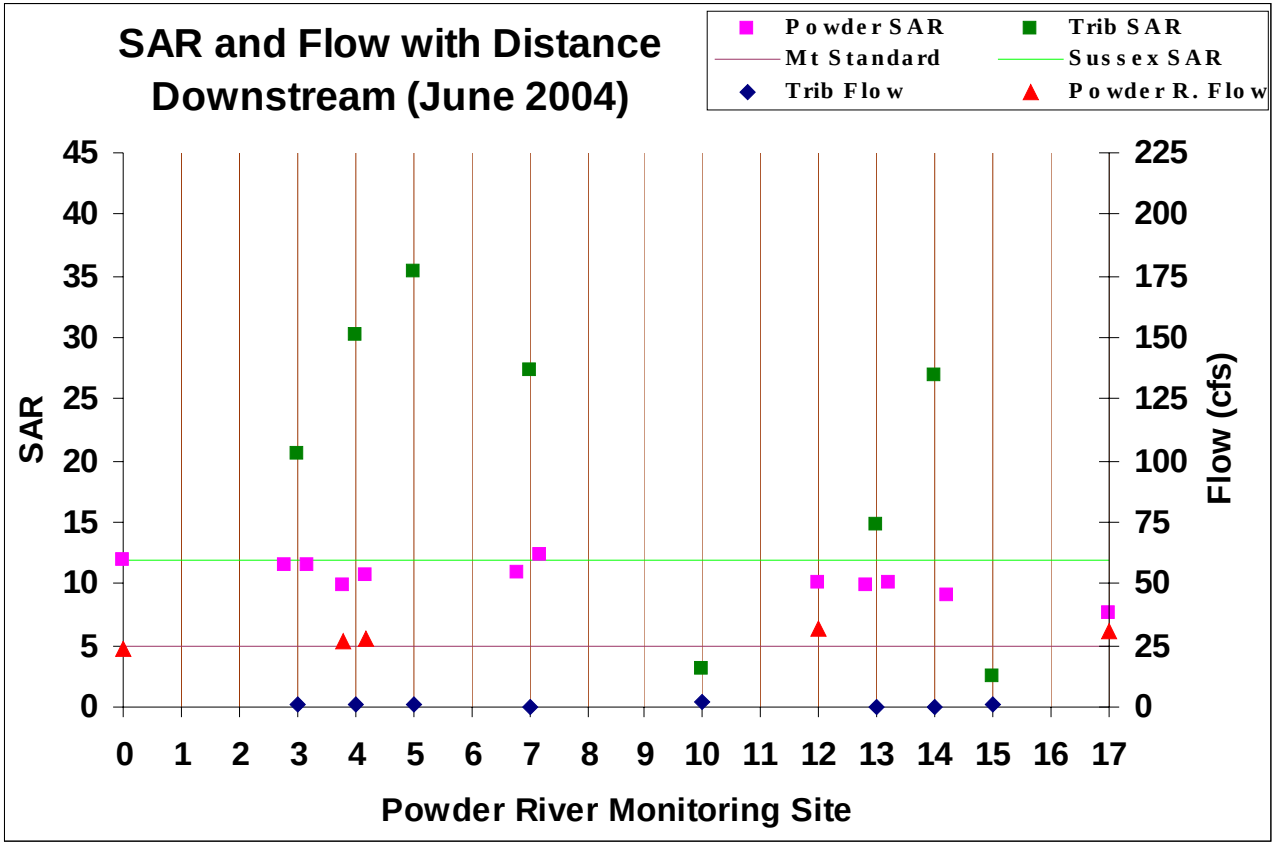
SAR Was Higher Before CBNG Discharges



Calculated SAR by Interval	Mean	SD	Median
Pre - 1990		1.45	4.59
2000 through 2004		1.14	3.73

SAR Level at Sussex and Clear Creek Flows Control SAR at Moorhead

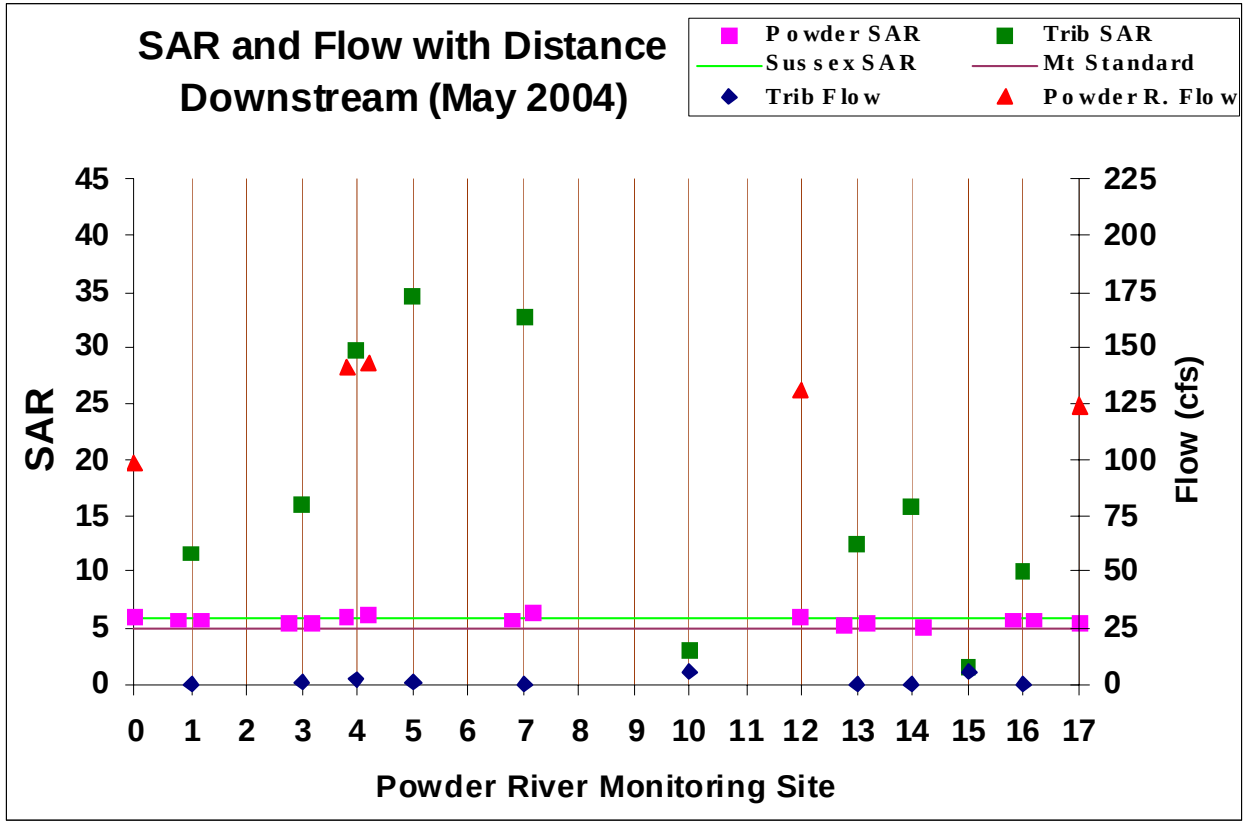
Case 2: Powder-Very Low Flow, & Clear Cr-No Flow



Data Shows No Impact Due to CBNG Discharges

SAR Level at Sussex and Clear Creek Flows Control SAR at Moorhead

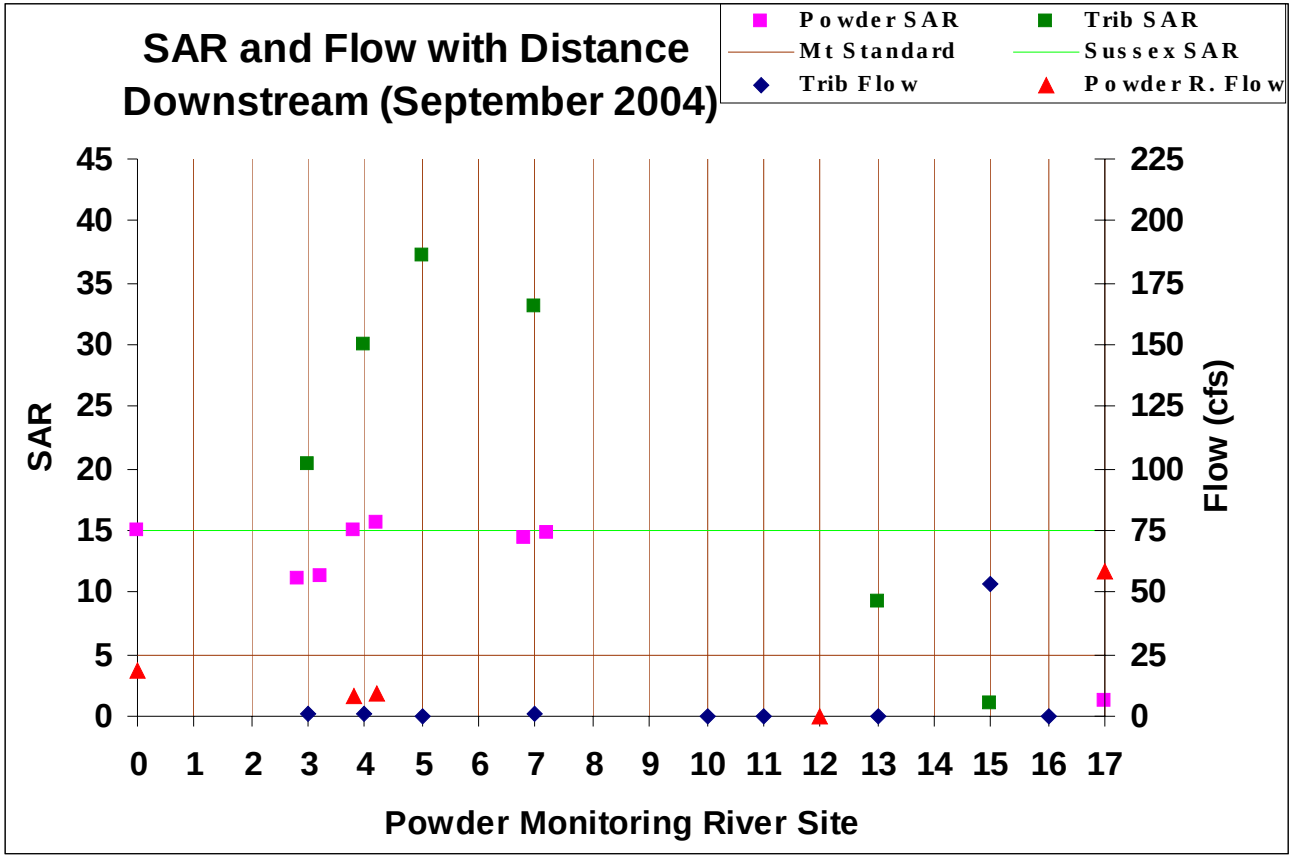
Case 3. Powder-Moderate Flow, & Clear Cr-No Flow



Data Shows No Impact Due to CBNG Discharges

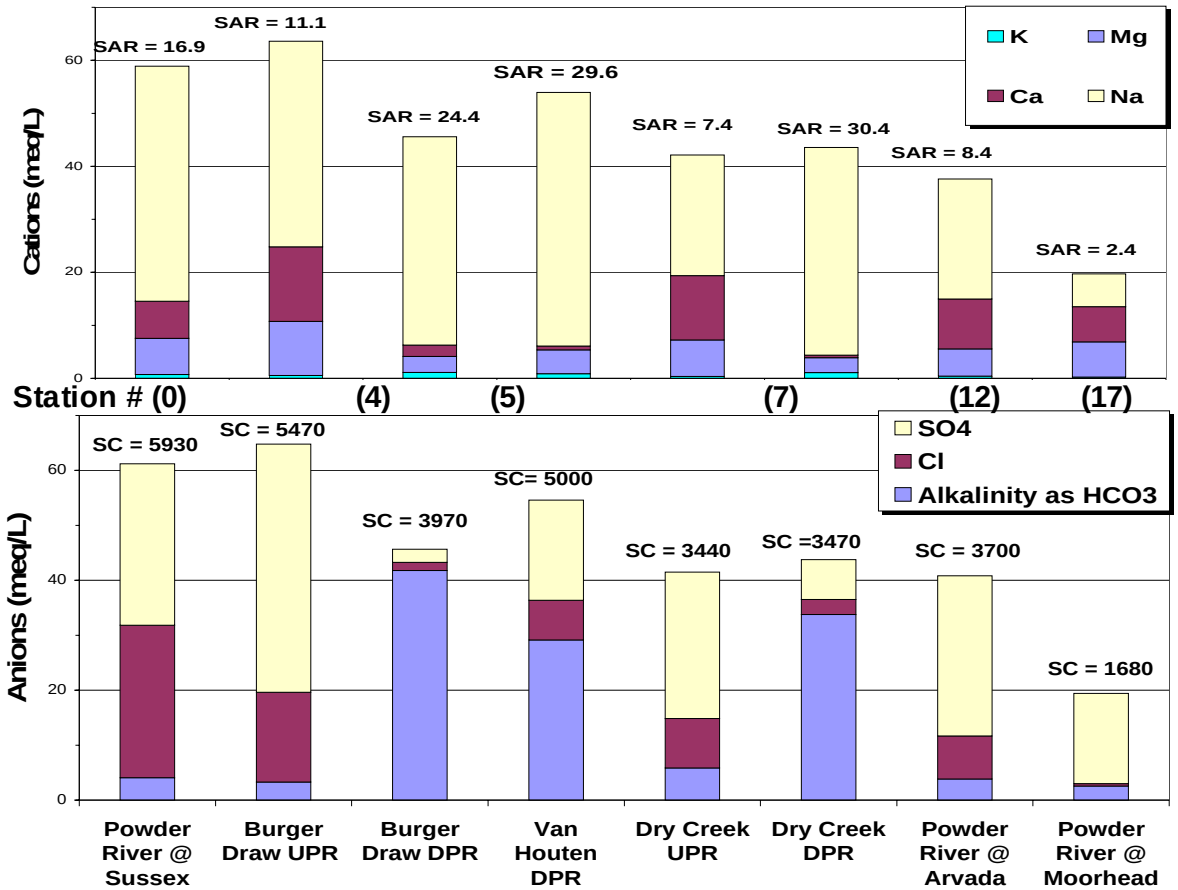
SAR Level at Sussex and Clear Creek Flows Control SAR at Moorhead

Case 4: Powder-Extremely Low Flow



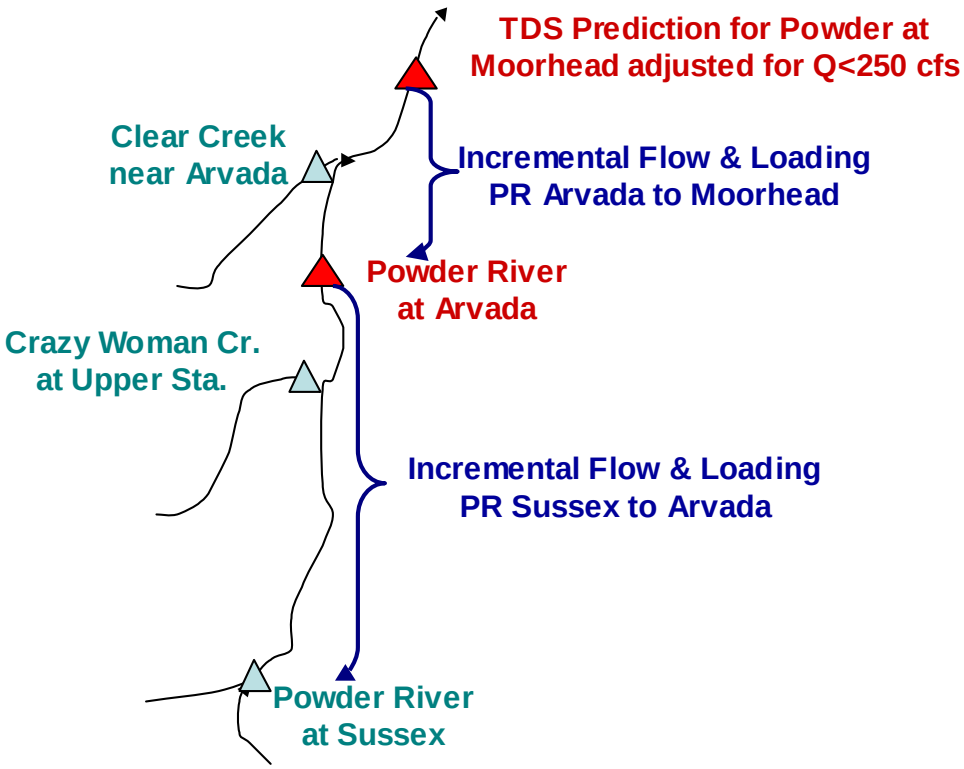
Data Shows No Impact Due to CBNG Discharges

Geochemical Influences Increase SAR Assimilative Capacity at Low Flows in Powder River

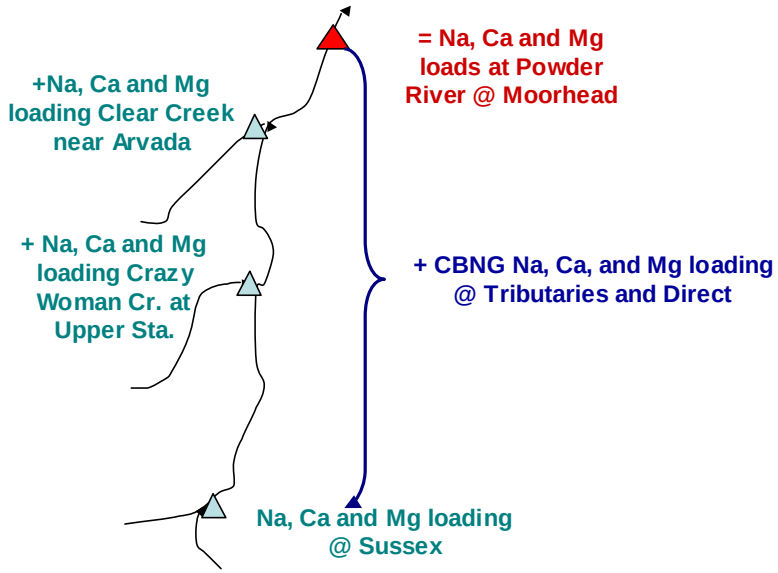


Water Quality Monitoring Sites - August, 2003

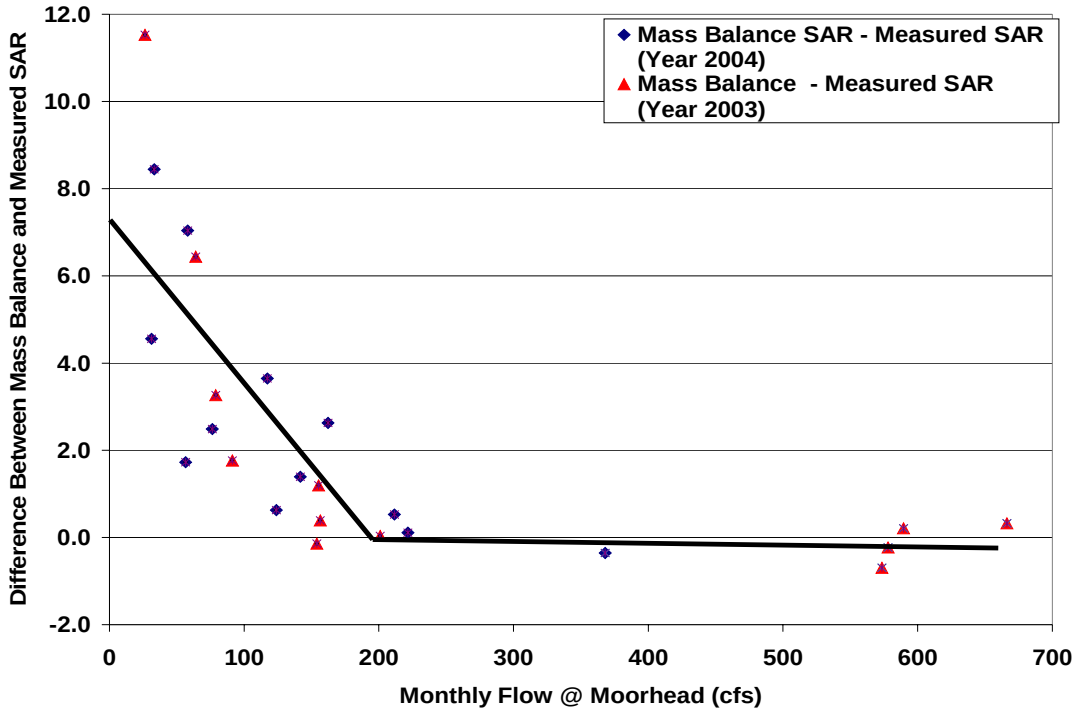
BSNMODY TDS Analysis for Powder River



Evaluation of Mass Balance Analysis for SAR Prediction Using Loading Measurements For Powder River



Mass Balance Over-Predicts SAR at Moorhead at Low Flows



Powder Moorhead Flows < 200 cfs for 67% of the months in 2003 and 2004

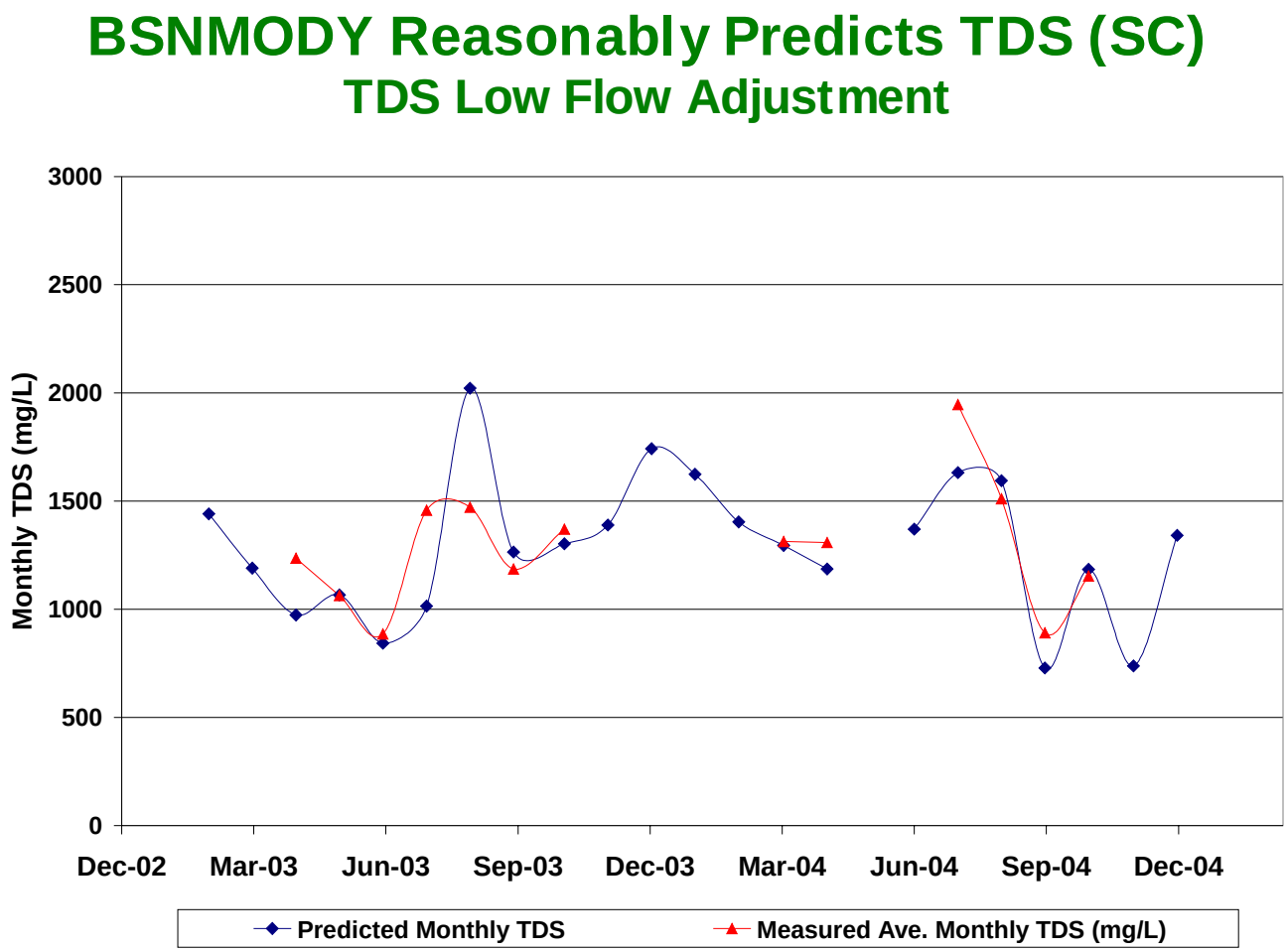


Figure 17. Comparison Between Predicted and Measured Average Monthly TDS Concentrations at Powder River, Moorhead

REFERENCES CITED

1. Lindner-Lunsfore, J.B., et al., "Chemical Quality of Surface Water and Mathematical Simulation of the Surface-Water System, Powder River Drainage Basin, Northeastern Wyoming and Southeastern Montana," *USGS Water Resources Investigations Report*, 91-4199 (1991).

QUANTIFYING LEASE STIPULATION IMPACTS ON FEDERAL OIL AND NATURAL GAS RESOURCE ACCESSIBILITY

John R. Duda and David Alleman
U.S. Department of Energy
National Energy Technology Laboratory

H. William Hochheiser
U.S. Department of Energy

Jeffrey F. Eppink and Ramon Alvarado
Advanced Resources International, Inc.

ABSTRACT

An analysis was completed that made innovative use of the Energy Policy and Conservation Act Inventory data base and model examined how changes in lease stipulation brought about by research could increase access to federal oil and natural gas resources in ten Rocky Mountain Basins. The analysis ranked classes of lease stipulations according to their potential impact on these resources and examined how equivocal modifications of the most important restrictions might increase access for development. Results indicate that big game winter range is the most significant stipulation type followed by sage grouse and raptor habitats. Hazardous geology/steep slopes and other wildlife habitat stipulations round out the top five. The largest changes in accessible resource volumes occur for the Greater Green River Basin. Taken individually, the stipulation types affect accessible federal natural gas and oil resources on the order of 7 trillion cubic feet equivalent. When examined using scenarios that integrate the top three stipulation types, accessible federal resources could increase by about 14.5 trillion cubic feet equivalent. The results (1) imply that significant impacts could be made for various stipulation types if non-environmentally compromising changes are made to lease stipulations and (2) provide direction to related research, development, and demonstrations designed to facilitate such changes.

INTRODUCTION

The U.S. Department of Energy (DOE) through its National Energy Technology Laboratory (NETL) and in collaboration with other federal and state agencies, and industry groups, develops technologies to minimize the environmental impacts of oil and natural gas exploration and production (E&P). The program – the Environmental Solutions Research and Development (R&D) program -- has taken on many faces and has tackled many environmental issues relating to oil and natural gas production since its inception in 1991. The program currently supports (1) development of advanced oil and natural gas E&P technologies and practices, (2) access to resources on Federal lands, (3) regulatory streamlining, and (4) innovative produced water management.

With much of U.S. potential oil and gas resources on federal lands[1], the Environmental Solutions program promotes strategies that will provide increased access to these resources while protecting the environment. Many of the concerns about federal land access involve land impacts such as surface disturbance and wildlife habitats although many others exist, too. In addressing these issues, the Environmental Solutions program facilitates responsible development by investing in small footprint advanced technologies, waste management, soil remediation, data collection and modeling, as well as partnerships to promote environment stewardship.

To support its efforts for evaluating and planning R&D activities related to federal lands access, DOE/NETL sponsored use the datasets and modeling capabilities developed during the Environmental Policy and Conservation Act (EPCA) Inventory[2] to identify potential high-impact research areas.

The objectives for this analysis included:

- Developing analyses of stipulations having potentially large impacts on federal land access and oil and gas resource development designed to assist the Department in evaluating the impact of DOE R&D activities on addressing these stipulations, aimed at improving access with minimal environmental impact.
- To identify and assess current data gaps within the EPCA Inventory datasets that, if addressed, would improve the analytical ability to address federal lands access and environmental/cultural considerations in the future.

It is important to note that the analysis described herein is complementary to a *metrics analysis* on this same topic. Further information on the *metrics analysis* can be found in the companion paper for this conference titled *Addressing Federal Lands Access Issues: Measuring Benefits from DOE's Oil and Natural Gas Environmental Research Program*.[3]

BACKGROUND

Geography of the Analysis

Geographically, the EPCA basins listed below were analyzed discretely.

- Paradox-San Juan Basin
- Uinta-Piceance Basin
- Greater Green River Basin
- Powder River Basin
- Wyoming Thrust Belt
- Denver Basin
- Montana Thrust Belt

For the contiguous states, the EPCA Inventory basins outside of the Rocky Mountains were excluded from the analysis. This was done due to the lesser amounts of oil and gas resources and the lesser degree of federal ownership of oil and gas resources in eastern basins (Black Warrior, Appalachian and Florida Peninsula). Alaska was also excluded from the current study.

This R&D planning analysis also incorporated three other basins that were not part of the EPCA datasets. These basins were examined by analogy and include:

- Williston Basin
- Big Horn Basin
- Wind River Basin.

As with the *metrics analysis*, drill depth considerations were retained in this evaluation of R&D planning and were expanded to include the Montana Thrust Belt, which had not been considered previously. Consideration of drill depth allows resolution of those portions of oil and gas resources that are too deep to drill within a single drilling season. To incorporate drill depth considerations, the EPCA Inventory categorization was modified slightly as shown in Table 1. The access categories were also aggregated as shown in the bottom of the table.

Rank-Ordering of Stipulations by Resources

To determine which lease stipulations have the largest potential effect on the access to oil and gas resources using the EPCA Inventory dataset, the oil and gas resources affected were discretely determined for each stipulation. Like-stipulations (e.g., big game species, sage grouse and sharp-tailed grouse, raptors, etc.) were then grouped to determine the relative impacts of stipulation types on oil and gas resources. Subsequently, and in order to better serve the interests of the Department's planning needs, all stipulations were binned into the following generalized types:

- Areas of cultural/historic resources
- Areas of high aesthetic value
- Big game habitat
- Hazardous geology/steep slopes
- Hydrologic resources
- Other wildlife habitat
- Raptors/accipiter habitat
- Recreation emphasis
- Sage and sharp-tailed grouse habitat

- Threatened, endangered, or special status species habitat.

Thereafter, these stipulation types were rank-ordered first by stipulation type within the EPCA Inventory study areas (Table 2), then by resource for all Rocky Mountain basins (Table 3). The resource allocation [in the tables] for each stipulation type is simply the sum of all oil and gas resources associated with each [stipulation type], independent of other stipulation types.

Working with the Steering Committee set up for the DOE R&D planning project (the same as that used for the EPCA Inventory, comprising officials from the Department of Energy, the Bureau of Land Management, the Forest Service and the Unites States Geological Survey) it was determined that the full EPCA Inventory model would be run on the following stipulation types:

- Big game habitat, which includes species that are largely managed for game hunting. Species include white-tailed deer, pronghorn antelope, elk and mule deer. These large area habitats include winter range, summer range, birthing and calving areas.
- Sage and sharp-tailed grouse habitat, which includes habitats critical to nesting, fledgling, and mating. These areas are typically buffered ¼ to ½ miles from the centroid representing the nest or propagation habitat.
- Hazardous geology/steep slopes, which includes areas of unstable geologic formations, sensitive soils, areas of critical environmental concern, and areas with slopes greater than at least 20 percent. These areas are protected due to the high potential of immediate environmental degradation due to mechanical disturbance.
- Other wildlife habitat, which includes areas that are critical to the survival of wildlife species other than big game (elk, deer, and antelope) or sage/sharp-tailed grouse. Excluded from this category are raptors and generic areas preserved for threatened, endangered or special status species. Commonly designated species include grizzly bear, mountain plover, wild trout, bats, black footed ferrets, and prairie dogs.

Areas of high aesthetic values were not assessed because they are dominated by controlled surface use designations, which are not restrictive relative to other EPCA Inventory categories. With the examination of the above stipulation types, approximately 540 individual stipulations were discretely modified for the analysis.

Important Stipulations for Which No GIS Is Available

Another objective of this effort was to identify and assess data gaps within the EPCA Inventory datasets. Specifically, for a significant number of environmental resources (e.g., cultural resources, wildlife), the requisite mapping has not been conducted. Specific stipulations and environmental resource types were inventoried to determine where data gaps exist, and a finite number were selected where surrogate

geographies of impact could be generated and assessed in the EPCA Inventory model base case.

The EPCA Phase II Inventory[4] incorporates over 2,100 lease stipulations, of which nearly 40 percent have no corresponding maps. For the Rocky Mountain region, the EPCA Inventory stipulations listings were analyzed to determine the preponderance of stipulations that are not mapped. These were ranked according to the following criteria: (1) number of occurrences, (2) importance of their EPCA Inventory categorization (e.g., no surface occupancy vs. timing limitations vs. controlled surface use), (3) the number of field offices affected, (4) an understanding of where stipulations might be related to high-category EPCA Inventory resources (e.g., grizzly bear habitat in Wilderness Areas), and (5) rudimentary estimation of the areas that stipulations might cover. Table 4 shows the stipulations listed in order of relative importance.

Based on an analysis of the stipulations for the seven EPCA basins, the big game and raptor stipulations were the most common stipulations missing GIS data, so these species were chosen for analysis in the EPCA Inventory model.

For big game species, maps from the state wildlife agencies that monitor big game activities were used to create stipulations for the missing data. Where state agency data were not available, USGS Gap Analysis Program (GAP)[5], which seeks to identify gaps between land areas that are rich in biodiversity and areas that are managed for conservation distributions, were used. Exception factors, the percentage of the time that an exception/waiver/modification was made for a given stipulation, determined by the BLM field office or Forest Service office in the EPCA Inventory were applied in the analysis for the base case for these maps.

To infill the missing raptor habitat, data for the missing stipulation maps came from a number of sources. GAP vertebrate distribution data were used for the following states: Colorado, Idaho, Montana, New Mexico, Utah, and Wyoming. This GAP data provides a geographical representation of the distribution of habitat preferences of native vertebrate species. In addition, data were used from the Montana Fish Wildlife & Parks, Colorado Department of Wildlife, Utah Division of Wildlife Resources and Wyoming Game & Fish.

Due to the generalization of the GAP data, it was determined that the GAP maps would need to be "discounted" in order to realize a more accurate picture of the actual impediment posed by the raptor stipulations. The discounting was incorporated into the EPCA Inventory model. Determination of the factors used for the adjustment is described as follows.

For the raptor data, this discounting was based on discussions with Dr. Gary P. Beauvais, Director of the Wyoming Natural Diversity Database at the University of Wyoming, where an adjustment factor was applied to the GAP data for various raptors. The discount factors were determined by a visual inspection of the GAP distributions and

compared with general knowledge of the actual occurrences of the species in Wyoming. For stipulations that included multiple species, the discount factors for all species were averaged and then applied to the model. Table 5 lists the discount factors utilized in the analysis.

Non-EPCA Basin Analysis

In addition to the EPCA Inventory basins, the Williston, Big Horn and Wind River basins were examined by analogy. Based upon experience with the Western basins, the following correlations were determined:

- Williston Basin, examination by analogy with the Powder River Basin
- Big Horn Basin, examination by analogy with the Powder River Basin
- Wind River Basin, examination by analogy with the Greater Green River Basin

To assess the portion of federal oil and gas resources in these basins, the percentage of federal land was determined using the Federal lands layer from the National Atlas[6], a collection of the geospatial and geostatistical data for the U.S. compiled by the government. The federal lands layer was clipped to each basin and the total acreage of federal land, excluding Indian lands, was divided by the total land in the basin. The mean resources (billion cubic feet equivalent [BCF_e]) in each basin were determined using the 1995 USGS National Oil and Gas Assessment[7] to derive the quantities, i.e., the sum of all plays within a given basin.

These basins were analyzed by comparison of the net federal oil and gas resources in these basins distributed within the Modified EPCA Inventory Access Categorization (see Table 1) relative to analog basins. Table 6 shows the resources and the relative portions of federal land in these basins.

Scenario Compilation and Analysis

As noted, the objective of this analysis was to ascertain, for specific stipulation types (for which various degrees of change were to be made to their geography, timing limitations or exception rates as a result of DOE's Environmental Solutions R&D program) if in fact improvements could result and to what degree. Specifically, the EPCA Inventory model allows one to strip away portions of a stipulation, allowing the calculation of the effects of the absence of that stipulation. In fact, other stipulations may co-exist at a site such that change in the stipulation in question could have little effect. Conversely, significant EPCA Inventory categorical changes to standard lease terms could occur if no other stipulations overlay the site. The EPCA Inventory model is specifically designed to capture the impacts of such changes.

The stipulation types of big game habitat, sage and sharp-tailed grouse habitat, hazardous geology/steep slopes, and other wildlife habitat were examined, independently, by basin. Three scenarios—representing changes in key parameters at levels of ten percent modification were examined, as shown in Table 7. Each of these scenarios

represents random reductions in stipulation geography. Geography is the most important parameter, as all stipulations in the model have a mapped area. Not all stipulations have timing limitations or exception factors.

The scenarios increase in order of the anticipated impacts — Scenario 1 [10 percent] is relatively modest, whereas Scenario 3 [30 percent] is very bullish. These scenarios were constructed to realistically capture the potential range of impacts from DOE R&D activities.

RESULTS

The initial results of the analysis show that big game winter range is the most significant stipulation type. Sage grouse and raptor habitats (within ranges of error) are essentially tied for second place followed by hazardous geology/steep slopes and other wildlife habitat. Table 8 illustrates this for Scenario 2 (the random 20 percent reduction), where the stipulation types have been examined independently.

Stipulations for different species often overlap; this is especially true for No Surface Occupancy (NSO) and timing limitations. By removing or reducing a stipulation, an area often defaults to another underlying stipulation affecting the categorization. After completing the initial analysis and examining the results of the single species stipulation runs, DOE decided to assess the potential cumulative impacts if R&D activities for several species were funded simultaneously and acceptable modifications were realized. By examining the impact of increased efficiencies of big game, sage grouse and raptor stipulation types, the three most significant stipulation types, the analysis sought to answer the question: Is the impact as expected and is the combined impact greater than the sum of the individual stipulation-type impacts, and by how much? As with the individual stipulation types, the modeling ascertains the degree of improvement that would result if significant changes were made to geography, timing limitations, or exception rates for big game, sage grouse and raptor stipulation types using 10, 20 and 30 percent changes.

Modeling of the integrated case (20 percent scenario) shows that a significant benefit results – shifting a significant 14.6 TCF_e into the accessible class. This is slightly more than twice the impact assessed for the largest individual stipulation type and an amount greater than the sum of the constituent independent runs. This increase is attributed to the effect of removing multiple timing limitation stipulations for the different species.

Figure 1 shows graphically the results for all basins (both individual stipulation types and the integrated stipulation cases) examined in a simplified fashion, showing the aggregated resource shifting out of Modified EPCA Inventory Access categories 5 through 8 and into categories 8a and 9. Individual basin results are presented in Figures 2 through 11.

CONCLUSIONS

The results of the DOE R&D planning analysis imply that significant impacts could be made for various stipulation types if non-environmentally compromising changes could be made to stipulation geography, timing, or exception rates. Targeted productive R&D has the opportunity to provide significant access to oil and gas resources in the Rocky Mountain basins—as much as 7 TCF_e of oil and gas resources could be made more accessible when stipulation types are examined independently. Notably, whenever the three most significant stipulation types are modified simultaneously the beneficial resource shift increases to 14.5 TCF_e.

In addition, the following conclusions are applicable:

- Each of the Rocky Mountain basins is unique in terms of the relative importance of stipulation types.
- Big game, sage grouse and raptors are important stipulations types that affect access in the Rocky Mountain basins.
  - Generally, big game winter range dominates in the basins.
  - In the southern basins, raptor habitat is relatively significant. This significance changes to sage grouse habitat in the northern basins.

Geohazards/steep slopes are significant for affecting net NSO but the "freed up" resources are typically subjected to other, lower order stipulations, especially timing limitations.

In summary, analyses such as the one described herein support the Department's goal of facilitating responsible development of domestic natural gas and oil resources. Results of the analysis can be used to guide RD&D supporting greater access to federal lands consistent with the Administration's drivers of economic growth, energy security, and environmental protection. Moreover, there is an acute need to access and produce additional quantities of oil and natural gas given the extremely high prices that these commodities are now commanding.[8]

Table 1. Modified EPCA Access Categorization

Level	Modified EPCA Access Category
1	No Leasing (Statutory/Executive Order) (NLS)
2	No Leasing (Administrative) (NLA)
3	No Leasing (Administrative) Pending Land Use Planning or NEPA Compliance (NLA/LUP)
4	Leasing, Net No Surface Occupancy (NNSO)
5	Leasing, Cumulative Timing Limitations (TLs) of >9 Months, Drill Depth Limited
5a	Leasing, Cumulative Timing Limitations (TLs) of >9 Months
6	Leasing, Cumulative Timing Limitations (TLs) of >6 to = 9 Months, Drill Depth Limited
6a	Leasing, Cumulative Timing Limitations (TLs) of >6 to = 9 Months
7	Leasing, Cumulative Timing Limitations (TLs) of >3 to = 6 Months, Drill Depth Limited
7a	Leasing, Cumulative Timing Limitations (TLs) of >3 to = 6 Months
8	Leasing, Cumulative Timing Limitations (TLs) of =3 Months (Drill Depth Limited) or Controlled Surface Use (CSU)
8a	Leasing, Cumulative Timing Limitations (TLs) of =3 Months or Controlled Surface Use (CSU)
9	Leasing, Standard Lease Terms (SLT)

Categories Aggregated Relative to Access
Inaccessible (Categories 1-4)
Accessible with Restrictions (Categories 5-8)
Accessible under Standard Lease Terms (Category 9) or with Minimal Restrictions (Category 8a)

Table 2. Ranked Stipulation Types by Study Area

STIPULATION TYPE	BCFe
Uinta Piceance Basin	
Big game habitat	3,295
Hazardous geology/steep slopes	1,499
Hydrologic resources	764
Areas of high aesthic value	559
Non-big game wildlife habitat	524
Paradox-San Juan Basins	
Big game habitat	5,689
Areas of cultural/historic resources	1,283
Hydrologic resources	604
Hazardous geology/steep slopes	410
Recreation emphasis	234
Montana Thrust Belt	
Hazardous geology/steep slopes	1,801
Non-big game wildlife habitat	1,596
Big game habitat	1,254
Recreation emphasis	1,169
Areas of high aesthic value	844
Powder River Basin	
Sage and sharp-tailed grouse habitat	1,528
Big game habitat	827
Hazardous geology/steep slopes	559
Areas of high aesthic value	257
Wyoming Thrust Belt	
Big game habitat	239
Hazardous geology/steep slopes	97
Sage and sharp-tailed grouse habitat	57
Hydrologic resources	46
Areas of cultural/historic resources	34
Greater Green River Basin	
Big game habitat	17,676
Sage and sharp-tailed grouse habitat	15,555
Areas of high aesthic value	4,925
Non-big game wildlife habitat	4,851
Hazardous geology/steep slopes	4,001
Denver Basin	
Big game habitat	51
Areas of high aesthic value	34
Hazardous geology/steep slopes	11
Raptors/Accipitor habitat	6
Threatened, endangered, or special status species	6

Table 3. Ranked Stipulation Types for the Rocky Mountains

STIPULATION TYPE	BCFe
Big game habitat	29,030
Sage and sharp-tailed grouse habitat	17,146
Hazardous geology/steep slopes	8,373
Other wildlife habitat	6,971
Areas of high aesthetic value	6,675
Hydrologic resources	1,419
Recreation emphasis	1,402
Areas of cultural/historic resources	1,317

Table 4. Stipulation Types with the Greatest Number of Data Gaps by Basin

EPCA Study Area	Stipulated Environmental Resource
Uinta Piceance Basin	Raptors and T&E/Sensitive Species
Paradox San Juan Basins	ACEC/SMAs and Raptors
Montana Thrust Belt	Big Game, Raptors and Historic/Cultural/Heritage areas
Powder River Basin	Raptors and Sage Grouse
Wyoming Thrust Belt	Big Game and Raptors
Greater Green River Basin	Big Game and Raptors
Denver Basin	Raptors and T&E/Sensitive Species

Table 5. Raptor Stipulation Factors Used for Discounting GAP Data

Species	Breeding	Winter*
Osprey	20%	
Bald Eagle	80%	70%
Golden Eagle	50%	70%
Merlin	80%	70%
Northern Goshawk	70%	70%
Peregrine Falcon	80%	
Swainson's Hawk	30%	
Mexican Spotted Owl**	54%	

*Exception factors for wintering species only calculated for those species that winter in Wyoming.

**The Mexican Spotted Owl does not occur in Wyoming therefore an average of the exception factors in the basins where it does occur was applied.

Table 6. Basins Analyzed by Analogy

USGS Basin	O&G Resources (BCFe)	Portion Federal Land	Portion Federal Resources (BCFe)
Williston	2,992	11%	329
Big Horn	451	68%	307
Wind River	1,007	51%	514

Table 7. Base Case and Scenario Parameters Used to Identify Potential High Impact Research Areas

Scenario	Changes			Remarks
	Geography	Timing Limitations	Exception Factors	
Base				EPCA II + Drill Depth Considerations
10%	-10% randomly	+2 weeks	+10%	Modest
20%	-20% randomly	+4 weeks	+20%	Significant
30%	-30% randomly	+6 weeks	+30%	V. Significant

Table 8. Aggregated Results—Beneficial Resource Shifting, All Basins

Rank	Stipulation Type	Delta BCFe (20% Scenario)
1	**Big Game**	**7,016**
2	**Sage Grouse**	**3,563**
3	**Raptors**	**3,291**
4	Steep Slopes	249
5	Other Wildlife	106

Figure 1. Potential Impact of R&D Programs on Stipulation Types on Federal Land Access—All Study Areas

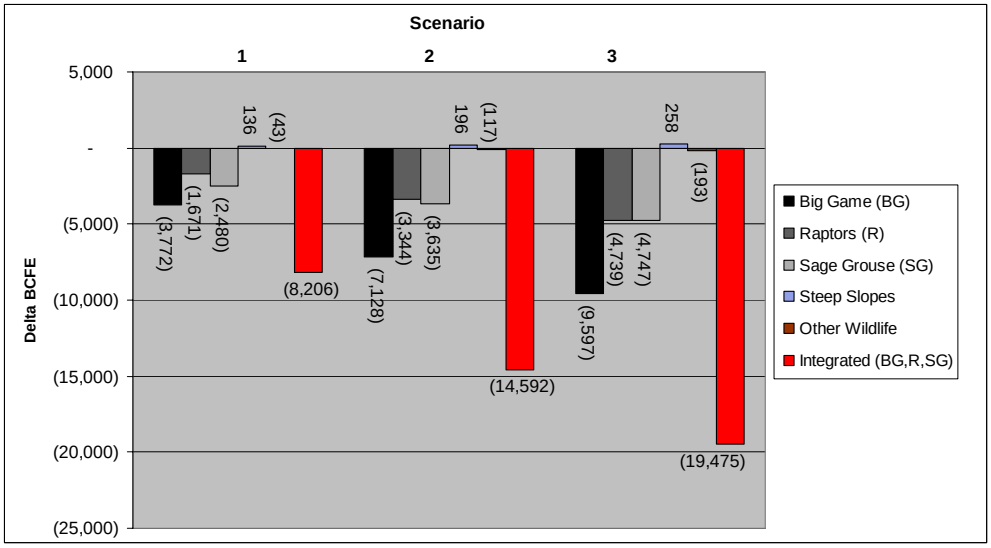


Figure 2. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Uinta-Piceance Study Area

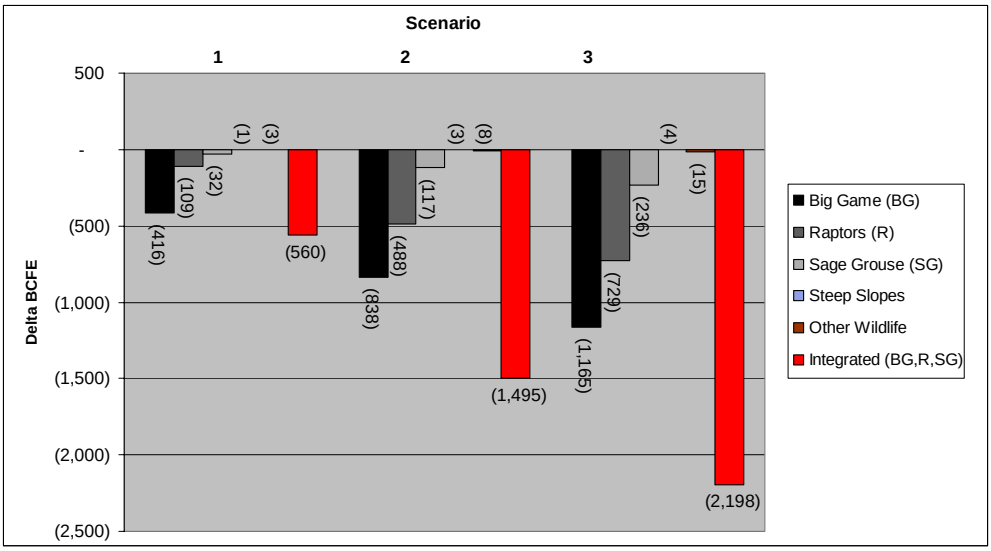


Figure 3. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Paradox/San Juan Study Area

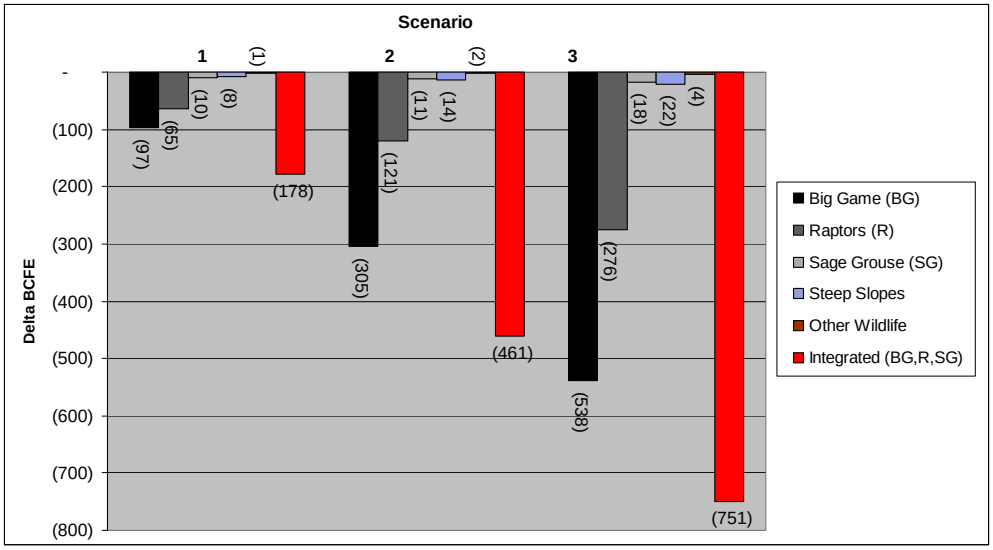


Figure 4. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Montana Thrust Belt Study Area

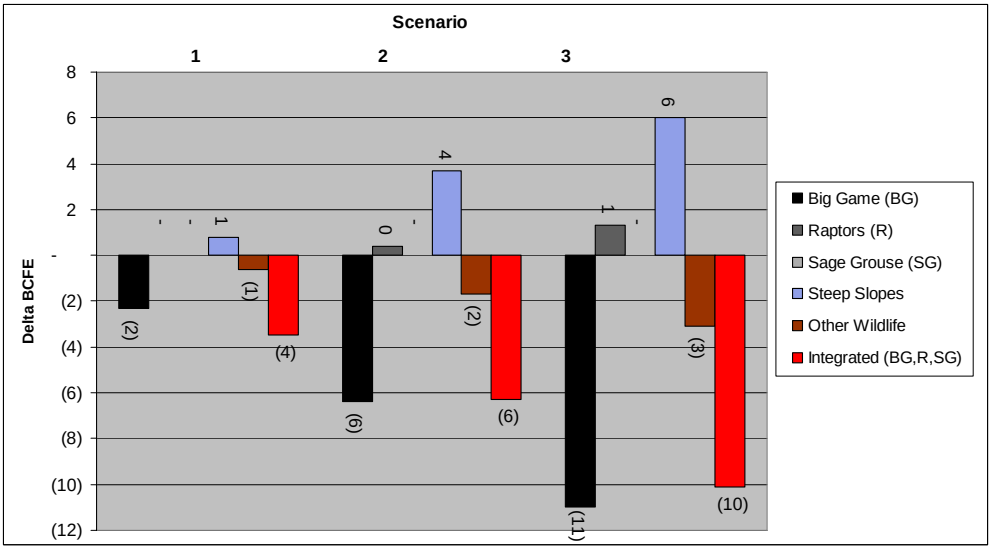


Figure 5. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Powder River Basin Study Area

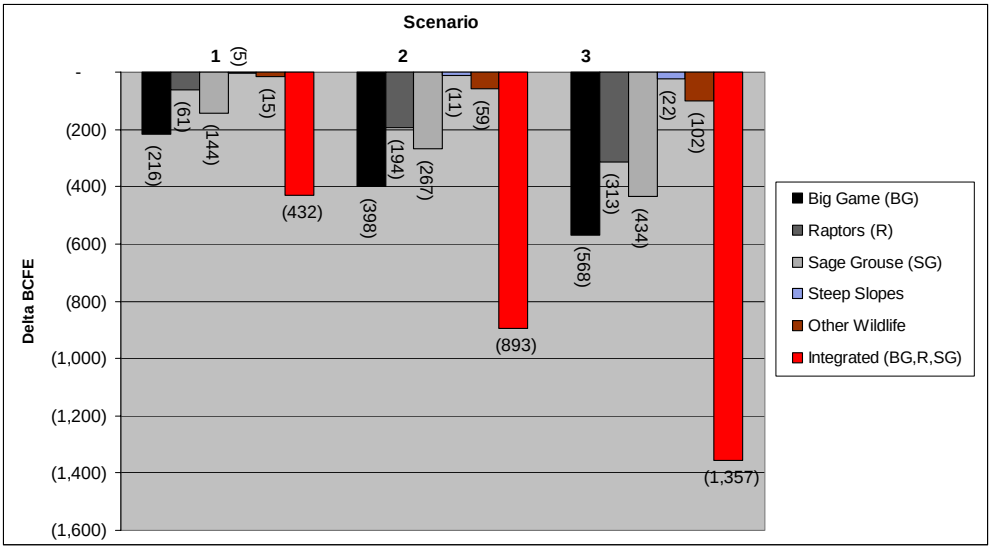


Figure 6. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Wyoming Thrust Belt Study Area

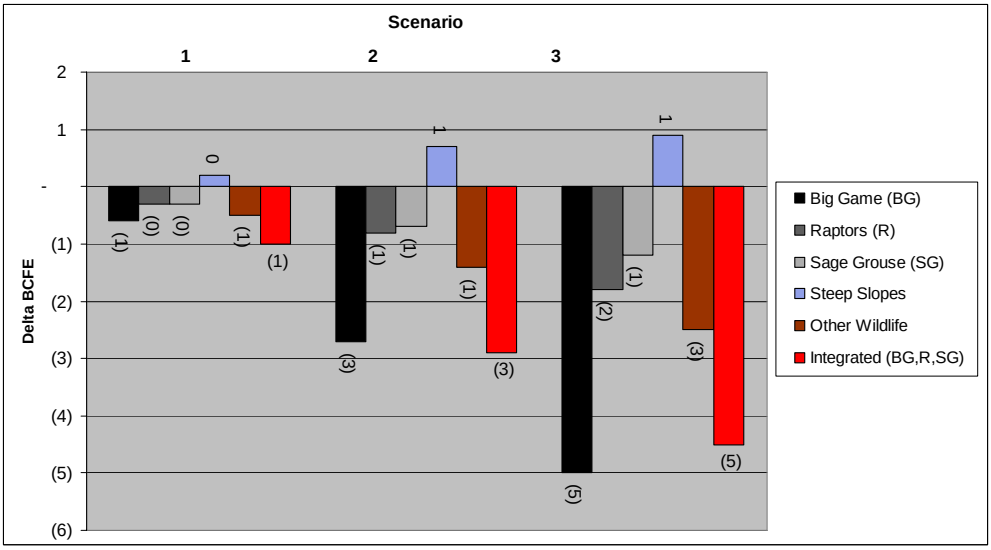


Figure 7. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Greater Green River Basin Study Area

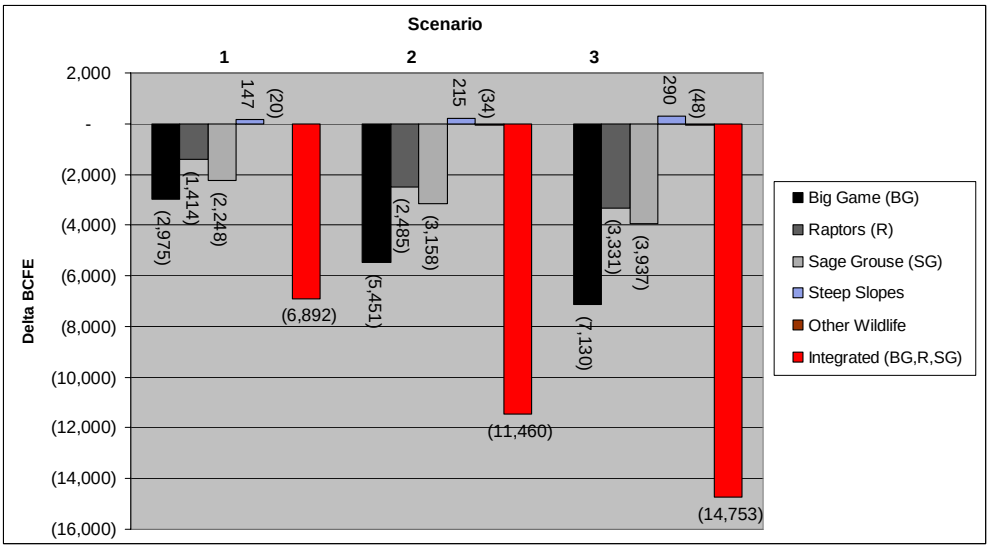


Figure 8. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Denver Basin Study Area

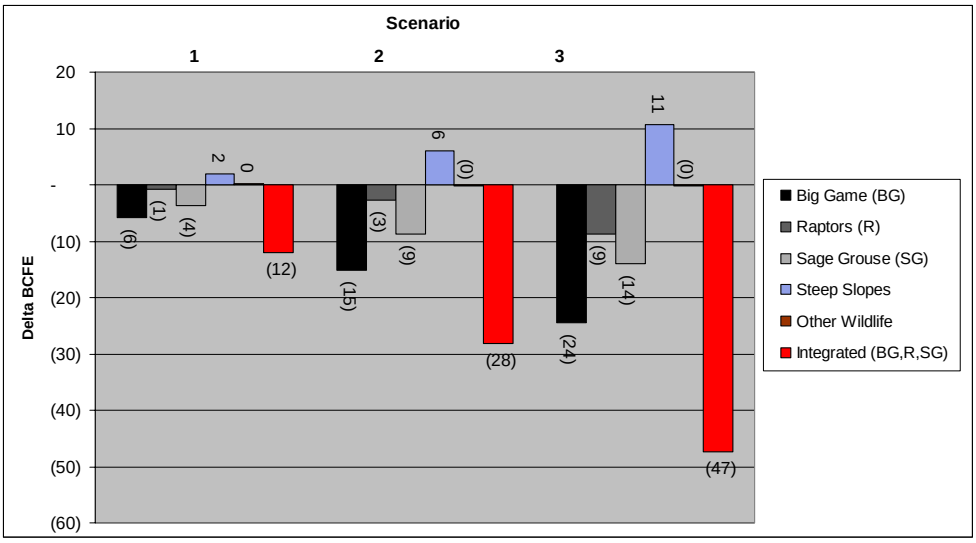


Figure 9. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Williston Basin

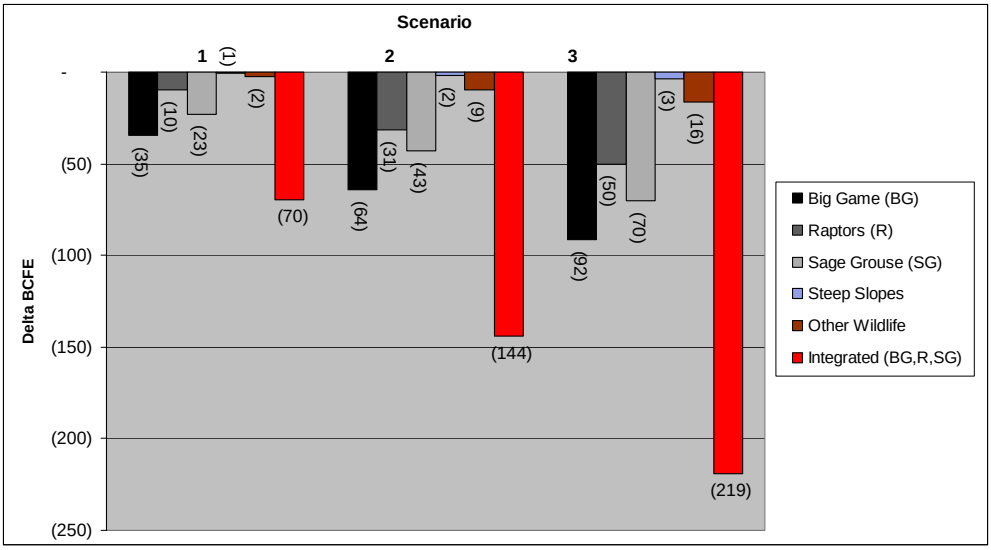


Figure 10. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Big Horn Basin

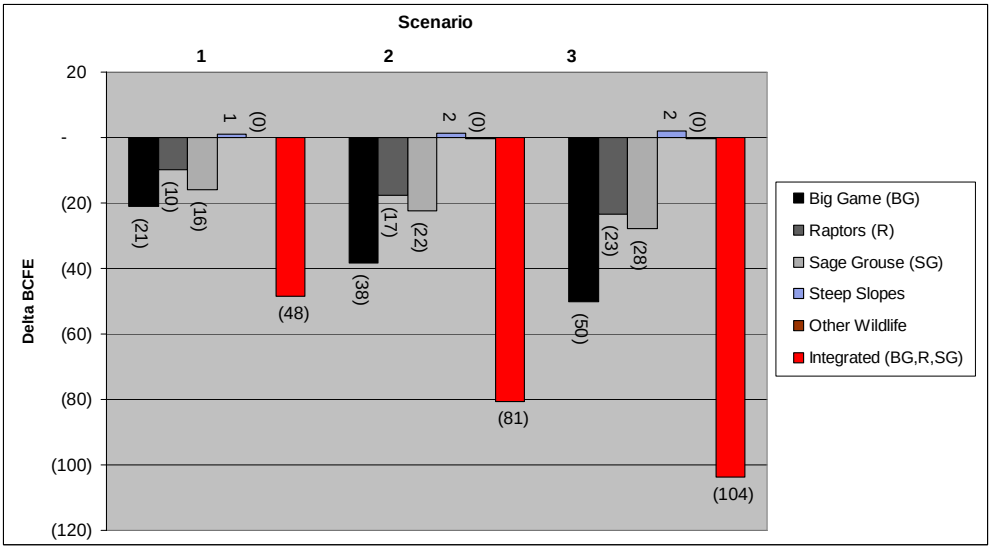
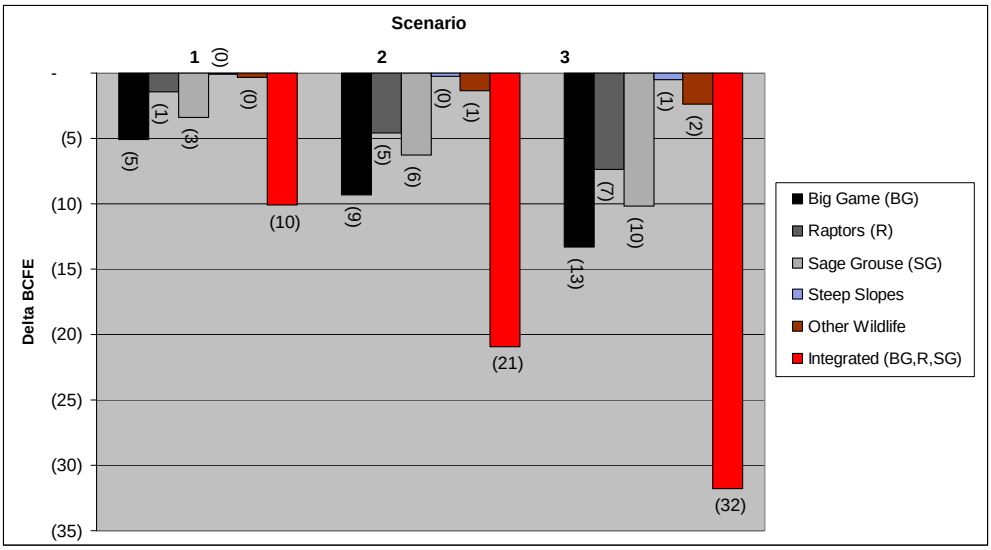


Figure 11. Potential Impact of R&D Programs on Stipulation Types on Federal Lands Access—Wind River Basin



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ENVIRONMENTAL POLICY AND REGULATORY CONSTRAINTS TO NATURAL GAS PRODUCTION

Deborah Elcock
Argonne National Laboratory
955 L'Enfant Plaza, SW, Suite 6000
Washington, DC 20024
Voice: 202-488-2451
Fax: 202-488-2413
Email: elcock@anl.gov

ABSTRACT

For the foreseeable future, most of the demand for natural gas in the United States will be met with domestic resources. Impediments, or constraints, to developing, producing, and delivering these resources can lead to price increases or supply disruptions. Previous analyses have identified lack of access to natural gas resources on federal lands as such an impediment. However, various other environmental constraints, including laws, regulations, and implementation procedures, can limit natural gas development and production on both federal and private lands. This paper identifies and describes numerous environmental policy and regulatory impediments to domestic natural gas production. For each constraint, the source and type of impact are presented, and when the data exist, the amount of gas affected is also presented. This information can help decision makers develop and support policies that eliminate or reduce the impacts of such constraints, help set priorities for regulatory reviews, and target research and development efforts to help the nation meet its natural gas demands.

INTRODUCTION

U.S. demand for natural gas is expected to continue into the future. Further, the U.S. Department of Energy's (DOE's) Energy Information Administration (EIA) has forecast that U.S. annual natural gas consumption will increase from 23 trillion cubic feet (TCF) in 2000 to 35 TCF in 2025 (EIA 2003). The factors driving this demand continue to mount. Foreign oil price instability related to tensions in the Middle East and Latin America could further shift demand from oil to less costly and domestically produced natural gas. Air pollution regulations favor the burning of clean natural gas over coal; while coal is more abundant, its use is of greater environmental concern. Energy price spikes and brownouts, such as those that occurred in California in 2001, could occur again if the delicate supply-demand balance is disrupted. Weather patterns can further increase demand.

In 1999, the National Petroleum Council (NPC) reported that the demand for natural gas was growing and that the resource base was adequate to meet this demand; however, certain factors needed to be addressed to realize the full potential for natural gas use in the United States (NPC 1999). In a 2003 update to the 1999 study, the NPC reported that government policies encourage the use of natural gas but fail to address the need for additional natural gas supplies (NPC 2003). The 2003 report states that a status quo approach to these conflicting policies will result in undesirable impacts to consumers and the economy. The Energy Policy and Conservation Act Amendments of 2000 (EPCA) required federal agencies to conduct an inventory of gas and oil resources beneath federal lands and to identify restrictions to developing these resources. The resulting study found that almost two-thirds of the land surveyed is restricted (DOI, 2003).

A key issue raised but not fully explored in these efforts was how environmental and regulatory policy constraints, which were developed to meet national environmental protection goals, can, at the same time, limit natural gas exploration and production (E&P) and transportation. Recent studies have examined limitations to accessing natural gas, particularly in the Rocky Mountain region, but even after the gas is accessed, numerous additional environmental policy and regulatory constraints can affect production and delivery to consumers. This paper identifies specific existing and potential environmental policy and regulatory constraints on E&P, transportation, storage, and distribution of natural gas needed to meet projected demands.

METHODOLOGY

To identify and assess environmental policy and regulatory constraints, existing studies were reviewed, and detailed issue investigations were conducted by examining existing and proposed statutes. Information published on proposed and final rules in the *Federal Register* was assessed, and issues were discussed with trade associations and industry and with state and federal government officials. Comments on proposed regulations and congressional testimony on issues and legislation that could affect natural gas production were reviewed. Information was also obtained from meetings on environmental policy relevant to natural gas conducted by the U.S. Commission on Ocean Policy, the Interstate Oil and Gas Compact Commission (IOGCC), the Minerals Management Service (MMS), the National Oceanic and Atmospheric Administration (NOAA), the Integrated Petroleum Environmental Consortium, the U.S. Environmental Protection Agency (EPA), and others.

Once potential policy and regulatory constraints were identified, an attempt was made to determine the nature of the impact and the amount of gas that each constraint could affect. It was

determined that a given constraint could affect the natural gas supply in one or more of the following ways: (1) make natural gas resources unavailable; (2) delay E&P or transportation; or (3) increase costs to the extent that some operators might stop operations, particularly if subjected to multiple costly regulations. To estimate the amount of gas a given constraint could affect, existing resource estimates were used. These estimates were reported in units of TCF and prepared by organizations such as the NPC, EIA, MMS, the U.S. Geological Survey (USGS), and an interagency group that studied U.S. oil and gas resources in five western basins (DOI, 2003). No attempt was made to develop independent estimates for amounts of gas that could be affected by the constraints, nor was an attempt made to normalize the estimates by year or form of estimate (e.g., technically recoverable, economically recoverable). As a result, these estimates can provide an indication of the order of magnitude of impact, but they should not be used to make direct comparisons among the various constraints. Some gas supplies are constrained by more than one factor. Therefore, the estimates are not additive, and eliminating one constraint may leave the gas supply affected by one or more other constraints.

FINDINGS

Numerous environmental policy and regulatory constraints currently affect natural gas E&P and transportation. Additional constraints may accrue as more environmental regulations are written. The constraints take several forms, including individual laws and regulations that directly affect natural gas access or production. They also include presidential policies and actions taken by implementing agencies. No priorities have been assigned to these constraints, and no inferences regarding priorities should be made from the order in which they are presented. Constraints that may limit access to gas supplies include the following:

- Coastal Zone Management Act (CZMA) consistency provisions,
- Endangered Species Act of 1973 (ESA) requirements,
- U.S. Department of Agriculture (USDA) Forest Service (FS) restrictions,
- Outdated Bureau of Land Management (BLM) land use plans,
- Lease stipulations,
- Monument designations,
- Outer Continental Shelf (OCS) moratoria,
- Permit restrictions,
- Bans on drilling in the Great Lakes,
- The “Roadless Rule,” and
- Wilderness Area designations.

Issues likely to produce delays include the following:

- Coal bed methane (CBM)-produced water and potential regulations to manage such water,
- Drilling permit delays,
- Essential fish habitat (EFH) regulations,
- Fracturing operations and the possibility of future rules that could limit this practice,
- Changes in nationwide permits (NWPs) issued by the U.S. Army Corps of Engineers (COE),
- National Environmental Policy Act of 1969 (NEPA) requirements,
- Pipeline certification issues,
- Pipeline safety regulations, and
- Wetlands mitigation issues.

Existing and potential issues likely to increase costs include the following:

- Regulations for cooling-water intake structures at offshore extraction facilities,
- Electronic reporting requirements,
- Lack of incentives to go beyond compliance,
- State waste disposal regulations,
- Maximum achievable control technology (MACT) rules,
- Mercury discharge regulations,
- Nitrogen oxides (NO_x) requirements,
- Noise regulations,
- Nonroad diesel regulations,
- Ocean discharge criteria,
- Particulate matter (PM) regulations,
- Pipeline gathering definitions,
- Regional haze rule,
- Spill prevention and control and countermeasures regulations,
- Standards for closing wells,
- Storm water construction permits, and
- Total maximum daily load (TMDL) regulations.

Constraints can arise from statutes; regulations written to implement a statute; Executive Orders; or from agency implementation of the statutes, regulations, or orders. Table 1 lists constraints, grouped by source of constraint, and identifies lead player(s) and production cycle phase(s). The lead player is the agency or other player that has control over the constraint, and can include various federal regulatory agencies (e.g., EPA, BLM, COE), states, the President, or Congress. Table 2 lists constraints, grouped by type of impact, and indicates the estimated TCF affected and the estimate type, date, and reference. Many of these issues have multiple impacts; to prevent duplication in presentation, constraints are grouped according to the impact deemed to be the most significant. Several of the constraints are highlighted or explained in the following paragraphs.

Legislative and Regulatory Constraints

Specific laws, such as the Coastal Zone Management Act (CZMA), whose consistency provisions can allow states to effectively prohibit development already approved by federal entities, and the ESA, whose court-interpreted definitions extend protected areas, can limit development on both private and federal lands. The Antiquities Act allows the President to designate national monuments on which no exploration or production may occur, even if the lands they overlie contain known natural gas resources. EFH regulations, whose requirements can duplicate those of other federal regulations, can delay leasing or permitting decisions, and the Roadless Rule, which prohibits road construction in roughly one-third (58.5 million acres) of the National Forest System, denies access to an estimated 11 TCF in the Rocky Mountain region.

Agency Actions

Once Congress passes a law and the responsible agencies have written the implementing regulations, local enforcement agencies can, through their own policies and procedures, delay or prohibit gas production. Federal land management agencies, such as the BLM and the FS, control development on their respective lands through land use planning documents. If these documents do not specifically provide for oil and gas drilling, the agencies can prohibit such drilling until the plans are updated, adding

months or years to the time before extraction from a leased site can begin. Similarly, when granting drilling permits, the land management agencies can impose stipulations, which, when added together at a given site, can narrow or effectively close the window of opportunity to drill. Compounding these problems are requirements to gain approval from other federal, state, and local agencies before a permit can be issued. As the number of permit applications grows, the ability to coordinate among the various agencies in a timely fashion diminishes, further increasing delays. This concern is particularly important for interstate natural gas pipelines, which are critical for transporting gas to users. Federal Energy Regulatory Commission grants certifications to build new pipelines, but only after it has received approval from other federal, state, and local agencies that have environmental jurisdiction.

Legal Constraints

The legal system can compound environmental regulatory constraints. When issues cannot be resolved among participating agencies, or when special-interest groups challenge a gas-related activity, legal action can delay projects for months or years. For example, the tendency for organizations to sue over Environmental Impact Statements has led agencies to prepare "appeal-proof documentation," which further delays the approval process.

Congressional and Presidential Actions

Typically, laws are developed after congressional debate, and regulations require a prescribed notice and comment period. However, at times, Congress and the President can impose constraints that may not follow the formal procedures designed to allow for the expressing of concerns by all interested parties. These initiatives can significantly decrease access to natural gas. For example, Congress has enacted and presidents have extended offshore drilling moratoria. These actions not only deny the extraction of natural gas, but also deny federal agencies and others the ability to determine the extent of the resources in waters off the coasts of most of the United States. Recently enacted congressional bans on drilling in the Great Lakes and lack of congressional action to determine the status of Wilderness Study Areas preclude the extraction and production of gas in these areas.

New Environmental Regulatory Constraints

A number of environmental rules are currently under development, and the potential impacts of these rules require active monitoring. For example, the EPA's "nonroad diesel engine" rule could increase costs for new engines used in natural gas E&P to ensure that they meet the required emissions reductions. The EPA is also writing regional haze rules designed to protect visibility in national parks and Wilderness Areas, which could apply to drilling and production equipment and affect the ability to produce natural gas in a timely and cost-effective manner. The Office of Pipeline Safety within the Department of Transportation is writing rules to ensure "integrity management," or structural safety of gas transmission lines. The implementation of these rules could disrupt supplies, as companies are forced to meet certain inspection deadlines using specific technologies that may not be available when needed. The EPA may require oil and gas E&P facilities covering 1 to 5 acres to obtain storm water permits under the Clean Water Act.

State and federal agencies are determining whether and how to address emerging environmental issues, many of which could affect or limit cost-effective production of natural gas. For example, the U.S. Commission on Ocean Policy, established under the Oceans Act of 2000, has developed recommendations that could include new policies and authorities to address the development of ocean resources, potentially including natural gas. Other issues are closer to regulation. For example, some states have written rules to address potential impacts of discharging produced water from CBM operations

to the environment. Others may follow, and such actions could severely restrict development of this source of gas, which many believe to be a significant future contributor to the nation's energy supply. A related issue is the use of hydraulic fracturing to increase the flow of gas, particularly CBM gas. This practice has been the subject of regulatory and legal action, and further regulatory activity can be expected. Other environmental regulations with potentially significant impacts on natural gas development include regulations for minimizing adverse environmental impacts from cooling-water intake structures at offshore oil and gas platforms; mercury regulations that could affect the use and discharge of mercury-containing drilling muds; and regulations to reduce noise generated by engines, drills, and compressors used in natural gas E&P and transportation.

CONCLUSIONS

A variety of environmental policy and regulatory constraints currently affect natural gas E&P and transportation, and more are likely to accrue as new regulations are written. The constraints take several forms, including individual laws, regulations, presidential policies, and implementing-agency actions. Some of these constraints can have significant impacts on natural gas production on an individual basis. Others, taken alone, may not have as great an impact, but when combined with other regulations or policies, could be so costly or produce so many delays that many small, independent operators may cease production. Whether the gas produced by these independents would then be extracted by other, larger firms, at an increased cost to them, or whether the gas would not be produced until prices increased sufficiently to warrant reentry into the market is not known. However, mitigation approaches should be developed to address not only the major impediments, such as access restrictions, but also to address the other regulations and implementing practices so that the ability to extract and distribute the gas to users in a cost-effective and environmentally protective fashion can be maintained, if not increased.

ACKNOWLEDGEMENTS

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Table 1. Environmental Regulatory Constraints, by Source of Constraint[a]

Source of Constraint	Constraint	Lead Player	Phase
Statutory/ regulatory/agency implementation	CZMA consistency provisions	NOAA	E&P, transportation
Statutory	Bans on Great Lakes drilling	COE, states	E&P
	Wilderness Areas	BLM	Exploration
Regulatory	CBM-produced water management	EPA, states	Production
	Cooling-water intake structures	EPA	Production
	Electronic reporting and record-keeping requirements	EPA	Production
	Fracturing operations	EPA, states	Production
	Lack of incentives to go beyond compliance	BLM	Production
	Louisiana E&P waste disposal regulations	State	Production
	MACT rules	EPA	Production, transportation
	Mercury discharge regulations	EPA	E&P
	Nationwide permits	COE	Production, transportation
	NEPA integration and lawsuits	States, BLM, FERC	E&P, transportation
	NO_x PSD increment consumption	EPA, states	Production
	Nonroad Diesel Rule	EPA	E&P
	Ocean discharge criteria	EPA	Production
	Particulate matter regulations	EPA, states	Production
	Pipeline gathering line definition	OPS	Production, transportation
	Pipeline safety (integrity management)	OPS	Transportation
	Regional haze rule	States, EPA	Production
	Roadless Rule	FS	Exploration

Source of Constraint	Constraint	Lead Player	Phase
	Spill prevention control and countermeasures	EPA	Production
	Standards for decommissioning or closing wells	States	Production
	Storm water construction permits	EPA	E&P
	TMDL regulations targeting oil and gas wells	EPA	E&P
	Wetlands mitigation	COE, states	Production, transportation
Presidential, statutory	OCS Moratoria — Atlantic Ocean	President, Congress	E&P
	OCS Moratoria — Eastern Gulf of Mexico	President, Congress	E&P
	OCS Moratoria — West Coast	President, Congress	E&P
Presidential	Monument designations	President	Exploration
	Ocean policy	President, Congress	E&P, transportation
Agency implementation	Drilling permits	BLM	Production
	ESA	USFWS	E&P
	Essential fish habitat	NMFS	E&P, transportation
	Forest Service restrictions	FS	Production
	Outdated BLM land use plans	BLM	E&P
	Lease stipulations	BLM, FS	Production
	Permit restrictions	BLM	E&P
	Pipeline certification	FERC, others	Transportation

[a] BLM = Bureau of Land Management; CBM = coal bed methane; CZMA = Coastal Zone Management Act; COE = U.S. Army Corps of Engineers; E&P = exploration and production; EPA = U.S. Environmental Protection Agency; ESA = Endangered Species Act; FERC = Federal Energy Regulatory Commission; FS = USDA Forest Service; MACT = maximum achievable control technology; NEPA = National Environmental Policy Act of 1969; NMFS = National Marine Fisheries Service; NOAA = National Oceanic and Atmospheric Administration; NO_x = nitrogen oxides; OCS = Outer Continental Shelf; OPS = Office of Pipeline Safety; PSD = Prevention of Significant Deterioration; TMDL = total maximum daily load; USFWS = U.S. Fish and Wildlife Service.

Table 2. Environmental Regulatory Constraints and Estimated Amounts of Gas Affected[a]

Issue Impact	Constraint	TCF Affected	TCF Type	TCF Date	TCF Reference
Unavailable gas, delay, cost	Ocean policy	Not estimated	NA	NA	NA
	Lease stipulations	108	Undeveloped gas resources	01/1998	NPC (1999)
Unavailable gas, delay	CZMA consistency provisions	362.2	Undiscovered conventionally recoverable resources	01/1999	MMS (2000)
	ESA	Not estimated	NA	NA	NA
	Outdated BLM land use plans	120.3	Technically recoverable	01/2003	DOI (2003)
Unavailable gas	Forest Service restrictions	10–30	Natural gas resources	01/2001	Fisher (2001)
	Monument designations	1	Technically recoverable	01/1995	Wilderness Society (2002)
	OCS Moratoria — Atlantic Ocean	28.0	Technically recoverable	01/2000	EIA (2001b)
	OCS Moratoria — Eastern Gulf of Mexico	11.3	Technically recoverable	01/2000	EIA (2001b)
	OCS Moratoria — West Coast	18.9	Technically recoverable	01/2000	EIA (2001b)
	Permit restrictions	86.6	Technically recoverable	01/2003	DOI (2003)
	Bans on Great Lakes drilling	1.1	Possible and probable reserves	09/2001	Shirley (2001)
	Roadless Rule	11	Technically recoverable	11/2000	Eppink (2000)
	Wilderness Areas	9	Technically recoverable	01/2003	DOI (2003)
Delay, cost	CBM-produced water management	74	Technically recoverable	01/1998	NPC (1999)
	Fracturing operations	293	Unproved technically recoverable	01/2000	EIA (2001b)
	Pipeline safety (integrity management)	Not estimated	NA	NA	NA

Issue Impact	Issue	TCF Affected	TCF Type	TCF Date	TCF Reference
	Wetlands mitigation	Not estimated	NA	NA	NA
Delay	Drilling permits	311.2	Assessed additional resources	01/1998	NPC (1999)
	Essential fish habitat	174.5	Technically recoverable	01/2000	EIA (2001b)
	Nationwide permits	Not estimated	NA	NA	NA
	NEPA integration and lawsuits	464.5	Technically recoverable	01/2000	EIA (2001a)
	Pipeline certification	23.3	Annual gas consumption	01/2003	EIA (2003)
Cost	Cooling-water intake structures	Not estimated	NA	NA	NA
	Electronic reporting and record-keeping requirements	Not estimated	NA	NA	NA
	Lack of incentives to go beyond compliance	86.6	Technically recoverable	01/2003	DOI (2003)
	Louisiana E&P waste disposal regulations	Not estimated	NA	NA	NA
	MACT rules	Not estimated	NA	NA	NA
	Mercury discharge regulations	Not estimated	NA	NA	NA
	NO_x PSD increment consumption	Not estimated	NA	NA	NA
	Noise regulations	Not estimated	NA	NA	NA
	Nonroad Diesel Rule	Not estimated	NA	NA	NA
	Ocean discharge criteria	Not estimated	NA	NA	NA
	Particulate matter regulations	7.2	Technically recoverable	01/1995	Whitney (2001)
	Pipeline gathering line definition	Not estimated	NA	NA	NA
	Regional haze rule	Not estimated	NA	NA	NA
	Spill prevention control and countermeasures	Not estimated	NA	NA	NA

Issue Impact	Issue	TCF Affected	TCF Type	TCF Date	TCF Reference
	Standards for decommissioning or closing wells	Not estimated	NA	NA	NA
	Storm water construction permits	5.75 per year	Economically recoverable	09/2002	Texas Alliance of Energy Producers (2003)
	TMDL regulations targeting oil and gas wells	Not estimated	NA	NA	NA

[a] Abbreviations: BLM = Bureau of Land Management; CBM = coal bed methane; CZMA = Coastal Zone Management Act; E&P = exploration and production; DOI = U.S. Department of the Interior; EIA = Energy Information Administration; ESA = Endangered Species Act; MACT = maximum achievable control technology; MMS = Minerals Management Service; NA = not applicable; NEPA = National Environmental Policy Act of 1969; NO_x = nitrogen oxides; NPC = National Petroleum Council; OCS = Outer Continental Shelf; PSD = Prevention of Significant Deterioration; TCF = trillion cubic feet; TMDL = total maximum daily load.

“Alternative Methods to Evaluate Volatile Organic Compounds in Soil: A Mexican Case Study”

Espitia C. A.*, Kondratenko N.*, Luna Baez J.L **

- *Universidad Autónoma Metropolitana – AZC.
- **PEMEX Gas y Petroquímica Básica

INTRODUCTION

- In January 24 of 2005 there was a spill of 481 barrels of natural naphtha light in a place located in the southeast of Mexico.
- The naphtha comes from wells of the region, as well as offshore facilities and the spill happened before it was distilled in a refinery.
- The natural naphtha light had traces of hydrogen sulfide as well as traces of heavy metals.
- The material disseminated on a slope land over the terrain and also a part was conducted to a small river
- The rupture point was in the elevated part of the terrain and the hydrocarbon spilled trough a mild slope with a difference of 10 m between the highest and the lowest point.

SITE CHARACTERISTICS

The soil in the site is heterogeneous, since in the past there was another spill, and the land was removed and filled with a non native soil and, In the moment of the new spill the soil was not consolidated.

The soil's surface is constituted of fine silica sand, with a reduced amount of clay, the sand is bad graduated, compacted with a clear brown color and with vegetable fossils, since was a lake deposit in the past.

The first layer is about 4 meters depth and the second layer is composed of gray clay with medium plasticity.

The soil affected started from the surface to the clay layer with an average depth of 4 meters.

Visual observations show in the pores of the soil a Light No Aqueous Phase liquid, LINAPL, which is lightly emulsionated by microbial activity.

Also a naphtha odor was detected.

Description of the problem

The spilled naphtha is a non polar, highly volatile with low solubility in water and low adsorption capability on inorganic fraction of soil.

The sand and clay contain exchangeable metal ions which makes their surfaces hydrophilic and consequently they are quite ineffective in sorbing nonionic organic compounds.

In spite of that the pollutant is easily detected by the senses. It is very difficult to measure by the methods for hydrocarbons light fraction (C_5 –C_{10}) of the Mexican rule NOM 138-Semarnat/SS-2003.

The Mexican standard establishes that for light hydrocarbons fraction, the sample obtained in the field, must be stored before analysis in a glass wide mouth jar with teflon seal cap.

Description of the problem

The standard also establish that the samples must be homogenized and screened in the field with a screen of ± 1.0 mm. before stored and transported to the analytical lab.

The rule establish for substances that have molecular weight between C_5 to C_{10} and boiling points between 60 °C and 170°C the methods EPA 8015B and 8020 for the analysis.

This work shows that we have losses of material in the sampling with this technique.

We also notice in the lab that there was losses as the material is adsorbed in the cap, and also we have losses when the jar is open

Legal Limits in Mexico

The Maximum Permissible Values, (MPV) in Mexico for hydrocarbon light fraction in soil of industrial use and in groundwater are:

Pollutant	TPH'S	Benzene	Toluene	Ethyl benzene	Xylene
MPV soil (mg/kg) (1)	500	15	100	25	100
MPV groundwater (ppm) (2)	1* (Quebec value)	0.01	14.3	1.4	NA

Source: (1) NOM 138-SEMARNAT/SS-2003
(2) "Criterios ecológicos de la calidad de agua", para calidad de agua potable. SEDESOL, 15 dic 1989.

* There is not a MPV for TPH's in Mexico

FIELD WORK:

- An initial area of 30 m x 30 m was divided in a grid of numbered 56 squared sampling points of 4m x 4 m.
- Topographic study in the initial impacted area. (693 m2 with 4 m of depth.)*
- Measure of the apparent electrical conductivity in the subsoil.
- Material Classification in the different subsoil layers.
- Drilling of 36 sampling wells for soil and subsoil and 23 sampling groundwater wells .
- Extraction of 162 soil and subsoil samples and 10 groundwater samples.
- Total petroleum hydrocarbons light fraction analysis in soil and water.
- BTEX analysis in soil and water.
- Heavy metals analysis in soil (Barium, Nickel, Lead and Zinc) in soil .
- Microbiological analysis in soil.

*In the field we observed free product and hydrocarbon odor and luminescence's in the subsoil and groundwater samples in this area.

FIELD WORK (cont.)

- In a preliminary study, using the rule criteria to obtain the samples we obtain values below the maximum limit value in points that shows free product and have a strong odor of hydrocarbons.
- In order to reduce the losses of compounds for volatility and have a more representative values.
- We took samples at the same points using vial's to head space analysis (EPA 3810) with the same analytical techniques.
- The results of this sampling were as follow measured in numbered areas of 16 m2:

RESULTS

Sampling points	DEPTH (cm)	MATRIZ	CONCENTRATION TPH's (ppm)	NO. of times that exceed the MPV
13	382	Soil	1603	2.2
	452	Soil	2219	3.4
16	1	Soil	1781	2.6
24	329	water	24	23
44	240	Water	18	17
57	702	Water	54	53
58	540	Soil	877	0.7
	600	Soil	1364	1.7

MPV soil = 500 mg/kg.
MPV groundwater = 1 mg/kg. (using Quebec values since in Mexico is not ruled)

RESULTS:

The results show that in some points the values are higher than the maximum permissible value.

The maximum values obtained were:

a) In soil

2219 mg/kg of TPH´s and

76.88 mg/kg of benzene;

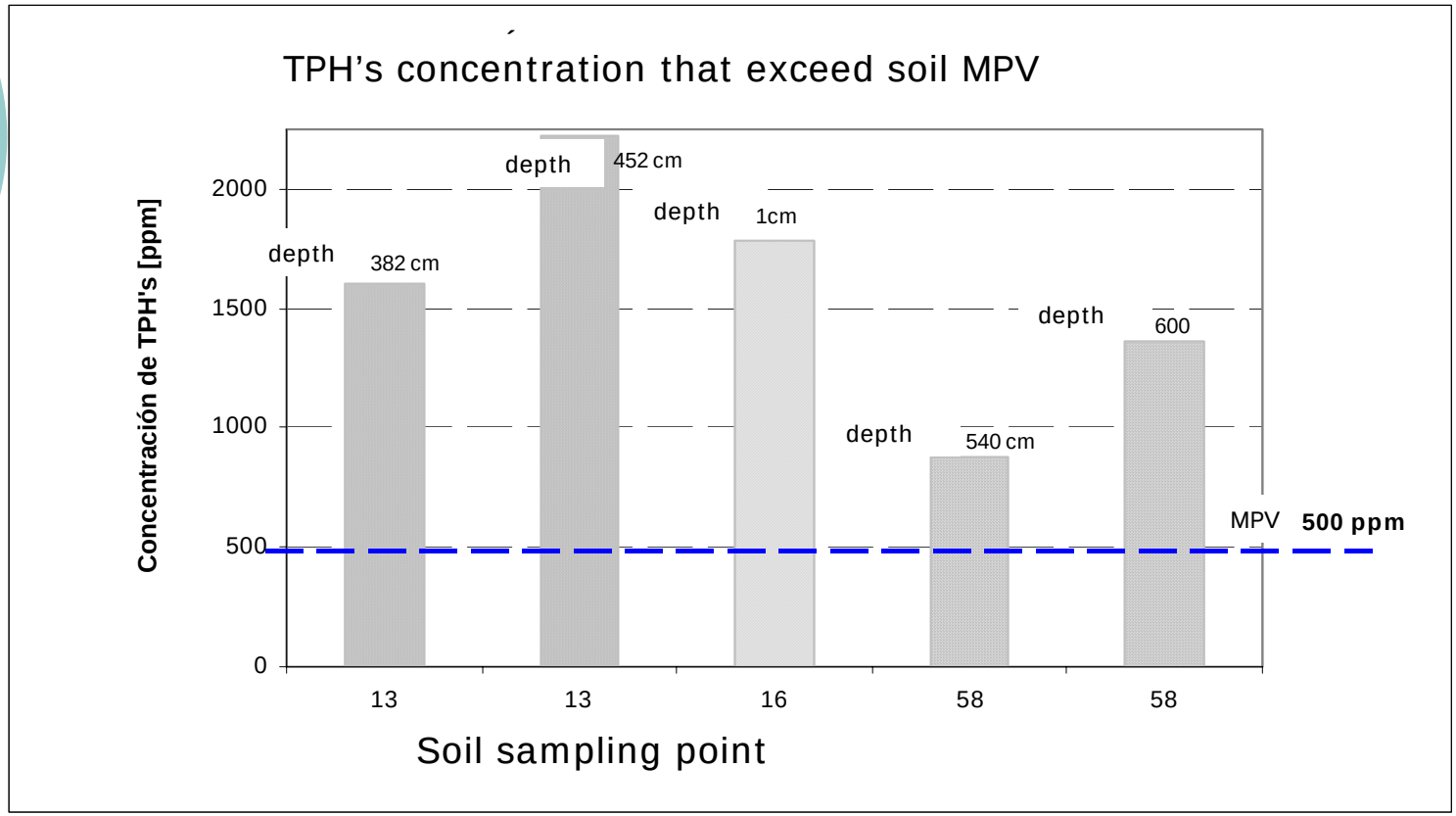
In water:

54 mg/kg of TPH´s and

8 mg/kg of Benzene.

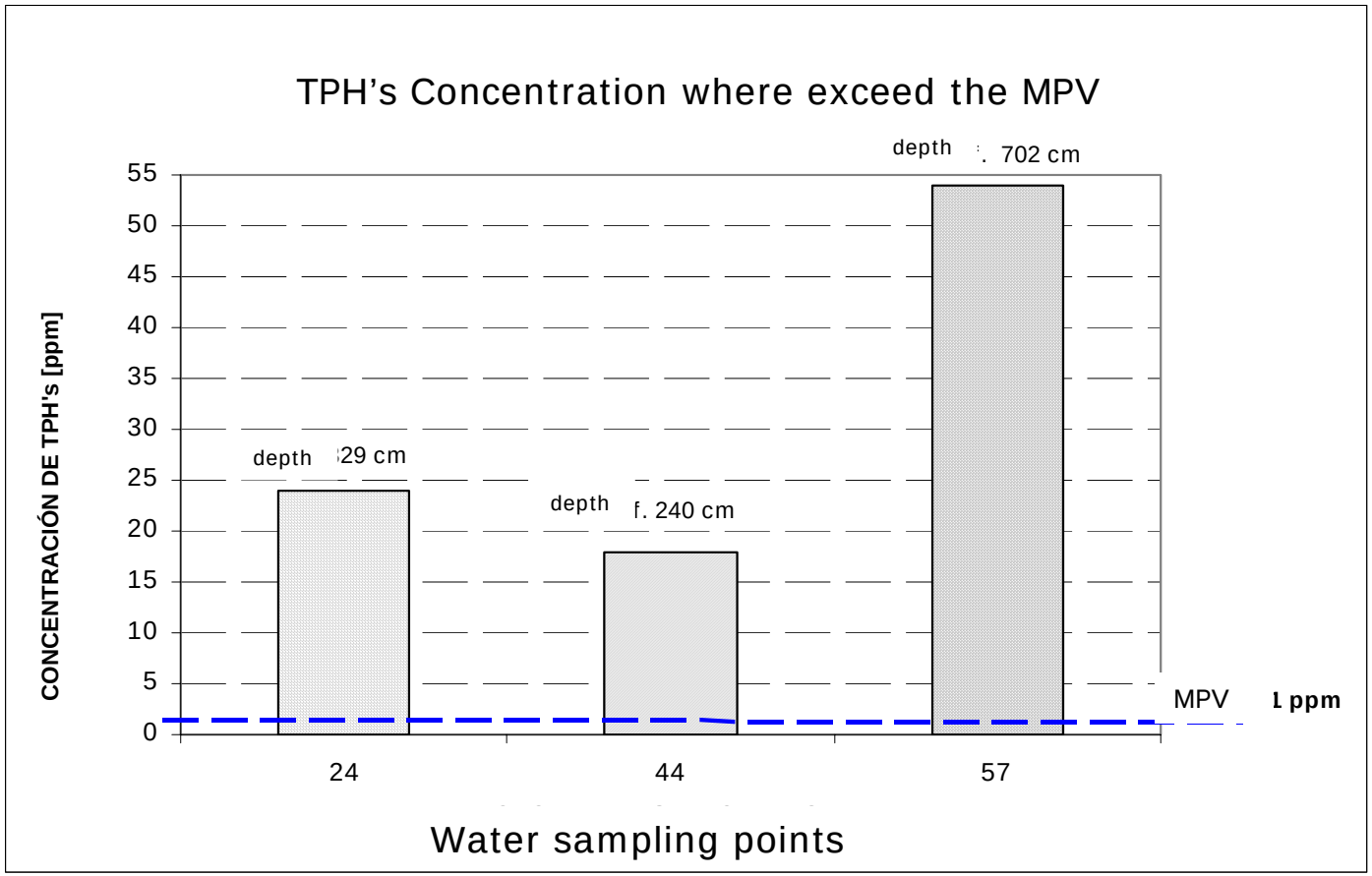
64 m2. is the affected area of soil that exceed the Mexican rule, according with the Mexican standard

RESULTS



TPH's polluted soil areas with sampling point and depth.

RESULTS



Points and depth of groundwater polluted with TPH's

RESULTS

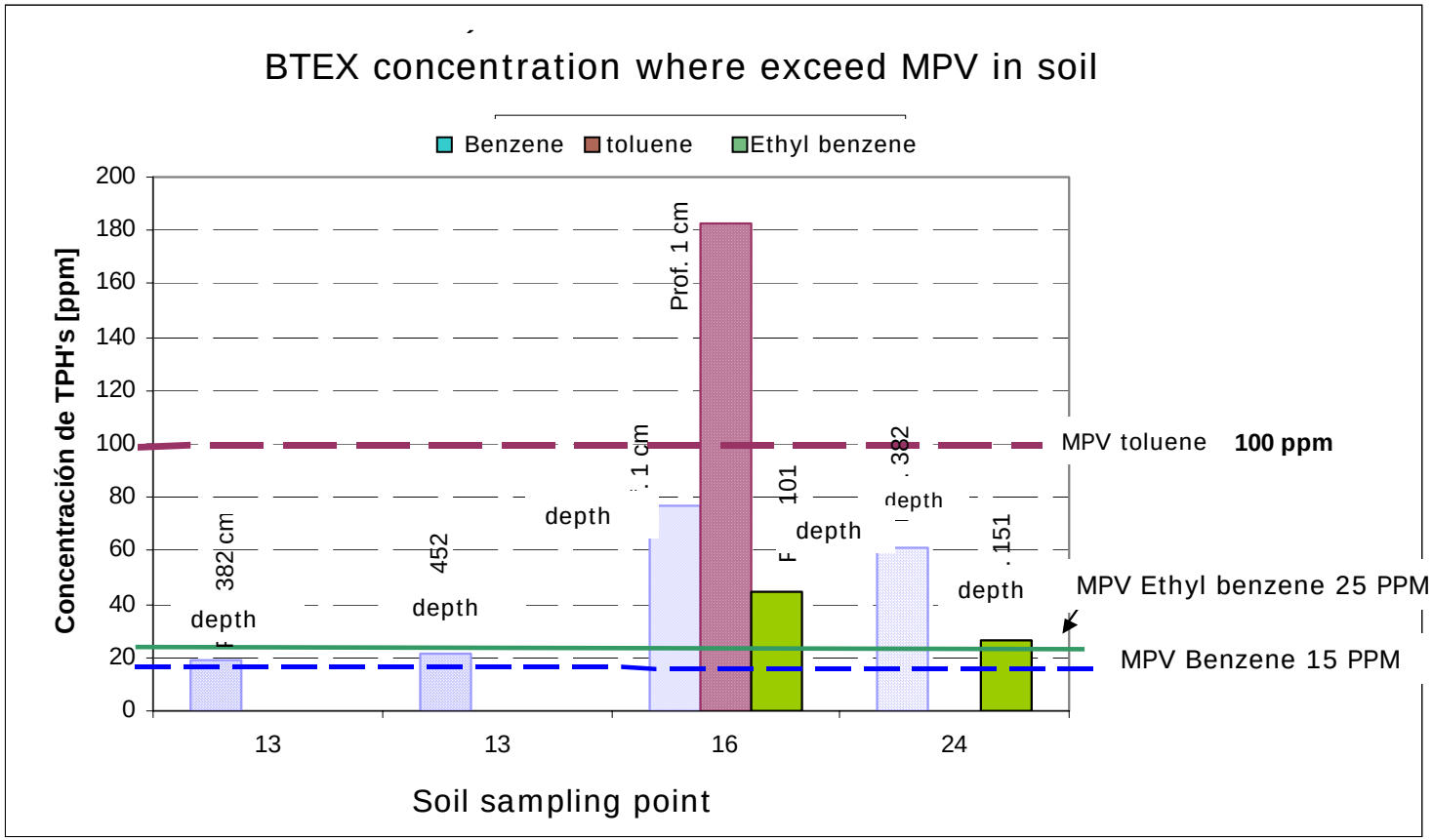
BTEX polluted areas

Sampling point	Depth (cm)	Pollutant	medium	TPH's concentration (ppm)	times that exceed MLV
6	548	Benzene	Water	6	622
13	382	Benzene	Soil	18.74	0.2
	452	Benzene	Soil	21.27	0.4
16	1	Benzene	Soil	76.88	4.1
		Toluene	Soil	182.51	0.8
		Ethyl benzene	Soil	45.03	0.8
24	101	Benzene	Soil	61.36	3.0
	151	Ethyl benzene	Soil	26.74	0.07
	329	Benzene	Water	3	296
44	240	Benzene	Water	8	781
57	702	Benzene	Water	6	589

MPV soil Benzene = 25 mg/kg, Toluene =100 mg/kg, Ethyl benzene =50 mg/kg, Xylene = 100 mg/kg.

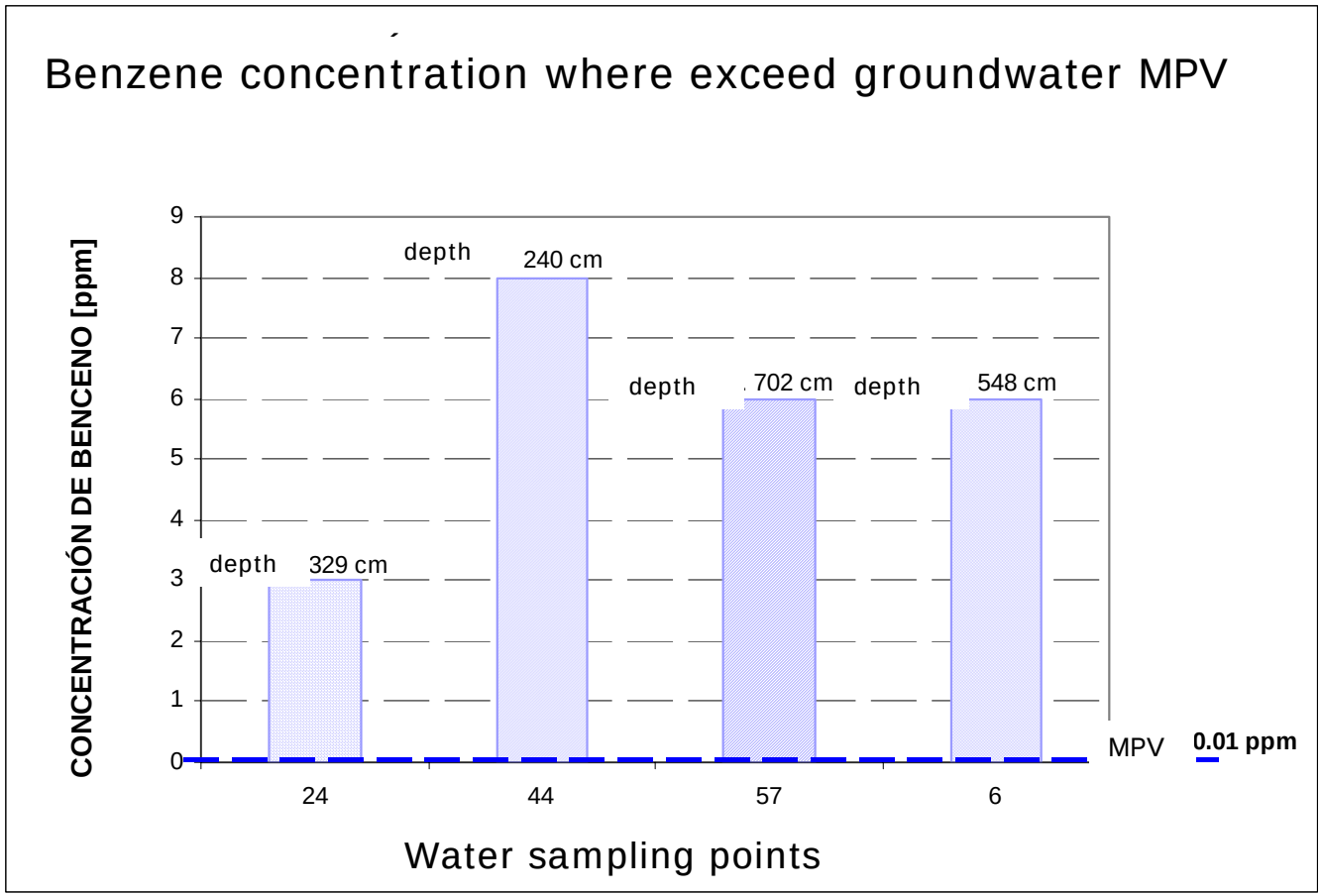
MPV water Benzene 0.01 mg/kg, Toluene 14.3 mg/kg, Ethyl benzene =14 mg/kg, not defined for Xylene.

RESULTS



BTEX Polluted soil areas with sampling point and depth

RESULTS



BTEX polluted areas with sampling point and depth.

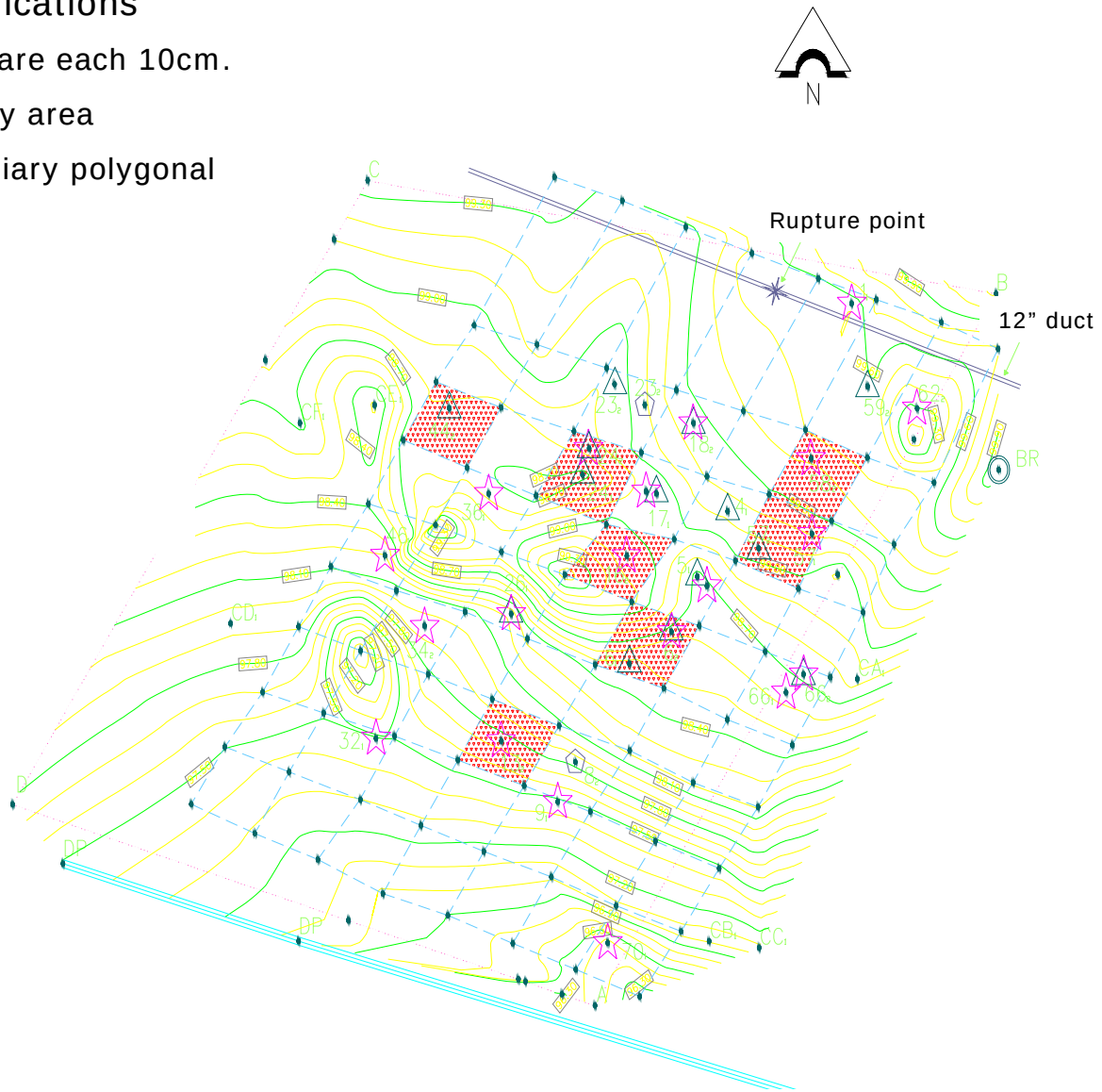
Specifications

Curve levels are each 10cm.

650 m2 Study area

864 m2 Auxiliary polygonal area

Scale 1:100



symbols

- Polluted point
- Soil sampling point
- Water sampling point
- mycrobiological sampling point
- $C_{A,B,C,D,E,F}$ blanks
- Drains for rain
- Reference bank
- Squares
- Reference points of level

Squares 13, 16 and 58 exceed soil MPV, squares 24, 44 and 57 exceed water MPV for TPH’s and BTEX.

study area of 693 m².

Alternative method

Initially, we evaluated an area of 900 m^2 with 4 m of depth, close of the rupture point, where we observed free product and a strong Hydrocarbon odor.

This area was suggested by the environmental authority, Who supervised the sampling work.

The results show values not credible, and also we observed that the spill began to disseminate and affected a big area.

As alternative method we measured an extended area of 20,000 m^2 with an average depth of 4 m. where we founded a clay layer not permeable.

In this area we detected hydrocarbon odor but not free product.

This evaluation was made using Photo ionization gasometry with direct reading (EPA 8021B)

RESULTS:

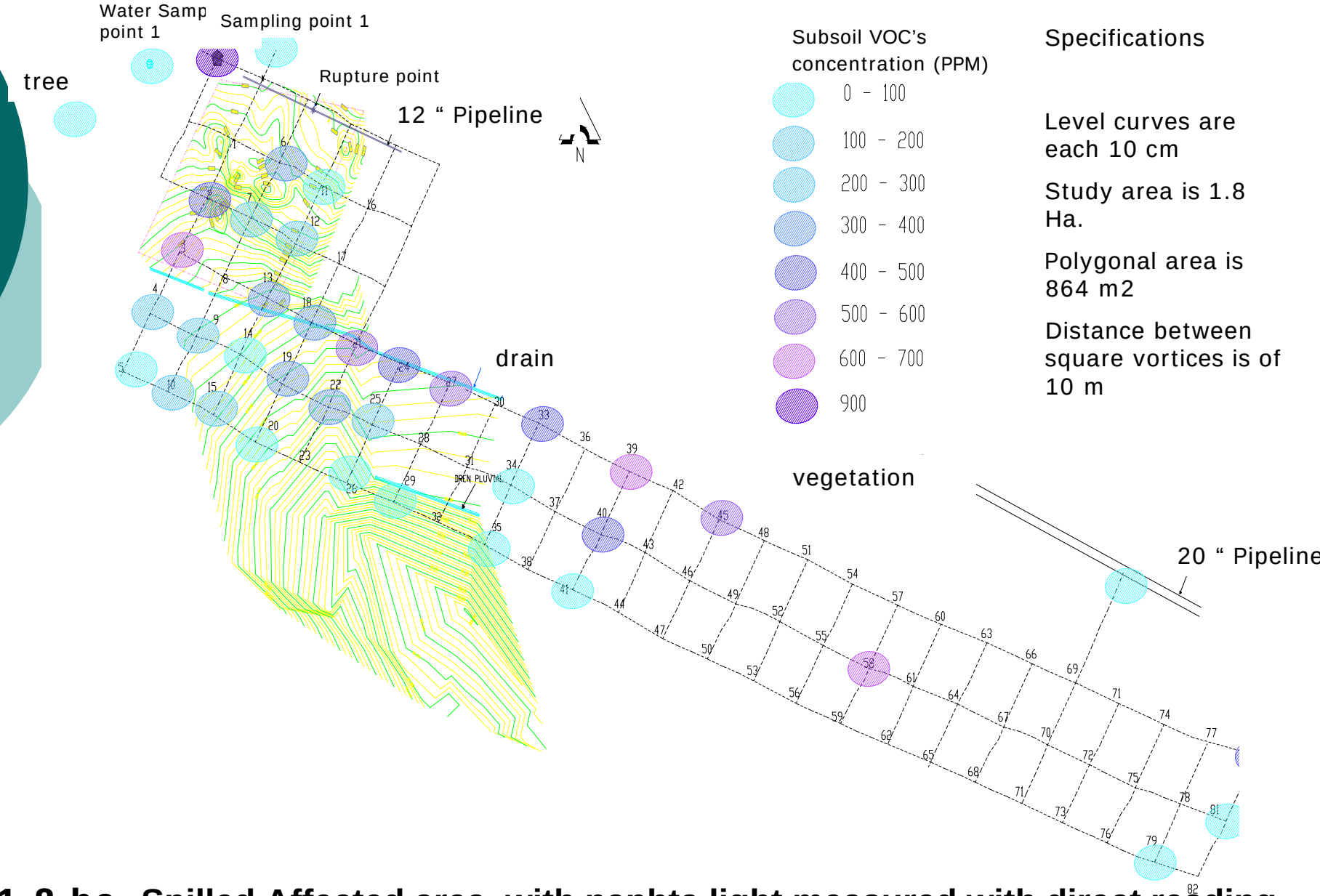
Volatile Organic compounds concentration in the subsoil measured with a photo ionizator calibrated with isobutylene .

Sampling points	VOC's soil concentration, ppm	localization, m		Maximum limit permissible as toluene, ppm
		X	Y	
2	498	66.3313	94.7522	100
3	616	60.4583	87.3038	100
4	188	54.1836	78.9139	100
5	16.2	48.4471	71.7184	100
6	341	81.8267	100.3537	100
7	249	75.7436	92.7997	100
9	117	64.0272	76.5138	100
10	245	57.9536	68.1788	100
11	15.1	90.8012	96.4714	100
12	158	85.266	89.2317	100
13	308	79.3168	81.15	100
14	49.9	73.4438	74.0606	100
15	102	67.7456	65.7618	100
18	339	88.7065	78.4101	100
19	361	82.4643	70.0563	100
20	49.8	76.8817	62.021	100
21	539	98.146	75.5045	100
22	338	92.3422	66.0233	100
24	428	107.6159	72.1016	100
25	154	101.6399	64.3759	100

RESULTS (cont.)

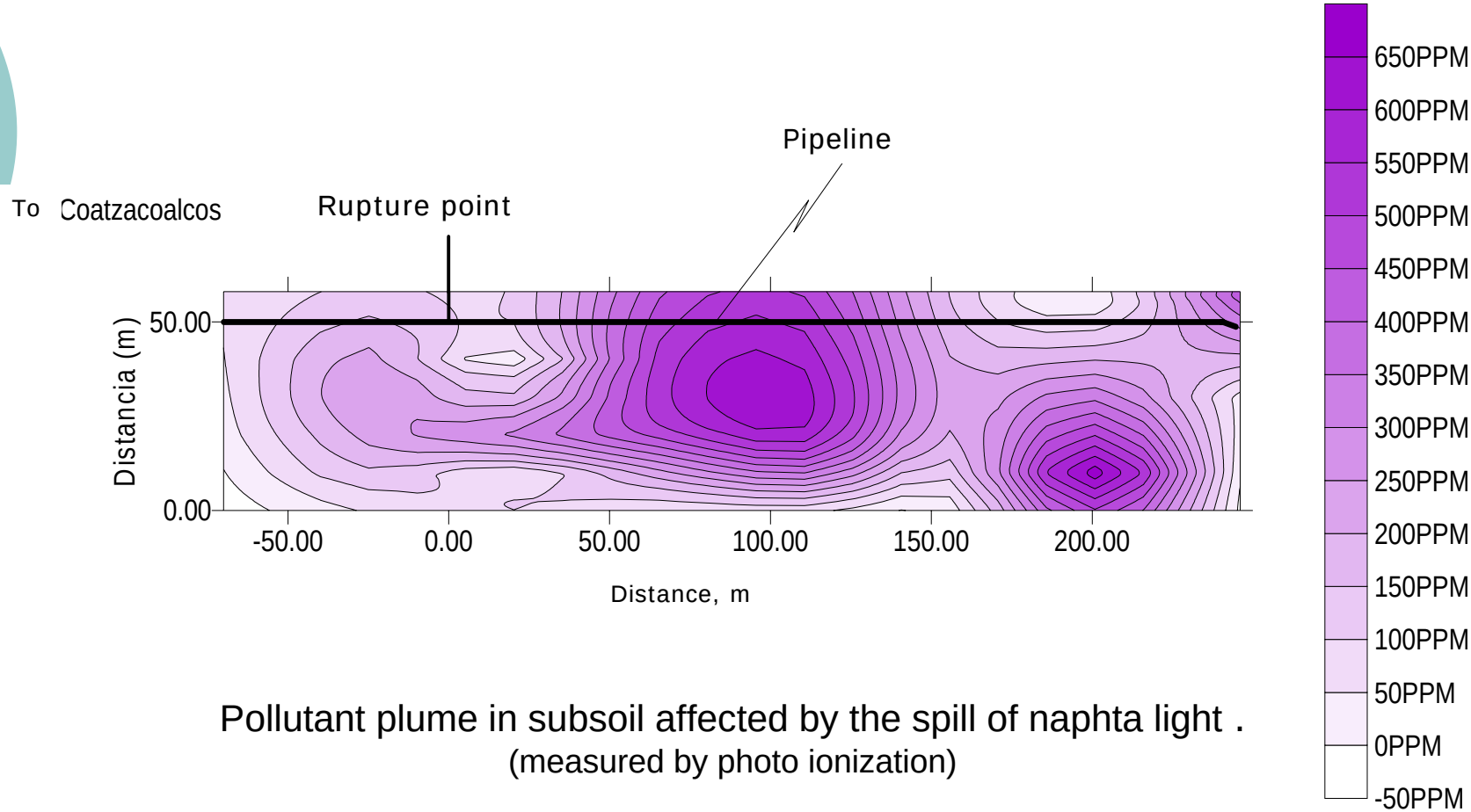
Volatile Organic compounds concentration in the subsoil measured with a photo ionizator calibrated with isobutylene .

Sampling points	VOC's soil concentration, ppm	localization, m		Maximum limit permissible as toluene, ppm
		X	Y	
26	29.3	96.2075	55.6626	100
27	535	118.27	69.3624	100
29	72.6	106.2454	53.0023	100
33	410	137.2122	63.8411	100
34	76.1	131.3449	55.3215	100
35	18.1	125.6242	47.145	100
39	606	156.6128	57.2027	100
40	401	150.6133	48.5029	100
41	15.1	144.4401	40.9775	100
45	589	175.7423	50.6115	100
58	690	207.888	30.1274	100
20" duct	9.7	268.1383	53.035	100
79	29.8	268.7652	3.5485	100
80	430	290.1712	100	100
81	10.7	284.0708	100	100
Water point 1	14.2	54.1169	100	100
Soil point 1	912		100	100
Tree	25.9		100	100
Behind 12" duct	16.7	81.1601	100	100



1.8 ha. Spilled Affected area with naphta light measured with direct reading photo ionization.

RESULTS:



Pollutant plume in subsoil affected by the spill of naphta light .
(measured by photo ionization)

CONCLUTIONS:

According with the Mexican legislation (NOM-138), this site shows pollution on soil and water only in a few points with a total area of **64 m^2** (256 m^3 or 676 ton of soil). And only this area is necessary to restore.

However, is detectable by the senses hydrocarbon odor as well as free product in the water sampling points.

Since the authorities notice this situation it was necessary to implement another sampling and analysis technique that measure the pollutant in the site.

Using photo ionization of direct reading in the site we detected an affected area of **1.8 ha** (72,000 m^3 or 190,080 ton).

Even the Mexican legislation do not establish limit permissible values for VOC's the authority at the end asked to restore this area, and in this time the area is in the process of restoration.

RECOMENDATIONS:

In this time Mexican authorities are encouraging to use a purge and trap extraction followed by gas chromatography to analyze Gasoline Range Organics (GRO). To obtain better results.

In this method oil or wastes samples are dispersed in methanol to dissolve the volatile organic constituents, and a portion of the methanolic solution is then analyzed by purge and trap GC.

However is also necessary to improve the sampling methods, otherwise there will be losses of the material due to the volatility of the compounds and the low capacity of adsorption of clay and sandy soils.

We suggest to explore this photo ionization method (EPA 8021B) as well as other direct reading on site methods in order to minimize the losses and have a more representative results

OPTIMIZATION OF A CRUDE HYDROCARBONS BIODEGRADATION PROCESS IN SOIL, USING A NATIVE BIOSTIMULATED BACTERIA CONSORTIUM IN A STATIC BIOPILE

[(1)]Espitia C. Alfonso, [(1)]Jiménez H., Rocío, [(1)]Torrecilla D. Virginia, [(2)]Cruz C. Ma. del Rocío, [(1)]Uribe H. Karina,

(1) Energy Department. Basic Science and Engineering Division.. Laboratorio del Grupo de Proyectos y Servicios Ambientales de la Universidad Autónoma Metropolitana Azcapotzalco. Av. San Pablo # 180, Col. Reynosa, Azcapotzalco, D.F. CP 02200. Tels: 5318 9006, 5318 9073. FAX: 5318 9538. e-mail: aec@correo.azc.uam.mx.

(2) Departmento de Ciencias Básicas. Laboratorio de Microbiología Ambiental de la Universidad Autónoma Metropolitana Azcapotzalco. Teléfonos: 5318 9596, 5318 9361. FAX: 5318 9573. e-mail: ccmr@correo.azc.uam.mx.

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Abstract

The enzymatic induction process was evaluated with a native bacteria consortium composed of *pseudomonae aeruginosa, Stenotrophomonae maltophilia, Acitenobacter iwoffi, Pseudomonae stutzeri y Flavobacterium oderatum*, previously isolated from a Tabasco Soil polluted 20 years ago, to degrade crude hydrocarbons in a soil with a texture of mud and sand. To enhance the biodegradation we used a mixture of nutrients with addition of vitamins

In a static reactor we prepared a soil mixed with Maya, Istmo and Olmeca crude to obtain an average concentration of 55,000 PPM of TPH's. We added in three stages to the soil: 1)surfactants to increase the hydrocarbon solubility and enhance the degradability; 2) nutrients with a relationship of C:N:P = 100:9:1 and 3) cofactors, and fulvic and humic acids to keep a high Cationic Exchange Capacity (CEC).

After that the degradation process was stabilized, we added Vitamin B to promote and accelerate the enzymes formation, controlling and optimizing the growth factors , pH, Temperature and Oxygen, that could interfere the enzyme induction.

According with the results, the biodegradation process increases in 43%.

INTRODUCCTION

Oil Spills are a source of pollution of soil and water. In México most of the pipeline network where the oil is transported is older than 40 years. The probability that spill happened is high.

In areas where spills had occurred, there is a bacteria tolerance to the oil inducing to a selectivity and decrement of diversity (Atlas *et al.,* 1991), the oil spills produces serious damages to the nature, where the microbial degradation is one of the best decontamination processes (Leahy y Colwell, 1990).

Most of the petroleum components are biodegradable but the process is very slow. (Atlas y Bartha, 2002), two of the most used techniques are: biostimulation and bioaugmentation. The biostimulation implies an environmental modification that eliminates factor that restrict the microbial growth velocity and metabolism. The biodegradation, is improved with the inoculation of native bacteria (bioaugmentation) from soils with the same characteristics to the soil that is to be treated (Levin y Gealt, 1997).

The bioaugmentation is very important when the pollutants are persistent, with a very slow degradation, with the possibility of toxic action on the environment or migration to subsoil and groundwater, with risk to pollute water to human use. If the degradation starts early the risk of pollutant toxic action to plant, animals and humans is reduced. (Alexander, 1999).

METHODS AND MATERIALS

Characterization of a polluted soil.

To this work we collected representative samples of soil polluted with hydrocarbons derivatives in order to isolate native bacteria. We took samples from the soil surrounding a visible polluted point, with a depth of 10 cm. (HMTRI, 1997). The place where the sample was obtained shows pollution with more than 20 years, located in the southeast of the country in a tropical climate,.

The initial analysis were made in the laboratory of the University where we determined texture, pH, temperature ,CEC, humidity, Nitrogen, phosphorous, field capacity, TPH's, density and organic fraction content. We made triplicate analysis. (Table 1)

Bacterium isolation

Culture Media: we used media A (Rojas *et al.,*1999) which contain in g/L the following compounds: KNO_3, 1.0; $FeCl_3$, 0.02; $MgSO_4$, 0.2; NaCl, 0.1; $CaCl_2$, 0.1; K_2HPO_4, 1.0; yeast extract, 0.05 y 1.0 % (v/v) crude oil previously emulsified with a Tween aqueous solution -20 (1:1) 1.0% (v/v). Media B with the same compounds with addition of bacterial agar 1.5 % (w/v). The media pH, were adjusted to 6.3 with a solution of HCl 0.1 N. the isolation technique was enrichment culture.

In a 250 ml. Erlenmeyer flask with 125 ml of ,media A, we putted by duplicate 30 g of crude oil polluted soil with a concentration of 55,000 mg/kg. After three days of shaking at 180rpm and 26 °C. The liquid resultant was transferred again to a 250 ml Erlenmeyer flask with a fresh Media A, and repeat the operation two times. The liquid resultant of the third operation was cultured in plates with Media B and incubated 24 hours at 26°C.

After the incubation period, the colonies were cultured in nutritive agar plates for isolation and identification. We also used control cultures in Erlenmeyer with Media A, but without yeast extract and crude oil to avoid false positives.

The morphological characteristics were determined and started Gram stain, Indole and Oxidase tests. After that, using a Becton – Dickinson identification kit, we compared the obtained profile with a profile database in a computer.

Tests in liquid media

The bacterium capacity of the isolated bacterium to growth in liquid media using soil polluted as energy source was determined in a qualitative mode at laboratory level, using Erlenmeyer of 250 ml with 50.0 ml of media A with saturated soil at 55,000 ppm of crude oil previously emulsified with a Tween 20.

A microbial consortium inoculate consisted of 5.0 mL of a bacterium suspension of each strain isolated previously growth five days in inclined agar of tripticasein soy.

The flasks were prepared by duplicate and were incubated 10 days at 26°C. Without shake it. The bacterium development was observed when skim appeared on the surface. It also were prepared test flasks without inoculate and crude oil, to eliminate false positives.

Soil Tests

To test the bacterial consortium in soil, we polluted a soil with a mixture of different crude oils. 66.67 k of soil was polluted with a TPH's concentration of 55,000 ppm. The mixture was prepared with 30% of Maya crude, %0% Istmo crude (light) and 20% of Olmeca oil, we added 4.14 l to the soil. The polluted soil feed an acrylic cell conditioned with PVC pipeline, where was used to air injection.

The soil was characterized in the following parameters: texture, pH, Temperature, CEC, Nitrogen, Phosphorous, humidity, field capacity, density, organic matter and TPH's.

Soil conditioned.

The polluted soil was conditioned with surfactants, nutrients (nitrogen and phosphorous), cofactors (minerals), hormones and vitamins.

4.5 l at 0.005 % of no ionic surfactant (Ether nonil fenil polietilenglicol) was added in the initial stage of the process. The soil had a relationship C.N:P of 100:9:1. To enhance the protein synthesis we added 2 mL of cofactors minerals (Zn, Fe, S, Mg, Mn, Cu, Co and Mb) and 5mL of hormones derivate of marine algae's.

Bacterium inoculation

With the soil conditioned. We inoculated the cultured bacterial consortium to reach a bacterial population in the range of 1.0×10^6 UFC/100 g of soil, capable to degrade the pollutant (Levin and Gealt, 1997). The inoculate was prepared adding 3.0 g/l to water with tripticasein soy, mixed until it was dissolved and sterilized. When the inoculate was cooled it was incubated 24 -48 hours at 25 °C. And when the culture was turbid (bacterial growth) it was added to the soil by a homogeneous aspersion.

Control Parameters

The control parameters were pH, Temperature, % humidity and % of field capacity in reason of the influence that have this parameters on the growth and survival of bacterium, the parameters were measured at five different points, as shows in table 3.

BIODEGRADATION ENHANCEMENT

When the degrading process decay and stabilized we added 19 mL of vitamin B complex to promote the acceleration of protein synthesis and the cycle of carboxylic acids.

RESULTS AND DISCUSSION

Results of soil characterization show that the bacterial population lived under limited conditions in nitrogen, organic matter and water. CEC also is low (7.2 meq/100 ml), and then the nutrient quantity fixed in the soil is limited. By this reasons the total count of bacterium integrated by yeast and mold report 6.6 x 10^{-4} UFC/g of soil for bacterium and 2.6 x 10^{-5} UFC/g of soil for yeast and molds.

We obtained 9 different strains identified with the number 1 to 9 and their properties are showing in the table 4, all the broths isolated were bacillus Gram negatives. To identify we used the system BBL Identification Crystal Becton and Dickenson and only 5 of them were characterized. The table 5 shows their properties according to biochemical tests that were applied.

The five broths isolated and identified were: *Pseudomonas aeruginosa* (B_2), *Stenotrophomonas maltophilia*(B_3), *Acitenobacter iwoffi*(B_4), *Pseudomonas stutzeri*(B_6) y *Flavobacterium odoratum*(B_{10}).We did tests on liquid media with this bacterial consortium as shows the figure 1.

From the liquid media tested after that were incubated the flasks, we can observed the microbial growth as supernatant over the surface of the culture media. The flasks without inoculate did not show any growth. The flasks without crude oil show bacterial growth, confirming the viability of the bacterial consortium. Figure 2 shows the results.

The bacterial consortium application on the soil was satisfactory, reducing with the simultaneously application of surfactant, the hydrocarbon concentration in 27%..

To compare the treatment efficiency we used a witness cell where the hydrocarbons concentration was constant all the time.

We also calculated the theoretical rate of hydrocarbon degradation to compare with the real obtained in the experiment, showing the results in the table 6.

The complex B vitamin enhances the degradation. We added this vitamin when the degradation process began to decrease and remain stable. After the addition, we observed immediately an acceleration of the process.

The fulvic acid promotes the micelles formation and increased the bioavailability of the petroleum molecules to the bacteria action

The tricarboxilic acid cycle was promoted by the addition of vitamin B and humic substances, increasing the electron transference through the increase of the coenzymes NAD^+ and FAD related with nicotinic acid and rivoflavin and synthesized by the cellules of vitamin B (Wilbraham A and Matta M, 1989).

The theoretical degradation calculated shows a degradation rate of 377 ppm/day. During the first six weeks we observe a rate of 720 ppm/day of hydrocarbon degradation.

According with the success of the experimental process, we decided to biostimulate the process with the complex B vitamin addition, as well as, with the addition of an agrochemical from marine algae's, starting in the seventh week.

Reaching a 43% increment in the biodegradability rate, obtaining a rate of 1029 ppm of hydrocarbon/day (figure 3).

Along the process the field parameters such as pH, Temperature, % of humidity show changes, resulting very difficult to adjust the pH , especially after the week number 6, were appears abrupt changes in this parameter and the buffer capacity of the soil disappears.

Simultaneously with decrement of pH, there were changes in the humidity, saturating the soil with decrements in the bacterial population (figure 4). Comparing the behavior of these parameters it is suggested that appears a catabolic activities, with a satisfactory advances in the mineralization of the hydrocarbons.

CONCLUTIONS

It was isolated five different bacteria species adapted to crude oil polluted soil, two of the species isolated (*Pseudomones and* y *Acitenobacter*) have been previously reported as hydrocarbons degraders. (Sugiura *et al.,* 1997).

Since we obtained development of the bacterium in a liquid media, with crude oil as the only energy source, the strains show capacity to be used in a remediation process with the bioaugmentation technique.

We observed that the bacterium survival at pH less than 5.0, since their number never was less than 1.0×10^6 UFC/100 g of soil, Besides it was demonstrated that the bacterial consortium isolated from a polluted soil was capable to be adapted and growth under controlled conditions C.N:P (100:9-17.2:1-1.2) and also keep a high degradation efficiency.

We believe that with this technique of biaugmentation with native bacterium the restoration of crude oil polluted soil could be obtained at low cost and short time.

Table 1 Soil Characterization for the bacteria isolation

PARAMETER	UNITS	VALUES
pH		7 ± 0.28
Temperature	° C	26 ± 1.41
Cationic Exchange Capacity, CEC	meq/100 g	7.2 ± 1.06
Humidity	%	0 ± 0
Total Nitrogen	%	0.065 ± 0.02
Total Phosphorous	mg/kg	6.7 ± 1.61
Organic Matter	%	0.085 ± 0.008
Field Capacity	%	41 ± 19.14
TPH´s	mg/kg	55,000
Real density	g/cm^3	1.91 ± 0.26

Table 2 INITIAL CONDITIONS OF POLLUTED SOIL

PARAMETERS	UNITS	VALUES
pH		7 ± 0
Temperature	° C	25.5 ± 0.57
CEC	meq/100 g	24.4 ± 2.12
Humidity	%	100 ± 0
Total Nitrogen	%	0.21 ± 0.02
Total Phosphorous	mg/kg	124 ± 0.80
Organic Matter	%	0.11 ± 0.10
Field Capacity	%	100 ± 0
TPH´s	mg/kg	55,135 ± 0
Real density	g/cm^3	1.99 ± 0

Table 3. Monitoring frequency in he reactor

PARAMETERS	Initial	Daily	Weekly	Final
Ph	X	X		X
Temperature	X	X		X
Field capacity	X	X		X
% Humidity	X	X		X
CEC	X		X	X
TPH´s	X		X	X
Real density	X			
% Organic Matter	X			X
Nitrogen	X		X	X
Phosphorous	X		X	X
Bacterial plate count	X		X	X

Tabla 5. Morphologic Characteristics of the Strain culture isolated

COLONY MORPHOLOGY	STRAINS ISOLATED								
	1	2	3	4	5	6	7	8	9
Form	Circle	Circle	Circle	Circle	Circle	Circle	Circle	Circle	Circle
Elevation	Convex	Convex	Convex	Convex	Plane	Plane	Convex	Convex	Plane
Surface	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth
Border	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
Color	Amarillo	Blanco	Amarillo	Amarillo	Blanco	Blanco	Amarillo	Amarillo	Blanco
Consistency	Viscous	Viscous	Viscous	Viscous	Mucous	Mucous	Mucous	Mucous	Mucous
Gram stain	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)
Spores stain	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)

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Table 5. Results of the biochemical proofs to identify the strains isolated
(+) positive ; (-) negative

Biochemical proof	STRAIN (B_2)	STRAIN (B_3)	STRAIN (B_4)	STRAIN (B_6)	STRAIN (B_{10})
Arabinose	-	-	-	-	-
Manose	-	-	-	-	-
Sucrose	-	-	-	-	-
Ramnose	-	-	-	-	-
Sorbitol	-	-	-	-	-
Manitol	-	-	-	-	-
Adonitol	-	-	-	+	-
Inositol	-	-	-	-	-
αβ̃-glucóside	-	+	+	+	-
β̃-galactóside	-	+	-	-	-
Prolina nitroalinida	+	-	-	+	+
Bis-phosphate	+	+	-	-	+
Xiloside	+	+	-	-	-
Phosphorilcoline	-	-	+	+	-
β̃-glucoronide	-	+	-	-	-
N-acetil-glucosamine	-	+	-	-	-
Esculine	-	+	-	+	-
p-nitro-fenilalanina	+	-	-	+	+
Urea	+	+	+	+	+
Glicine	+	+	+	+	+
Citrate	+	-	-	+	+
malonic acid	-	-	-	-	-
Tetrasodium thriphenyl Chloride	+	+	-	-	+
Arginine	+	-	+	+	+
Lisine	+	-	+	-	-

Table 6. TPH's theoretical and real Biodegradation

DÍA	THEORETICAL TPH´s Ppm	REAL TPH´s Ppm	σ
0	55,135.30	55,135.30	± 4,712.31
10	51,367.9	40,046.5	± 800.20
20	47,600.5	34,388.2	± 1,333.67
30	43,833.1	21,185.5	
40	40,065.7	16,784.6	
50	36,298.3	8,297.15	± 622.38
60	32,530.9	5,468.00	± 177.82
70	28,763.5		
80	24,996.1		
90	21,228.7		
100	13,693.9		
110	13,693.9		
120	9,926.5		
130	6,159.1		
140	2,391.7		

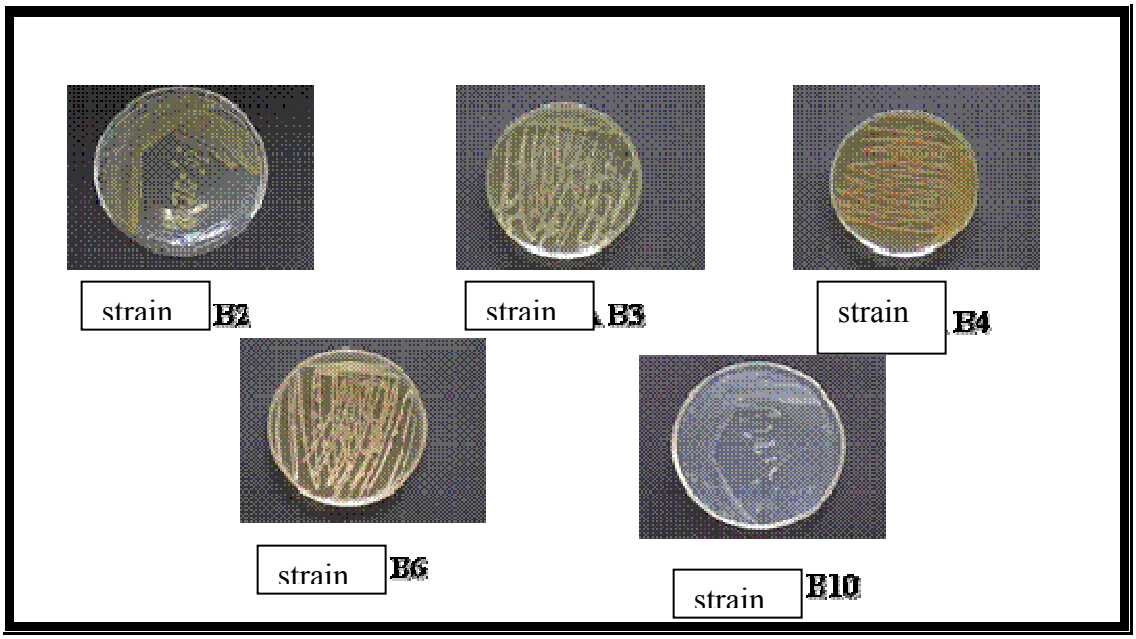

Figure 1. Strains developed in plates

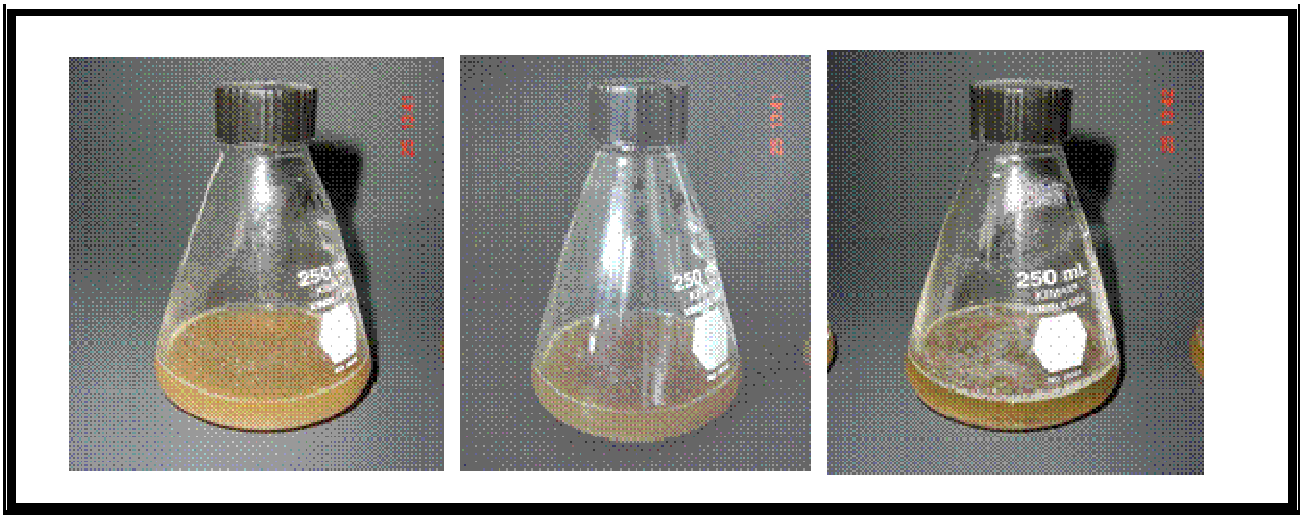

Figure 2. from left to right test without crude oil, test without microbial consortium inoculum's, and microbial consortium develop of the 5 strain, 10 days after incubation

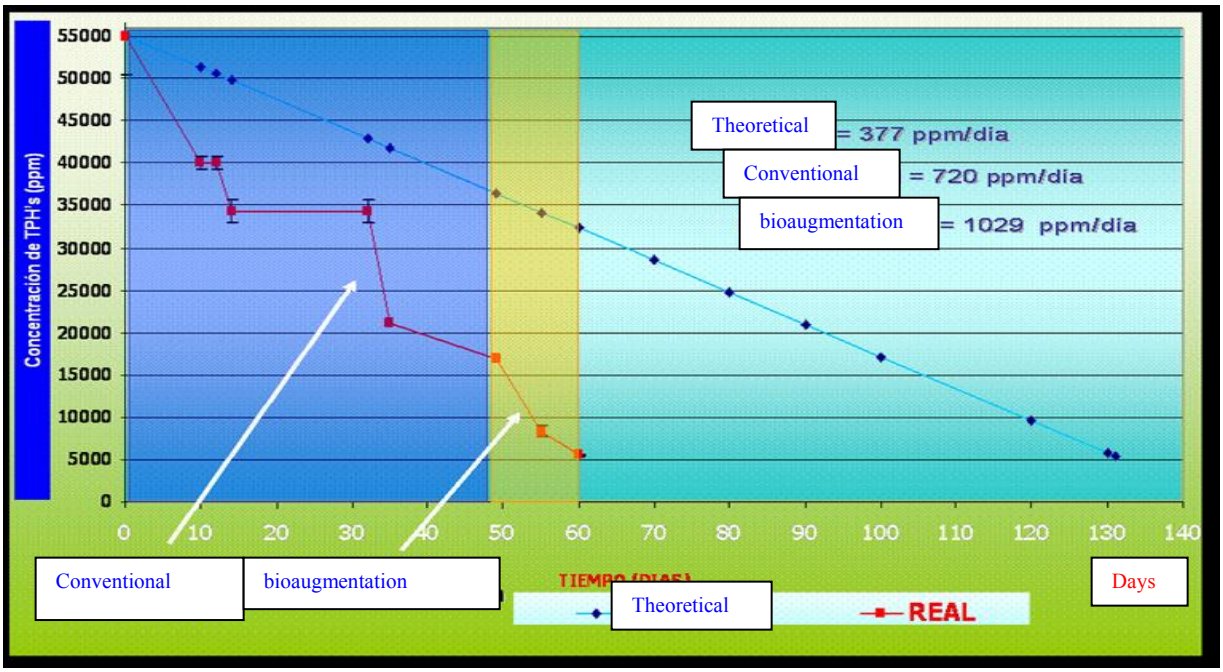

Figure 3. crude oil degradation

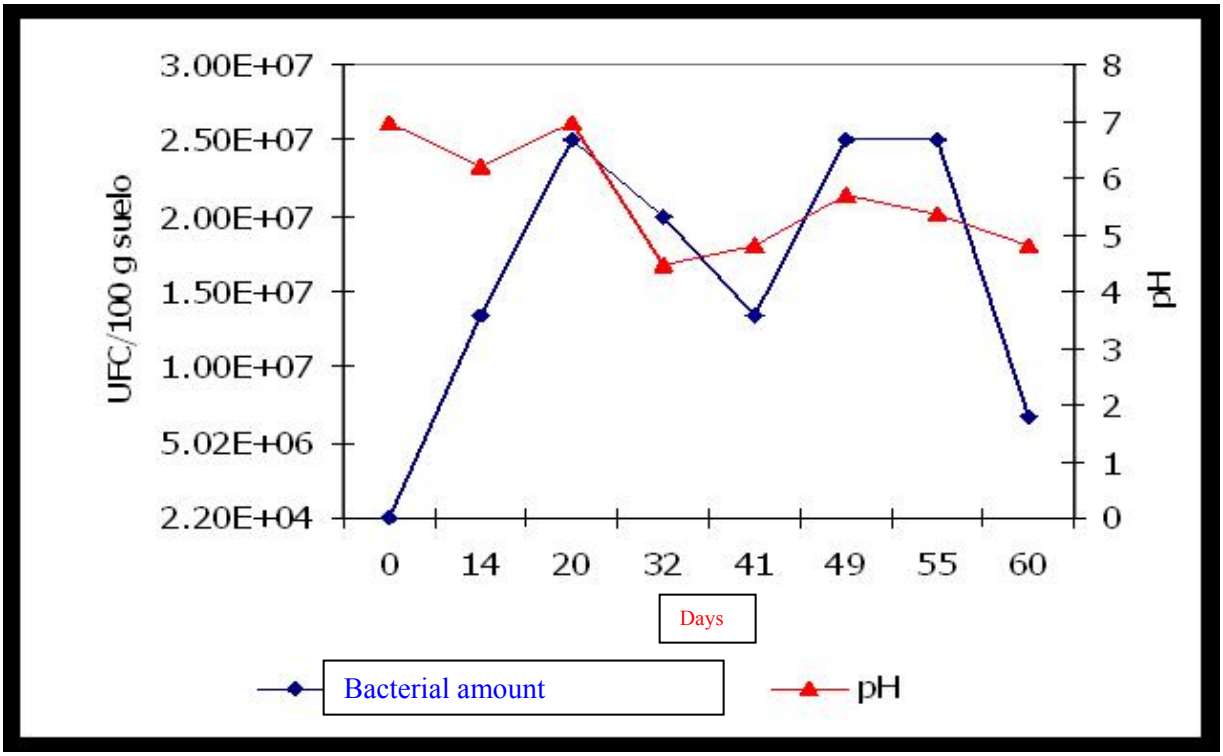

Figure 4. Behavior of the microbial consortium against pH

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DIAGNOSING AND RESOLVING CHEMICAL AND MECHANICAL PROBLEMS WITH PRODUCED WATER TREATING SYSTEMS

Dr. Ted Frankiewicz, V. P. Liquid Process Solutions
Dr. Joseph Lee, Sr. CFD Research Engineer
Dr. Chang-Ming Lee, Sr. Process Consultant

Natco Group
2950 North Loop West
Houston, Texas 77092

ABSTRACT

An approach is described for diagnosing chemical and mechanical limitations of produced water treatment systems. The methodology is predicated upon the development of a fundamental understanding of the produced water contaminants, the mechanical limitations of installed equipment, and process operations. Examples are presented to illustrate how this fundamental understanding has been applied to identify the causes of and to resolve field problems. In each case the operator was successful at improving the operation of their water treatment systems.

Introduction and Background

Two primary drivers are forcing oil and gas producers to give more consideration to the treatment of produced water. First, water production is increasing as fields mature. The result is that many facilities are required to handle water volumes substantially above the rates for which they were designed. Second, environmental regulations are becoming more restrictive over time. Thus produced water must be cleaner than ever prior to being discharged overboard from a platform or FPSO. Alternatively, regulations require the disposal of produced water by reinjection either into a suitable aquifer or into the reservoir from which it originated. For reinjection, the water quality must often be substantially better than that required for overboard disposal.

For overboard disposal, the US NPDES permits require that Total Oil and Grease (TOG) be less than 29 mg/liter as determined by the gravimetric analytical method US EPA 1664. For the North Sea, the limit is in the process of being reduced from 40 mg/liter to 30 mg/liter as determined by solvent extraction and an IR measurement. Other areas of the world, including much of South America, and West Africa (two very large growth areas for oil production), the TOG discharge limits are <20 mg/liter TOG with the measuring method often not defined.

The cleanliness of water to be injected depends upon the character of the reservoir that will receive the water. For fractured and for carbonate reservoirs, almost no restrictions on water quality are required. However, for sandstone or other low permeability formations, solids removal down to the 2 – 5 micron range may be required. Otherwise it will be impossible to inject substantial volumes of produced water below the formation fracture pressure for substantial lengths of time between expensive well work-overs.

Value of Produced Water

As a “non-revenue” fluid, produced water is generally considered as a cost burden by the operator. However, viewed from another perspective, recoverable reserves can be substantially enhanced if one is willing to produce more barrels of water per barrel of oil recovered. Thus, in one sense, the “value” of produced water can be defined by the volume (value) of incremental oil recovery as a result of water production.

From the disposal side, the “value” of improving the produced water cleaning facilities can be defined by the alternative cost of, for example, injection well maintenance. Often, an improvement in water treating facility performance will pay for itself by avoiding the cost for a single well work-over.

Cleaning Produced Water

There are two interactive aspects of produced water treatment: process hardware and chemical treatment. The selection and operation of process hardware requires knowledge of the chemical and physical characteristics of both the produced water and of the contaminants in that water. Similarly, to properly select a robust chemical treatment program that successfully augments the performance of the water treating equipment, those same chemical and physical characteristics

must be known. Table 1 lists key information that is required to diagnose problems with water treating systems.

Much of the information listed in Table 1 is only accessible on the production site itself. The determination of oil droplet size distributions, $CO_3^{=}/HCO_3^{-}$ concentrations, and Total Suspended Solids (TSS) on site is essential. Generally, it is recommended that water samples be pressure filtered directly from a process sample point when possible to avoid subsequent scale mineral precipitation or ferrous to ferric oxidation. Where process pressure is insufficient, laboratory pressure filtration of fresh samples at the field/platform location is far preferable to vacuum filtration.

The design of a gas/oil/water separation process as well as the selection of upstream process hardware is critical for produced water treatment. The diagnosis of a water treating problem and the selection of means to mitigate the problem require

- An understanding of how the mechanical aspects of upstream operations are impacting water quality
- An understanding of the impact that process operating conditions may have on produced water quality
- Knowledge of how the overall process design is impacting water quality. Of particular concern here is the presence of contaminant recycle streams.

The selection of equipment to treat produced water is, for the most part, dependent upon the size distribution of the contaminants to be removed. Table 2 lists commonly used water treating equipment and the oil droplet sizes that are removed by that equipment.

On shore, where space is not an issue, residence time in large tanks is a favored technology. Unfortunately, until recently, the hydraulics of fluid flow through large tanks was poorly understood. Recent studies using Computational Fluid Dynamics (CFD) has revealed much about how water flows through large tanks and suggested designs for tank internals that virtually eliminate this short circuiting.[1] With these designs, fluid residence times in large tanks can be increased from <50% of theoretical to over 90% of theoretical. The CFD studies also show that separating oil droplets <50 microns diameter in these tanks is inefficient.

Offshore, where equipment weight and space must be minimized, the most commonly installed equipment for cleaning produced water is the combination of hydrocyclones and induced gas flotation. Where possible, upstream separator pressure is used to drive water through the hydrocyclones. By installing the hydrocyclones close to the flotation cell, dissolved gas that breaks out of the water as pressure is reduced can be used for the first stage of flotation.

To limit the space required for a flotation cell, single cell vertical flotation units are increasingly popular. One of these designs, illustrated in Figure 1, utilizes both dissolved and dispersed gas in order to effectively provide two stages of flotation in a single vessel.[2] Figure 2 shows a combination deoiling hydrocyclone and induced gas flotation system with a capacity of 40,000 BWPD that is currently operating in the Gulf of Mexico.

Diagnosing and Resolving Water Treating Problems

Table 3 is adapted from a recent article published in World Oil.[3] This table outlines a step by step approach for first identifying the root causes of a water treatment problem and then proscribing a workable and robust solution to the problem.

Example 1

In this example, key fundamental produced water contaminant characterization data allowed an unambiguous solution to a water treating problem to be developed.

An operator requested that a process audit be conducted in order to determine why the deoiling hydrocyclones on his platform were "not working" as expected. Prior to conducting the audit, the operator was asked to conduct a Jorin Analyzer Survey to determine the oil and solids particle size distributions at several points in the process. The Jorin Analyzer is an on-line sampling device that takes several hundred photomicrographs of flowing water. Image analysis software is then used to determine the size distribution independently for oil droplets and solids.

The Jorin survey showed that the oil droplets in the produced water had a median droplet size of 9 to 15 microns and that these droplet sizes persisted from a point just downstream of a high pressure separator operating at about 450 PSIG. The high shear experienced by the produced water across the control valve for this separator generated the small oil droplets which then had insufficient process time to coalesce prior to entering the deoiling hydrocyclones. The hydrocyclones on the platform were of a low efficiency design and were, in fact, performing better than their manufacturer would have specified.

The recommended solution was to replace the low efficiency hydrocyclones with a newer, high efficiency design capable of removing the small oil droplets now known to be present in the produced water.

Example 2

An operator constructed a water treating process on a floating platform that consisted essentially of deoiling hydrocyclones and induced gas flotation. The feed water specification stated that no solids were to be present in the produced water. Unfortunately, this was not the case and the presence of oily solids in the produced water made it all but impossible for the operator to clean the water to <20 PPM TOG. A flow diagram for the process as installed and with a subsequent upgrade is shown in Figure 3.

An audit of the water treating process revealed that fluids from the reject stream of the deoiling hydrocyclones and fluids from the skimming of the IGF were being returned to an upstream separator and recycled through the process. This practice had two significant impacts on water quality. First, fine, oily solids in both of the reject streams were being recycled and sheared into the water phase by pumps and control valves. Second, demulsifier and water clarifier chemicals were also being recycled via the two reject streams. Together, the chemicals and problematic solids were generating interface emulsions that further interfered with contaminant removal.

The solution in this case was to install on the platform, an accumulator vessel to permit oil and oily solids to be removed from the process instead of being recycled. Once the accumulator

vessel was installed, it was determined that the location for injection of water treatment chemical could be moved and the treat rate reduced. Subsequent to implementation, the TOG of the overboard discharge water dropped from typical values >30 mg/liter to typical values around 15 mg/liter.[4]

Example 3

An operator installed a new IGF on a floating platform in the Gulf of Thailand. However, when placed into service, the vessel initially appeared to have no impact on water quality. Thus a process audit was requested by the operator in order to ascertain the source of the problem. The audit revealed the following:

- As a result of the presence of methanol in the produced water, there was a high concentration of soluble organics in the produced water, some of which were detected when the water was analyzed by solvent extraction and IR spectroscopy. However, these hydrocarbons were not detected by EPA 1664.
- As in the above example, hydrocyclone and flotation reject streams were being recycled within the process to the detriment of overboard water quality
- The water clarifiers in use did not target the oil-wet scale mineral precipitates present in the water and were thus only marginally effective.
- Water clarifier injection was upstream of a skim tank and was being removed from the system ahead of the IGF. In essence, the performance of the IGF was not augmented by this chemical injection.
- Highly variable water flow rates were experienced as a result of incorrectly sized interface control valves on an upstream separator.

The first action required was to change the analytical method used on the platform so that representative water quality data could be obtained and water quality data could be correlated with other actions and activities on the platform. Next, the contaminant recycle streams were eliminated from the process and control valve sizes changed to match the produced water flow rate. Finally, a higher molecular weight polymer was used as a flocculent water clarifier and this chemical was injected immediately upstream of the flotation cell. The water quality discharged from the IGF over several months time is summarized in Table 4.[5]

Summary

A systematic approach is presented for evaluating the performance of an oil treatment facility and developing recommendations for upgrading performance. The approach is predicated upon first identifying and resolving mechanical issues, then introducing the appropriate process chemistry. Problem solutions are developed based upon an understanding of the fundamentals of both fluid chemistry and process operations. Examples discussed show that this approach can be used successfully to develop recommendations for upgrading process systems. With this approach, investment risk is minimized since the upgrade recommendations are based upon a fundamental understanding of both process capabilities and fluid chemistry.

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Table 1. Chemical and physical characteristics of produced water that should be known in order to assess problems with water treating systems

Cation content	Na^{+}, Mg^{++}, Ca^{++}, Ba^{++}, Fe^{++}/Fe^{+++}, etc.
Anion content	sulfate, chloride, carbonate, bicarbonate, sulfide
Organic acids	acetate, proprionate, naphthenic acids
Soluble organics	methanol, other alcohols
Solids	precipitated scale mineral phases formation mineral phases particle size distribution for solids
Dispersed oil	droplet size distribution wax & wax appearance temperature asphaltenes
Upstream chemicals	Corrosion inhibitor, scale inhibitor, biocide, demulsifier, "soap stick", anti-foam, etc.

Table 2. Commonly used equipment for cleaning produced water are listed along with oil droplet sizes typically removed by that equipment.

TECHNOLOGY	**REMOVES PARTICLES (MICRON)**
API Gravity Separator	> 150
Long Residence Time Skim Tanks	> 50
Corrugated Plate Separator (CPI)	> 30
Deoiling Hydrocyclone	> 10
Desanding Hydrocyclone	> 5
Induced Gas Flotation	> 25 without CHEMICALS
Induced Gas Flotation	> 3 with CHEMICALS
Mesh Coalescer	> 10
Nutshell or Media Filter	> 5
Centrifuge	> 2
Membrane Filter	> 0.01

Table 3. A systematic approach is outlined for diagnosing produced water treating problems and developing viable solutions.

1. Review all aspects of a facility's mechanical operations. Fix mechanical problems prior to addressing chemical treating issues

2. Review the facilities process flow diagram to identify issues that may impact water quality, e.g., high pressure drops and contaminant recycle streams.

3. Correlate the appearance of water treating problems with operational practices

4. Take fluid samples for analysis both on site and at a remote laboratory. Jorin Analyzer Surveys have proven to be particularly valuable.

5. Conduct diagnostic tests in the field to understand how the produced water may respond to a particular technology, e.g., sparge tube flotation test.

6. Review data and information developed with operators and asset engineers.

7. Provide relevant data to equipment and chemical suppliers. Work with suppliers to select and test candidate solutions.

8. Where possible, pilot test to confirm proposed solutions prior to committing to the purchase of equipment or a change in the chemical treating program.

Table 4. Water quality discharged from a VersaFlo 1-cell induced gas flotation vessel installed on a spar in the Gulf of Mexico. TOG was measured by EPA Method 1664.

Date	Inlet TOG	Outlet TOG
02-03	52 mg/liter	27 mg/liter
02-03	48	19
02-03	37	13
10-03	47	15
10-03	55	23
01-04		12
02-04		14
03-04		6
04-04		20
06-04		12
07-04		19
08-04		12
09-04		14
10-04		Hurricane Ivan
11-04		low water flow
12-04		13

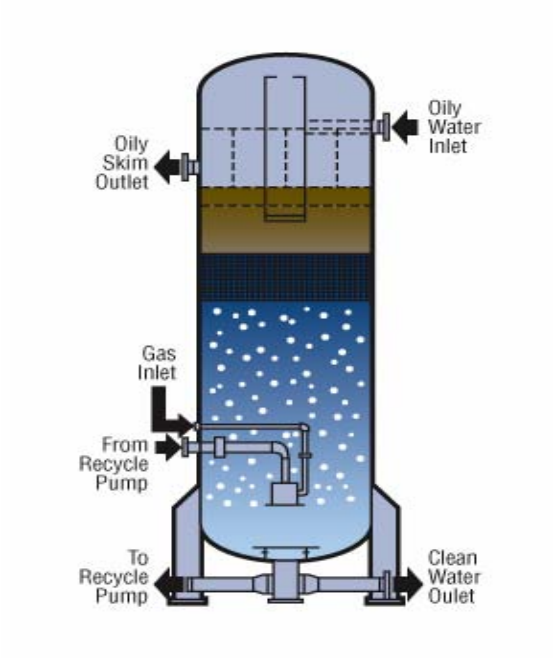

Figure 1. A schematic of a 1-cell VersaFlo IGF that incorporates two stages of flotation in a single vessel.

Figure 2. A 40,000 BWPD water treatment skid is shown that closely couples deoiling hydrocyclones and a vertical IGF vessel.

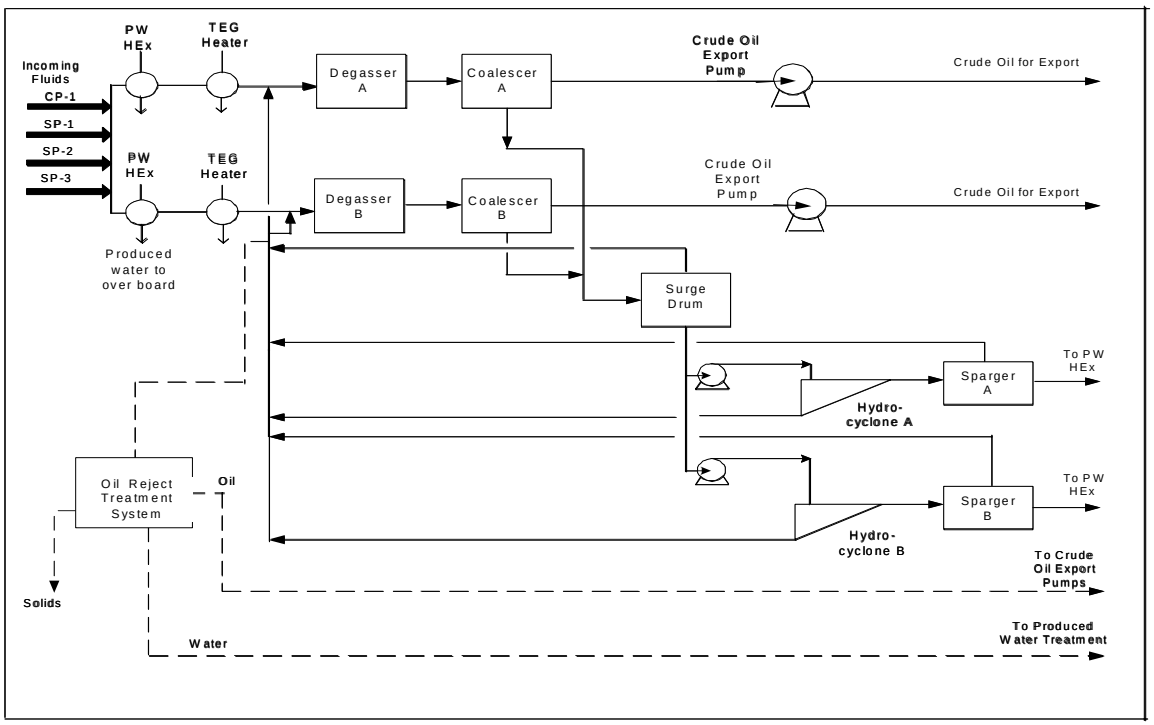

Figure 3. The Process Flow Diagram is shown for a water treatment system before and after the installation of an oil reject accumulation system designed to eliminate contaminant recycle within the process.

DISSOLVED METHANE IN GROUNDWATER, SAN JUAN BASIN, LA PLATA COUNTY COLORADO: ANALYSIS OF DATA SUBMITTED IN RESPONSE TO COGCC ORDERS 112-156 & 112 -157

Anthony W. Gorody, Ph. D., CPG-9798 (Universal Geoscience Consulting, Inc.)
Debbie Baldwin (COGCC) and
Cindy Scott (Consulting Hydrogeologist)

ABSTRACT

Since the Colorado Oil and Gas Conservation Commission (COGCC) approved orders 112-156 and 112-157 issued on July 11, 2000, operators in the Ignacio Blanco Field of the San Juan Basin have been sampling domestic groundwater wells prior to and following drilling additional optional wells in the Fruitland Formation. The objective of this independent study was to determine whether infill drilling has had any impact on methane concentrations dissolved in groundwater.

The COGCC data base of water samples from the San Juan Basin contained data from 2109 groundwater samples that were collected from 1034 different water wells in the San Juan Basin. There were 292 water well sites with data from samples collected both prior to and after drilling additional optional Fruitland wells. We compared the statistical variance in dissolved methane concentrations prior to and after drilling Fruitland wells with the short term variance observed among 87 paired samples collected from individual sites within sampling lag times of up to 3 months. Results show that 61% of the 292 sites sampled did not contain any dissolved methane. Of the remaining 39% of samples, 21% had pre-drilling concentrations that were greater than post-drilling concentrations; 18% had higher post-drilling concentrations. Only 14 sites contained post-drilling methane concentrations exceeding the calculated maximum value predicted from the short term variability regression analysis. Chromatography and stable carbon and deuterium analyses of dissolved gas from 10 of those samples establish that dissolved methane in groundwater did not originate from the underlying Fruitland Formation. Methane concentrations in the other 4 samples were too small to be characterized.

Infill drilling has had no detectable impact on dissolved methane concentrations found in groundwater throughout the Colorado portion of the San Juan Basin. Observed short and long term changes in dissolved methane concentrations are due to a combination of sampling error, environmental variability, aquifer mixing dilution, mixed biogenic and migrated thermogenic gas sources, and bacterially-mediated methane oxidation.

INTRODUCTION

The Colorado Oil and Gas Conservation Commission (COGCC) orders 112-156 and 112-157 issued on July 11, 2000, require operators in the Ignacio Blanco Field of the San Juan basin to sample the 2 closest domestic groundwater wells within a ½ mile radius of each planned additional optional well in the Fruitland Formation. The results are treated as "baseline" data used to evaluate potential future impacts on shallow groundwater resources that may result from drilling operations. Each water well then becomes a "monitor" well which is subsequently sampled within one year, three years, and six years after the additional Fruitland well has been drilled.

Several types of analyses are routinely run for each sample collected at a water well site. These include standard field parameters, dissolved major ion concentrations, dissolved methane concentrations, stable carbon and deuterium isotopic analyses of dissolved methane when exceeding concentrations of 2 mg/L, and fixed gas and hydrocarbon chromatography of samples sent for stable isotopic analysis. Some operators, such as BP, supplement the data required by the COGCC with stable isotopic analyses of oxygen and deuterium in water, and stable isotopic analyses of dissolved inorganic carbon. When measured methane concentrations exceed 10 mg/L or increase by 5 mg/L in successive samples, operators are required to determine if the dissolved methane is of thermogenic or biogenic origin. If the stable isotopic values appear thermogenic, then the produced gas from the additional optional Fruitland Formation well is sampled and compared with the dissolved gas composition extracted from the water well sample.

The COGCC's objectives for this commissioned study were as follows:

1. Determine whether drilling of optional additional wells in the Fruitland formation has had any impact so far on the methane concentration in groundwater;
2. Compare baseline data before drilling with monitor data after drilling;
3. Address causes for observed variability in methane concentrations;
4. Post results on the COGCC web site;
5. Make public presentations of the information.

Groundwater data made available for this study are now part of the COGCC database and include samples collected and data reported since 1990 by various state and federal organizations, and industry. These data are available on line through the COGCC web site. The analyses reported here are based on the data available through March 2004. Up to that time, approximately 2109 data records containing measurements of dissolved methane concentrations in groundwater were available in the COGCC database.

The data used for this study was compiled by various sources including industry operators, the Bureau of Land Management, the United States Geological Survey, and the COGCC (1,2,3). Groundwater samples were collected from 1034 different sites. Of those, there were 445 sites with single methane analyses, and 589 sites with multiple methane analyses. Methane was detected at 674 water well sites (65% of all wells sampled). Detection limits are approximately 0.004 mg/L.

SHORT TERM VARIABILITY

To evaluate the significance of long term changes in methane concentrations, we first evaluated changes typically observed in water well samples over the short term. The COGCC data base contained 87 pairs of multiple methane concentration measurements from 43 different water wells. The sample data shown in Figure 1 were collected within a maximum period of 95 days. At 32 of the water wells, there were only 2 consecutive analyses available within that period. Each data point represents the lag time between consecutive measurements, and the difference between the maximum and minimum methane concentration values between consecutive samples. Results indicate that short term variability between consecutive samples is large.

Figure 2 shows the results of a least squares regression analysis of the minimum and maximum methane concentration values observed between consecutive sample pairs. The majority, or 64%, of paired samples vary in concentration by less than 1 mg/L, and the short variability in methane concentration increases with increasing methane concentration. This variability is far greater than the analytical detection limit of 0.004 mg/L. On average, we can predict the minimum and maximum methane concentration at any give water well as:

EQ.1: Maximum Methane Concentration= 0.55 * 1.14 Minimum Methane Concentration

Although there are many data points outside of the 95% confidence level for the regression shown in Figure 2, the mean regression value provides a reasonable estimate for short term variability. We use the regression result to address changes in pre-drilling and post-drilling methane concentrations among water well sites sampled within a period of one year or more.

The Bureau of Land Management and COGCC (2) recognized that measured methane concentrations in samples from a single water well can vary significantly. The authors of the San Juan basin water study (2) attributed such variability to a combination of sampling error, and environmental factors. Sampling variability was attributed to the following factors:

- Differences in the number of water well volumes purged prior to taking samples;
- Intensity of methane effervescence relative to time required to collect a sample
- Laminar vs. turbulent flow through tubing when collecting samples;
- Intensity and timing of mechanical pump action.

Environmental variability was attributed to the following factors:

- Changes in specific yield;
- Changes in barometric pressure;
- And seasonal changes in static water levels;

The BLM-COGCC report concluded that variations of between 50 and 100% should be considered “normal”, whereas changes of an order of magnitude or more should be considered to be outside the “normal” range.

METHANE CONCENTRATIONS BEFORE DRILLING AND AFTER DRILLING

There were 292 sample pairs used for this analysis representing methane concentrations measured prior to and after drilling optional additional Fruitland wells. The average time lag between paired sample measurements was 378 days. 179 of those sample pairs (61%) had consecutive measurements below detection limits. There were 113 sample pairs for which there were detectable amounts of methane measured at least once. Of those, 21% of the samples had methane concentrations that were higher in wells sampled before drilling than after drilling; 18% of the samples had higher methane concentrations after drilling (pie chart inset Figure 3). The approximately equal partitioning of sample pairs with either increasing or decreasing methane concentrations suggests that the observed changes are random.

Using equation 1, we can calculate an expected maximum methane value based on the minimum value of a sample pair. Figure 3 shows that 14 sample pairs with higher post-drilling dissolved methane concentrations exceeded the predicted maximum methane concentration calculated on the basis of the regression equation 1.

There were 16 water wells which were tested a second time after the pre drilling baseline measurement (usually during the second year after new well was drilled). Of these, 10 (63%) did not contain detectable amounts of dissolved methane. Of the 6 water wells with detectable methane, only three had methane concentrations higher than that measured the previous year. Of those, none had maximum methane concentrations above that predicted using the short term regression equation. Of those 6 sites, only site #811 contained more than 2 mg/L of dissolved methane (Figure 4).

ADDRESSING THE ORIGIN OF DISSOLVED GAS

COGCC orders 112-156 and 112-157 do not require either chromatographic analysis of dissolved gas or stable isotopic analysis of methane if concentrations are below 2 mg/L. Of the 14 sample pairs found to exceed the average predicted maximum methane concentration after drilling, only 10 contained at least one sample with 2 mg/L or more of methane. These samples were analyzed using GC chromatography, mass spectrometric analysis of stable carbon isotope ratios in methane and carbon dioxide, and mass spectrometric analysis stable deuterium isotopes in methane.

Stable carbon and deuterium isotopes of methane (CH_4) are used in the oil and gas industry as a diagnostic tool to determine methane origin (5,6,7). Methane originating from the burial of organic sedimentary matter at high temperatures and pressures is defined as thermogenic. Methane originating from bacterial fermentation or from the bacterially-mediated reduction of carbon dioxide is defined as biogenic. Biogenic methane is a common constituent of groundwaters around the world. Approximately 20% of the world's commercial natural gas reserves is biogenic (4).

By convention, isotope ratios are expressed in delta (δ) notation indicating the difference in the molar ratio of the heavy to light isotope of a sample relative to the molar ratio of the heavy to light isotope of an National Bureau of Standards standard (5). In natural gases such as methane

and carbon dioxide, this difference between samples and a standard, for both deuterium and carbon isotopes, is very small and expressed in per mil or parts per thousand. Also by convention, negative values indicate that samples are less heavy than the standard. When comparing samples, differences are expressed as being either relatively enriched or relatively depleted in the heavier isotope.

The range in stable isotope ratios for dissolved methane in water wells far exceeds the range in values reported from producing Fruitland Formation gas wells (Figure 4). The range in carbon isotope ratios for produced Fruitland Formation gases is between delta -53 and -37 per mil, and the range in deuterium isotope ratios is between delta -266 and -179 per mil (as indicated with the shaded ellipse). Among the 10 sites with significant methane concentrations above predicted averages, only two (site 595 and site 895) have carbon and deuterium isotope ratios that are in the measured range of produced Fruitland Formation gas samples throughout the Ignacio Blanco gas field. Stable carbon isotope values of delta -55 per mil have historically been used in this basin as an arbitrary cut off value used to differentiate between more thermogenic and biogenic gas (1,2).

Site #595 is one of the water wells monitored for the optional additional Medina Presentacion A#2 Fruitland Formation gas well. High methane concentrations were present in this well prior to drilling the additional well. Chromatographic and isotopic data are used to show that the dissolved gases in the domestic water well are not derived from the underlying Fruitland Formation (Figure 5). Fruitland Formation gas, sampled from three closest surrounding producing wells in the area, is composed of methane (C_1) with trace quantities of ethane (C_2); dissolved gases sampled from the monitor well contain C_1, C_2, propane (C_3), butane (C_4), and pentane (C_5). The isotopic composition of the methane in the monitor well is also different from that in the Fruitland Formation. Although the stable carbon isotope ratios are similar to those measured in methane produced from the Fruitland Formation, the stable deuterium isotope ratios differ by more than 22 per mil. Accordingly, the dissolved hydrocarbons found in water well site 595 do not originate from the underlying Fruitland Formation.

Site #895 is one of the monitor water wells for the optional additional Streeter Gas Unit B#1 Fruitland Formation producing gas well. Variably high dissolved methane concentrations were present in this water well prior to drilling the new Fruitland Formation well. In this area of the San Juan Basin, both methane and ethane are present in produced Fruitland Formation gas. Both dissolved methane and ethane are also present in the water well. However, the C_1/C_2 ratio is significantly different between the two types of samples. The stable isotopes of methane are also significantly different. Thus the dissolved hydrocarbons in the water well do not originate from the underlying Fruitland Formation.

We can also compare the stable isotopic ratio of $\delta^{13}C$ in CO_2 in water samples and produced gas samples to evaluate gas origins. Stable isotope values for dissolved gaseous CO_2 used in this study were calculated on the basis of the measured stable carbon isotopic composition of dissolved inorganic carbon (DIC) precipitated from water samples. The $\delta^{13}C_{DIC}$ data were converted to a $\delta^{13}C_{CO2}$ ratio by using known fractionation factors that account for the partitioning of stable isotopes between the gaseous and dissolved phases of CO_2 (5). Such a conversion allows direct comparison with the $\delta^{13}C_{CO2}$ ratios obtained when analyzing gaseous CO_2 in produced Fruitland Formation gases.

Gas produced from the Streeter Gas Unit B#1 Fruitland Formation well contains small amounts of CO_2 (0.93% by volume). Here again we can observe that $\delta^{13}C$ in CO_2 found dissolved in water well site #895 is typical of soil gas values of the basin, in the range of delta -25

to -27 per mil, and unlike that which is produced from the Fruitland Formation. Accordingly, we can conclude that the dissolved gas found in water well site #895 does not originate from the Fruitland Formation.

FACTORS AFFECTING DISSSOLVED METHANE CONCENTRATION

Dilution

Having established that the dissolved gases in site #595 are not derived from the underlying Fruitland Formation, we can use the dissolved major ion data to determine why dissolved methane concentrations appear to have increased systematically at this site since 1994. Samples collected and analyzed from water well site #595 provide an excellent example of the influence that fluid mixing and dilution have on dissolved methane concentrations.

There are 5 sets of available historic data for site #595 that include both measured dissolved methane concentrations and major ion chemistry. The water well now contains high dissolved methane concentrations, and since 1994 the concentrations have steadily increased (Figure 7). Figure 7 also shows how the normalized relative concentration of total alkalinity (% HCO_3^-), dissolved sulfate (% $SO_4^=$), and dissolved chloride (Cl^-) ions have varied with time. The change in the relative concentration of dissolved sulfate is inversely proportional to the change in methane concentration.

Shallow aquifers in this area of the San Juan Basin have a vertical distribution of water types. In order of increasing depth, water composition changes from being predominantly composed of Na_2SO_4 (dissolved thenardite), to dissolved $NaHCO_3$ (dissolved bicarbonate), and finally to dissolved NaCl (table salt). Such changes in dominant water types are typically observed over a depth range of 50-300 feet. Accordingly, the aquifers in this area are layered, confined, and not well vertically mixed.

Although most water wells are only screened at the bottom of the well, the permeable gravel pack in a well bore annulus can allow water to enter the screened interval from multiple water-bearing zones. The domestic water well at site #595, 327 feet deep, is among the deeper water wells in the area. Since 1994, the relative amount of sodium sulfate has continually decreased from a value of 40% of the total dissolved anion milliequivalents to 10% of the total dissolved anion milliequivalents. Conversely the relative amount of sodium chloride has increased proportionately from 40% to 70% of the total dissolved anion milliequivalents. Thus relative to sulfate, the sodium chloride concentration has increased by 175% since 1994. Over the same period, the measured dissolved methane concentration has increased by 177% from an average value of 13 mg/L to an average value of 23 mg/L. This proportionate relationship clearly shows that the more saline NaCl type waters entering this well carry dissolved methane, whereas the $NaHCO_3$ and Na_2SO_4 type waters do not. Chemical analysis of the water allows us to conclude that since 1994, the amount of Na_2SO_4 type fluids available to dilute the methane-bearing NaCl type waters has systematically decreased. Mixing of fluids, sourced from different water-bearing layers in a well bore, can therefore significantly affect methane concentrations.

Methane Oxidation

Bacterially-mediated methane oxidation is a common phenomenon observed in oceans, shallow surface waters, and aquifers throughout the world (7,8,9). Different bacterial groups oxidize methane via different biochemical pathways depending on whether dissolved oxygen, or bound oxygen in sulfate is used for their metabolism. It is beyond the scope of this paper to discuss the source of oxygen used by subsurface bacteria to oxidize methane. However, available data indicate that anaerobic methane oxidation in the presence of dissolved sulfate ions is the dominant metabolic mechanism in water well environments throughout the San Juan basin. Ratios of dissolved O_2/Ar in most domestic water well samples from this area tend to be extremely low, indicating that the domestic wellbore environment tends to be stagnant.

Bacterially-mediated methane oxidation is recognized on the basis of a direct relationship between decreasing methane concentrations, enrichment of heavy stable carbon and deuterium isotope ratios in residual methane, and a corresponding depletion of heavy stable carbon isotope ratios of carbon dioxide (CO_2) (7,8,9). Bacterial consumption rates are greater for molecules of methane containing lighter isotopes than for those containing heavier isotopes. This phenomenon, referred to as a kinetic fractionation process, occurs because the chemical bond between atoms containing heavy isotopes is stronger and requires more energy to break than the bond between atoms containing lighter isotopes. Methanotrophic bacteria generate CO_2 as part of their metabolic process. Because such bacteria preferentially consume the light isotopes of methane, the carbon dioxide they produce becomes progressively depleted in heavy isotopes.

At site 895, the chemical composition of water containing the lowest concentration of dissolved methane, contains sulfate ions, whereas the composition of water containing the highest concentration of dissolved methane does not contain sulfate. Figure 6 shows a trend of decreasing methane concentration, increasing $\delta^{13}C_{Methane}$ and $\delta D_{Methane}$ ratios, and decreasing $\delta^{13}C_{CO2}$ ratios (inset graph B). Thus methane oxidation by methanotropic bacteria accounts for the additional loss of methane that cannot be explained by mixing alone.

The effects of bacterially-mediated methane oxidation are evident in most water well sample data for which there are one or more pairs of samples with stable isotopic analyses. Figure 8 shows a reduced three dimensional plot of stable isotope ratios in methane, and methane concentration. The vertical z axis of dissolved methane concentration is represented with contour lines generated by fitting a quadratic surface through the available methane concentration data for each sample point. Also shown on Figure 8, are white arrows connecting one or more sample points obtained at various times from a unique water well sample site. Figure 8 allows us to observe that the shift towards lighter stable isotope ratios in all white arrow sample pairs occurs in the direction of decreasing methane concentration.

Figure 9 shows that the characteristic enrichment in stable carbon and deuterium ratios resulting from bacterially-mediated methane oxidation can be approximated as follows:

$$\text{EQ 2: Change in } \delta D_{Methane} = 7.4 * \text{Change in } \delta^{13}C_{Methane} + 2 \text{ per mil}$$

Although there is scatter in the data, the Pearson's correlation coefficient for this regression is significantly high. The regression value compares well with other published empirical and laboratory data (8,9).

The observed scatter in data shown in Figure 9 is surprisingly low considering the dynamic well bore environmental conditions affecting dissolved methane concentrations. A permeable, uncemented water well annulus provides the cross flow environment needed to allow reduced fluids carrying methane to mix with fluids carrying either the free or bound oxygen that

methanogens need to oxidize methane. The amount of residual, oxidized methane present at any given time can be expected to vary significantly. For example, when the rate of methane oxidation is greater than the rate of fresh methane influx, then dissolved methane concentrations will decrease and the effects of kinetic fractionation will be most evident. On the other hand, when the rate of fresh methane influx is greater than the rate of oxidation, then methane concentrations will appear to increase and the effects of kinetic fractionation will be less evident. Mixtures of oxidized and fresh aquifer methane account for much of the scatter of stable isotopic data observed among water sample pairs.

Mixed Methane Sources

There is third source of variability in methane stable isotope ratios observed among water sample pairs. Up to this point, our discussion has been predicated on the assumption that a single water-bearing interval provides a source of methane in a water well. However, there are areas in the basin where both thermogenic and biogenic methane sources are present. Figure 8 shows a black arrow connecting the stable isotope ratios from consecutive samples collected from one water well. This arrow clearly shows the influence of mixing between thermogenic (more positive stable isotope ratios) and biogenic (more negative stable isotope ratios) methane sources. It is likely that such a trend in sample pairs is indicative mixing between water containing dissolved biogenic methane and water containing dissolved thermogenic methane.

CONCLUSIONS

The results of this study demonstrate that multiple types of analyses are required to address whether domestic water wells are being impacted by drilling operations in the San Juan basin. At a minimum, these include field parameters measured on site, (e.g. water temperature), analysis of the dissolved major ion concentration in water samples, analysis of dissolved methane concentrations, stable isotopic analyses of dissolved methane and carbon dioxide in water samples, and stable isotopic analysis of methane and carbon dioxide produced from producing Fruitland Formation gas wells. Together, such analyses can be effectively used to determine whether drilling additional optional Fruitland Formation wells has impacted water quality in shallow aquifers. As demonstrated here, the same methods could be used in any basin to evaluate the potential impact of oil and gas operations on shallow groundwater resources.

Based analyses of pre-drilling baseline and post-drilling water well samples, predominantly acquired within a year after a Fruitland well was drilled, the results of this study demonstrate that production operations have not had any detectable impact shallow groundwater resources in the Colorado portion of the San Juan Basin. Observed short and long term changes in dissolved methane concentrations are due to a combination of sampling error, environmental variability, aquifer mixing dilution, mixing of biogenic and thermogenic gas sources, and bacterially-mediated methane oxidation.

FIGURES

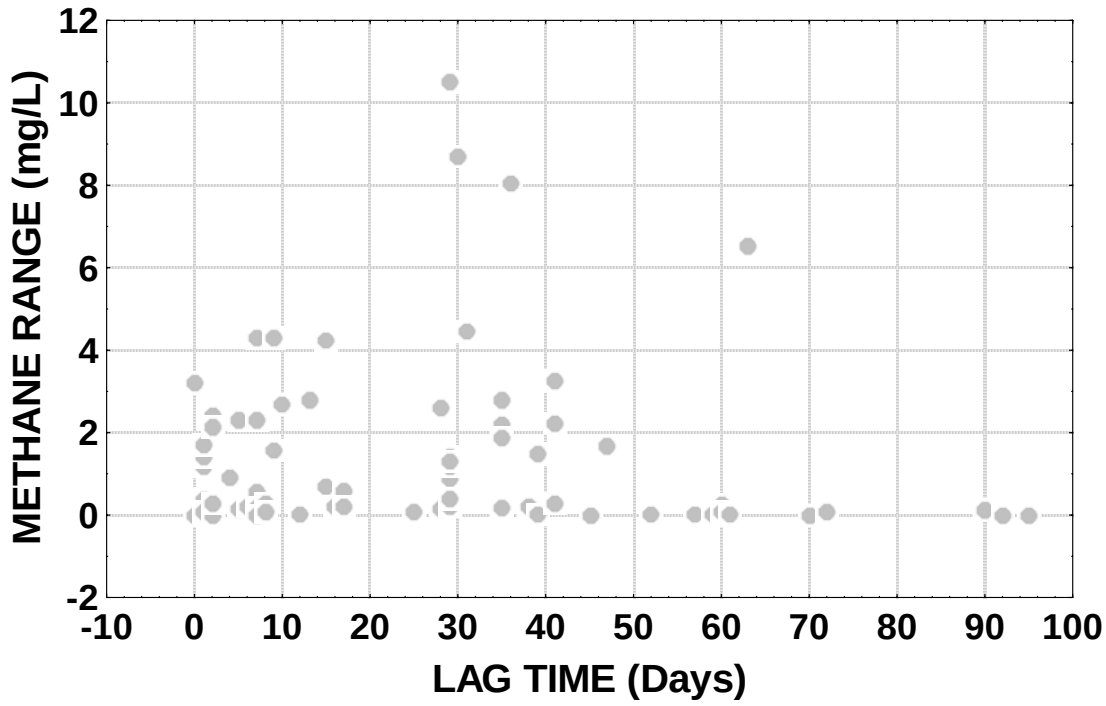

Figure 1. Difference between minimum and maximum methane concentration values in water well sites sampled multiple times within a period of 95 days. Sample pairs with consecutive non-detect values are not included.

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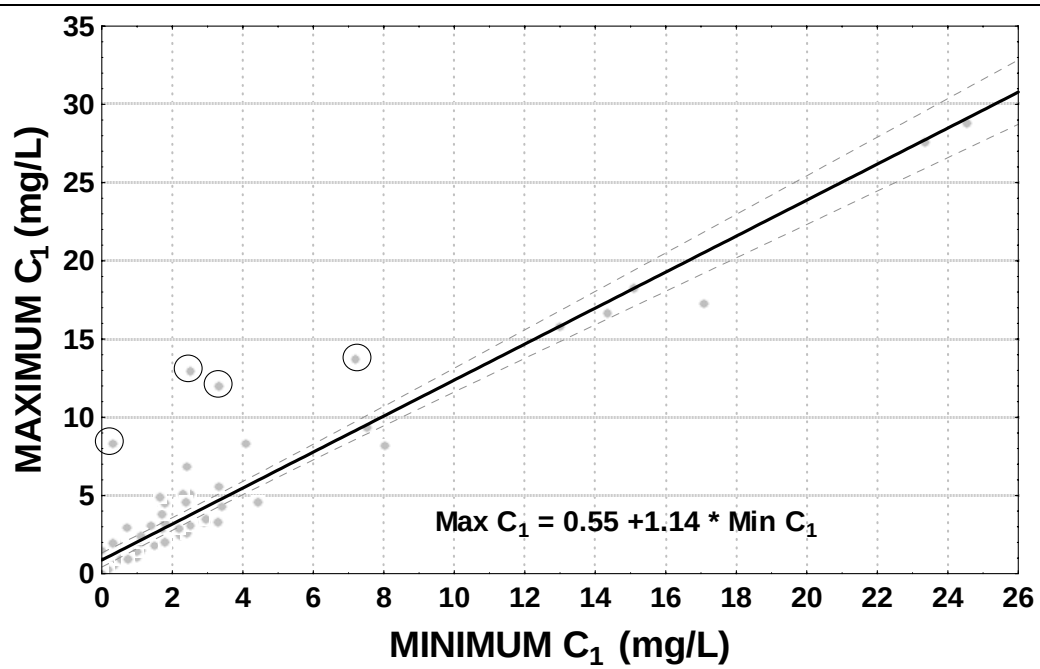

Figure 2. Regression analysis of the data shown in Figure 1 with 4 large outliers (circled) removed. The dotted line represents the 95% confidence level for the regression.

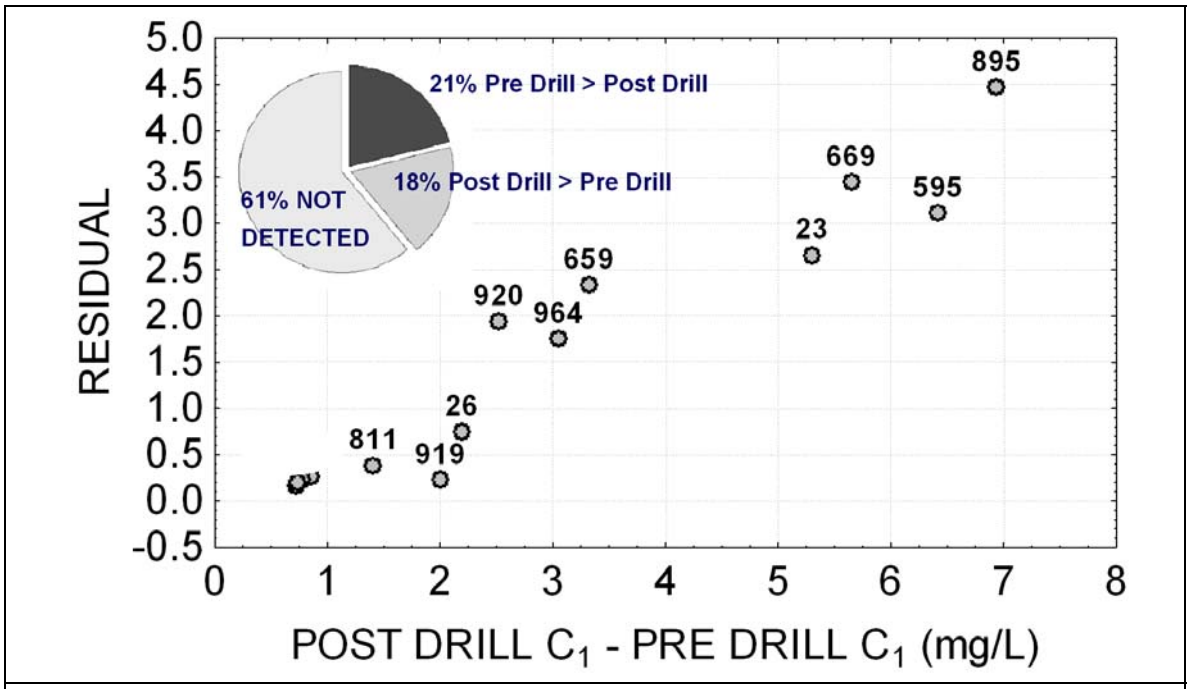

Figure 3. The difference in methane concentration between sample pairs from a single well site plotted against the residual value calculated on the basis of the regression equation in Figure 2. The residual value is the difference between the actual maximum methane concentration and the predicted value. Also shown is a pie chart showing the change in methane concentration observed among 292 sample pairs collected within an average period of 357 days.

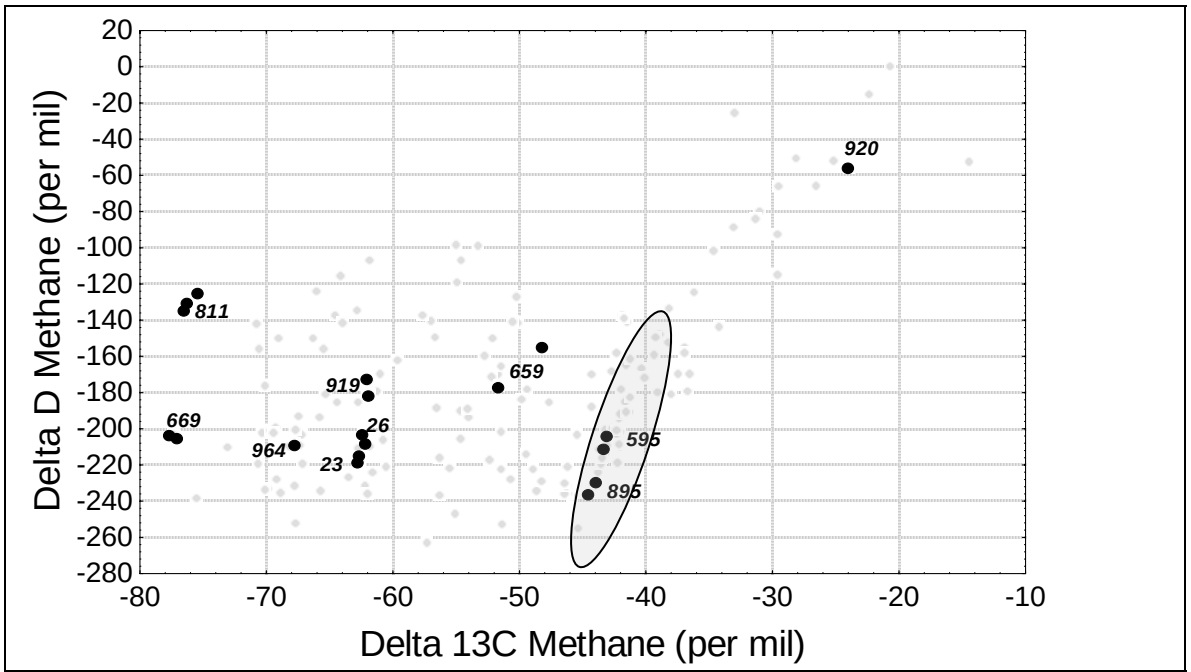

Figure 4. Stable carbon and deuterium isotope ratios for the 10 sample sites with higher post-drilling methane concentrations are highlighted within the values measured for all samples in the COGCC data base. The range in values of methane from the Fruitland Formation generally falls within the shaded ellipse.

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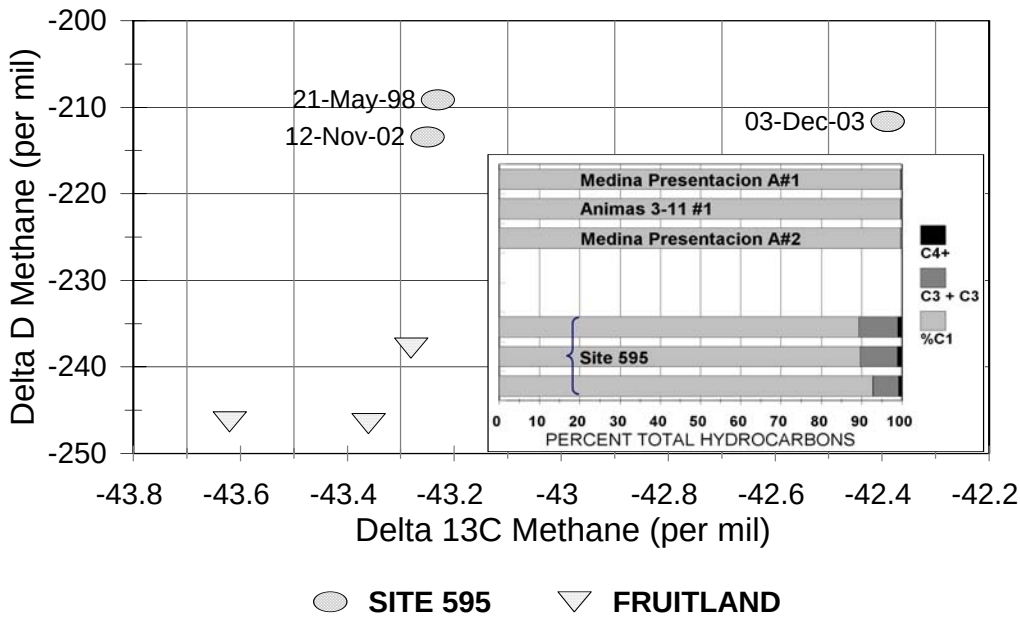

Figure 5. The dissolved gas composition (inset) and the stable isotopic composition of methane at site 595 does not correspond to that in underlying Fruitland Formation gas.

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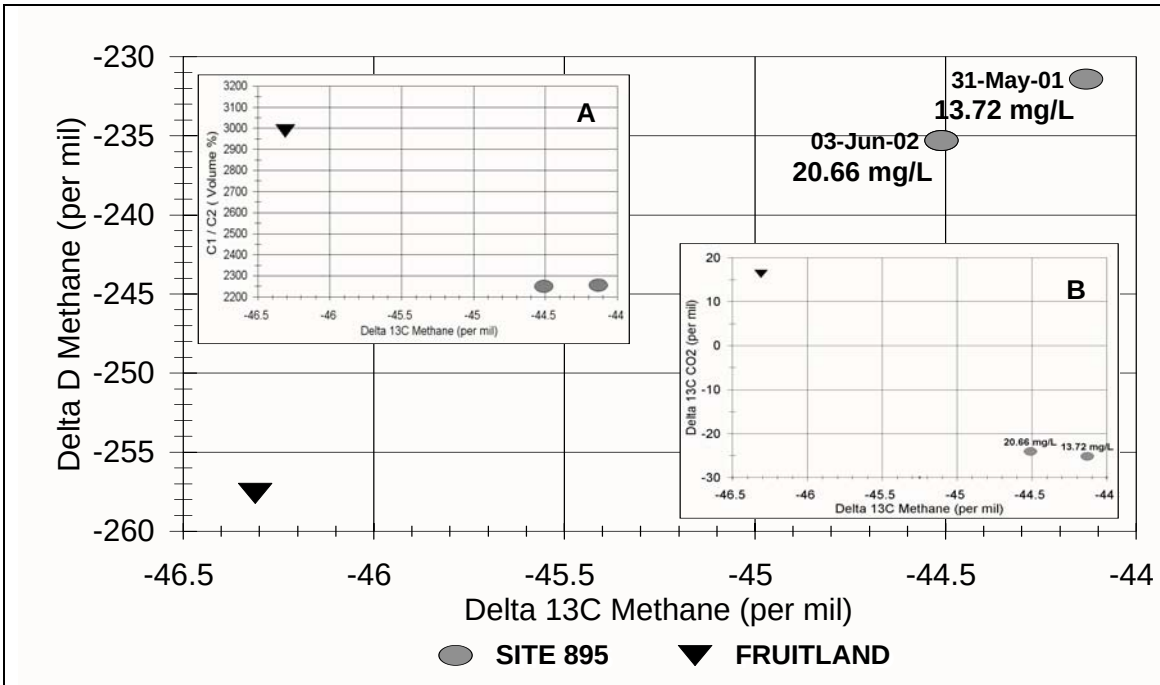

Figure 6. The dissolved gas composition (inset) and the stable isotopic composition of methane and CO_2 at site 895 does not correspond to that in underlying Fruitland Formation gas. Decreasing methane concentrations correspond with more positive (enriched) stable carbon and deuterium ratios in methane, and more negative (depleted) stable carbon isotope ratios in CO_2.

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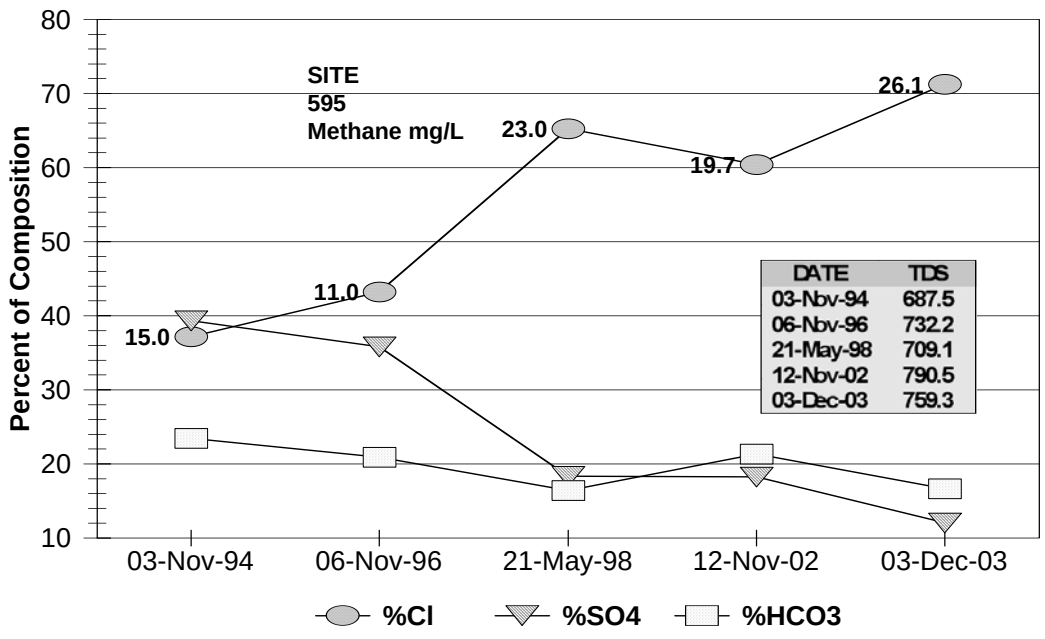

Figure 7.

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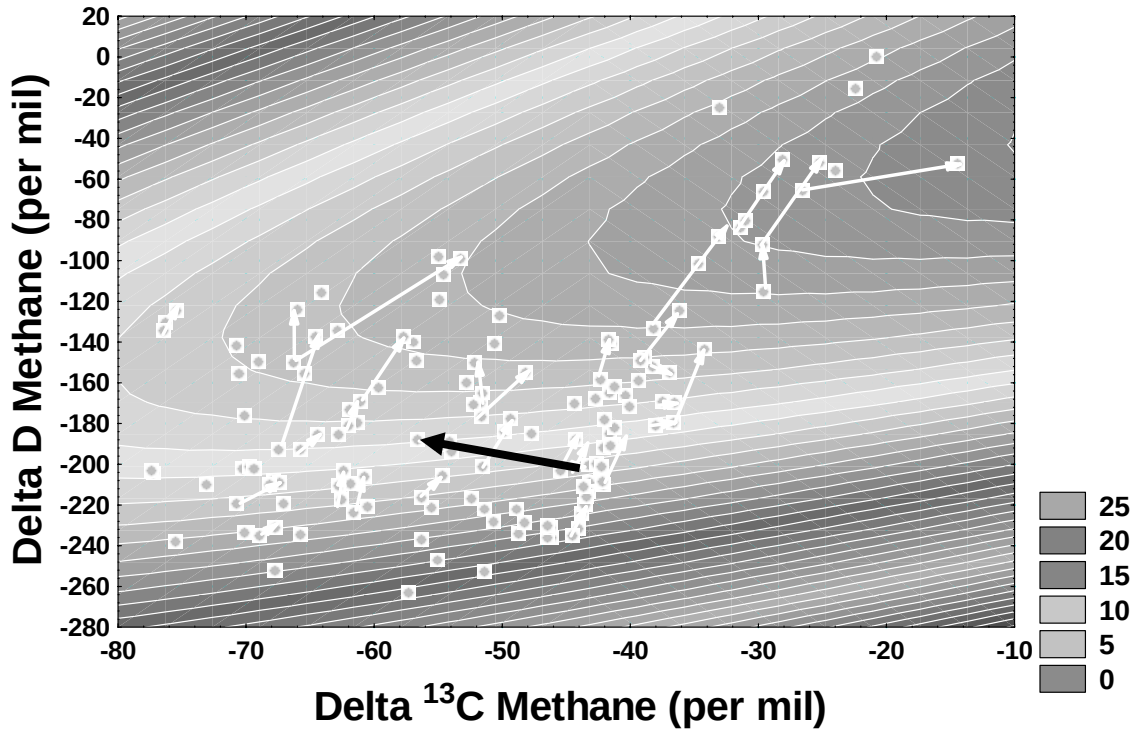

Figure 8. Quadratic surface of decreasing methane concentration. Stable isotope ratios from paired samples collected in a water well site are indicated with connecting arrows.

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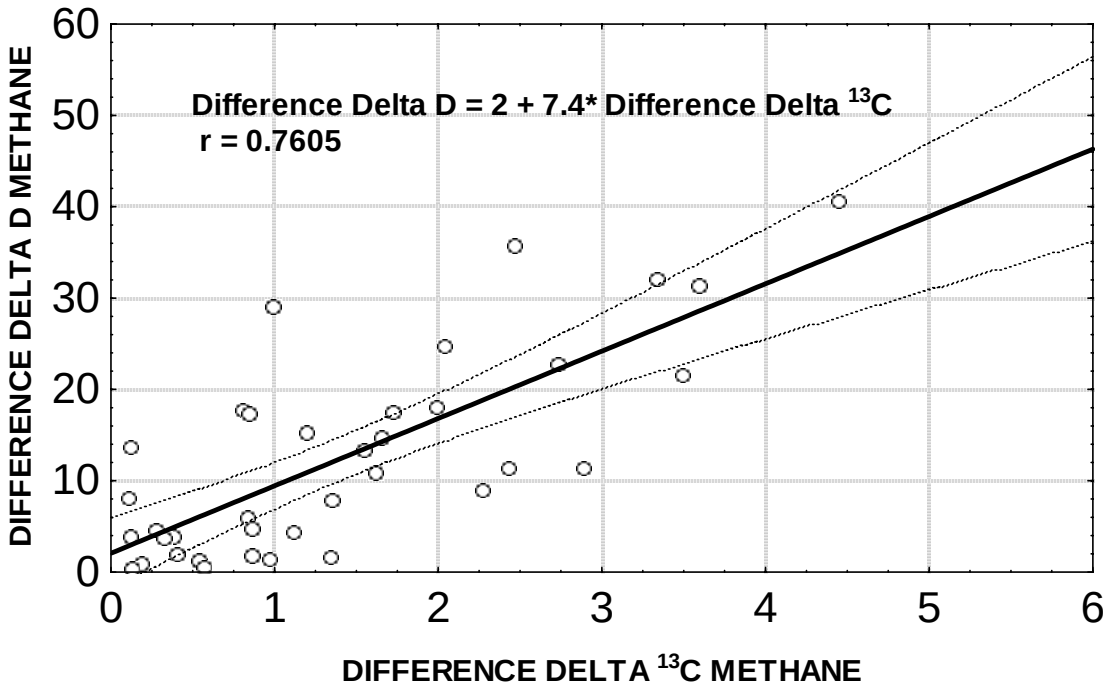

Figure 9. Regression analysis of the per mil difference in stable carbon and deuterium isotope ratios for consecutive water well sample pairs

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NITROGEN-REJECTING MEMBRANES TO INCREASE GAS HEATING VALUE AND RECOVER PIPELINE NATURAL GAS: A SIMPLE WELLHEAD PROCESS APPROACH

Ankur Jariwala,
Kaaeid A. Lokhandwala
Membrane Technology & Research, Inc.
1360 Willow Road, Menlo Park, CA 94025 USA
Tel: 650 328-2228; Fax 650 328-6580
Email- ankur @mtrinc.com,
www.mtrinc.com

ABSTRACT

The Gas Research Institute (GRI) has estimated that approximately 17% of the natural gas reserves in the United States cannot be used because of high nitrogen content. Besides naturally occurring N2, even in normal gas production processes, in many cases during well workups N2 gas is used to fracture and increase production. Significant amount of N2 –rich vent gases that cannot be piped are produced at the wellhead and need to be vented for several days. This represent an environment issue as well as a significant product loss.

At present, the only proven technology available to upgrade this gas to pipeline specification is cryogenic separation. However, cryogenic plants are complex, require numerous moving parts and have high capital and operating costs. Furthermore, these plants must process a relatively high volume of gas before they are economical, typically in the range of 50 to 500 million standard cubic feet per day. As a result, smaller gas fields cannot be economically treated.

Membrane Technology and Research, Inc. (MTR) has developed a membrane-based separation process to remove excess nitrogen from natural gas. The process is particularly suitable for small fields, with production rates up to 10 to 15 million standard cubic feet per day. The MTR process is also skid-mounted and movable from one location to another. This makes this process very suitable for well head processing of gas produced during venting after a well work-up.

This paper describes the membranes and processes used, provide data from tests, and discuss commercial installations as case studies.

NITROGEN-REJECTING MEMBRANES TO INCREASE GAS HEATING VALUE AND RECOVER PIPELINE NATURAL GAS: A SIMPLE WELLHEAD PROCESS APPROACH

A recent Gas Research Institute study showed that about 17% of known U.S. natural gas reserves are sub-quality due to high nitrogen content (1). Naturally-occurring nitrogen is the most common cause of high nitrogen content in natural gas, but in addition, nitrogen content can increase to unacceptable levels even in normal gas production processes. For example, in many cases during well work-ups, nitrogen gas is used to fracture and increase production. Significant amounts of nitrogen-rich vent gases that cannot be piped are produced at the wellhead and need to be vented for several days until the gas quality is at a level which can be used. This represents an environmental issue as well as significant product loss. The transient nature of the high nitrogen content gas released during well work-ups is very well suited to membrane processing. In this application for example, feed gas nitrogen content can be as high as 50 mole% at the start of the work-up and will decline to 6-10 mole % in the due course of time. Figure 1 represents the typical nitrogen content and flow rate in a high rate nitrogen- rich foam fractured horizontal well.

Until recently, the only technology available to upgrade nitrogen-rich natural gas to pipeline specification has been cryogenic technology. However, cryogenic plants are complex, require numerous moving parts and have high capital and operating costs. Furthermore, these plants must process a relatively high volume of gas before they can be run economically, typically in the range of 50 to 500 million standard cubic feet per day. Also cryogenic plants are designed very specifically for fixed inlet gas composition and cannot be used when the inlet conditions vary widely over a short period of time.

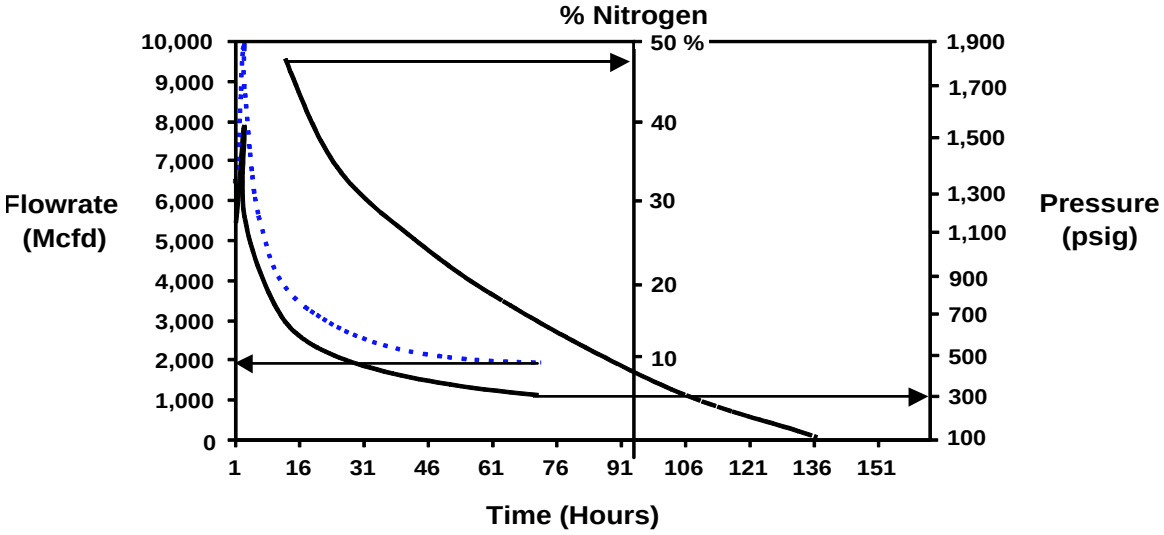

Figure 1. Nitrogen content and blow down flow rate in high rate nitrogen rich foam fractured horizontal well.

In the mid-1980s, membrane systems for the removal of carbon dioxide from gas were first introduced to the natural gas processing industry. These membranes separate gases primarily by virtue of molecular size, and permeate carbon dioxide 10-15 times faster than methane. Unfortunately, the difference in size between methane and nitrogen is very small (kinetic diameter CH_4 = 3.8A^0; N_2 = 3.64 A^0), so size-selective membranes were not able to achieve economically useful separations. About five years ago, MTR developed membranes that perform separations by virtue of differences in the solubility of the two gases in the membrane. Methane, being more condensable than nitrogen, is about seven-fold more soluble in certain polymers. This difference in solubility has been used to produce membranes that are three- to fourfold more permeable to methane than nitrogen.

Selection of Membrane Materials [2]

The ability of a membrane to permeate gases is measured by its permeability, *P*, defined as the rate that a gas permeates a membrane (cm^3(STP)cm^2.s) of standard thickness (1 cm) under a standard driving force (a pressure differential of 1 cmHg). Permeability of gases is most commonly measured in Barrer, defined as 10^{-10} cm^3 (STP)cm/cm^2.s.cmHg and named after R.M. Barrer, a pioneer in gas permeability measurements.

The membranes used industrially to separate gases are dense polymeric films that contain no pores. The permeating gas molecules dissolve in the polymer film as in a liquid and then defuse through the membrane down a gradient in concentration created by the pressure difference across the membrane. Gas permeabilities, *P*, can be expressed as the product of two terms

$$P = D_i K_i \qquad (1)$$

The diffusion coefficient, D_i, reflects the mobility of the individual molecules in the membrane material; the gas sorption coefficient, K_i, reflects the number of molecules dissolved in the material.

The most basic factor determining the ability of a membrane to separate two gases, *i* and *j*, can be expressed as the ratio of the gas permeabilities, α_{ij}, called the membrane selectivity

$$\alpha_{ij} = [D_i/D_j][K_i/K_J] \qquad (2)$$

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio K_i/K_j is the ratio of the sorption coefficients of the two gases and can be viewed as the sorption or solubility selectivity, reflecting the relative condensabilities of the two gases.

In all polymer materials, the diffusion coefficient of a gas decreases with increasing molecular size, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity always favors the passage of small molecules over large ones. Another important factor affecting overall membrane selectivity is the sorption or solubility selectivity. The sorption coefficient of gases and vapors, which is a measure of the energy required for the permeant to be sorbed by the polymer, increases with increasing condensability of the permeant. This dependence on condensability means that the sorption coefficient also increases with molecular diameter because large molecules are normally more condensable than smaller ones.

In the case of high-nitrogen-content natural gas, nitrogen is smaller but less condensable than methane, so membranes can be made that preferentially permeate *nitrogen* by relying on the mobility selectivity term or that preferentially permeate *methane* by relying on the solubility selectivity term.

In our work, we have chosen to use hydrophobic rubbery polymers with small diffusion selectivity terms and solubility selectivity terms close to the theoretical maximum of 6 to 7. Under these conditions, we obtained membranes with a selectivity of three to four. Some data obtained in the laboratory and then at a pilot plant installed at a Butcher Energy gas field in Ohio are shown in Figure 2. Membrane selectivity increases somewhat at lower temperatures because of changes in the relative solubility of methane and nitrogen.

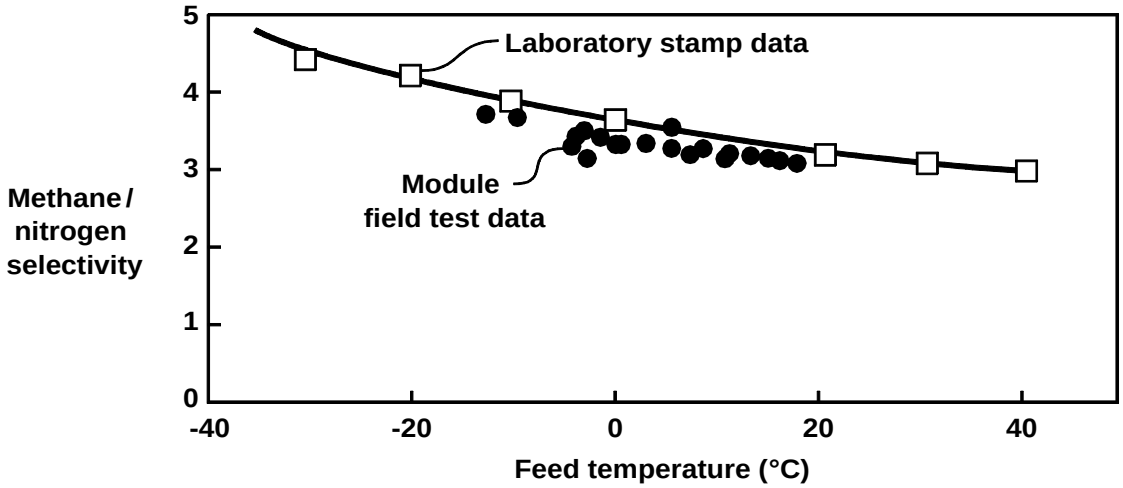

Figure 2. Methane/nitrogen selectivity as a function of gas temperature in laboratory membrane stamp tests and module tests performed over a six-month period at Butcher Energy's Ohio gas field.

Membrane and Module Preparation

For a variety of reasons, membranes used to separate nitrogen from natural gas typically require the use of composite membrane structures. First of all, the optimum materials for methane-permeable membranes are made of rubbery polymers that are not mechanically strong. Furthermore, to obtain high permeation rates, the selective membrane must be very thin, typically between 0.5 and 5.0 µm thick. Finally, the membrane must be able to comfortably support a pressure differential of 500 to 1,500 psi. These contradictory needs are met by forming multilayer, composite membranes of the type shown in Figure 2. The nonwoven polyester paper provides the mechanical strength required. The surface of this material is too coarse and porous to be directly coated with the ultra thin selective layer, so the paper is first coated with a microporous polymer layer. The surface of this microporous layer has pores 0.01 to 0.1 µm in diameter, so these pores are easily bridged when they are coated with the thin selective layer.

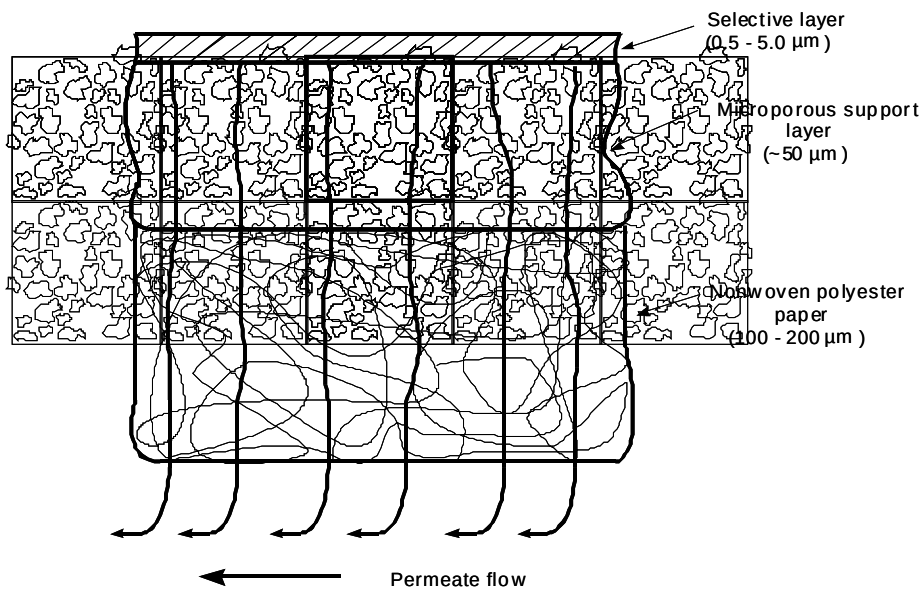

Figure 3. Schematic diagram of a multilayer composite membrane (not to scale).

Even though membranes of the type shown in Figure 3 have extremely thin selective layers, many square meters of membrane are required to separate a useful amount of gas. he units into which large areas of membrane are packaged are called membrane modules In this nitrogen separation process, we chose to use spiral-wound membrane modules of the type illustrated in the exploded view shown in Figure 4.

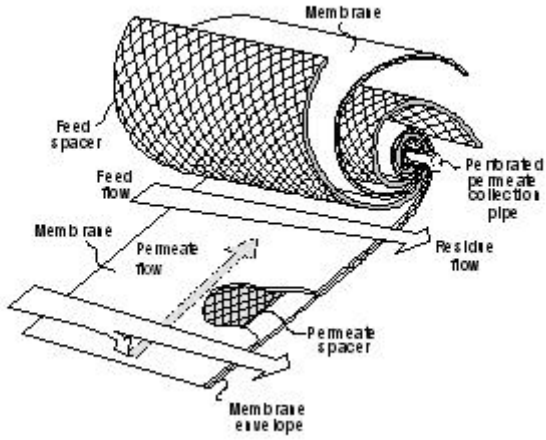

Figure 4. Exploded view of a spiral-wound membrane module. The wound module is contained in a tubular pressure vessel. High pressure, nitrogen-contaminated gas passes across the membrane surface. Methane and other hydrocarbons preferentially permeate the membrane, producing a nitrogen-depleted permeate. The residue gas is enriched in nitrogen.

Spiral wound modules are manufactured on an industrial scale and are standardized in sizes at 8" and 12" diameter modules. A complete separation plant may use from 10 to several hundred modules, depending on the size of the gas stream to be treated.

Process Design

The complexity and cost of the membrane process increases with the nitrogen content of the gas, especially if the product gas contains low mol% nitrogen. If the gas contains less than 6 mol% nitrogen , a single bank of modules can be used to produce the separation required. A typical process is shown in Figure 5(a). Pressurized feed gas passes across the surface of the membrane: the permeate, depleted in nitrogen, is re-pressurized while the residue is used as fuel. The process achieves higher than 90% methane recovery in the product gas and even higher Btu recovery since the membrane permeates essentially all of the ethane, propane and higher hydrocarbons from the residue gas. The product gas consists of nitrogen, methane and very little else.

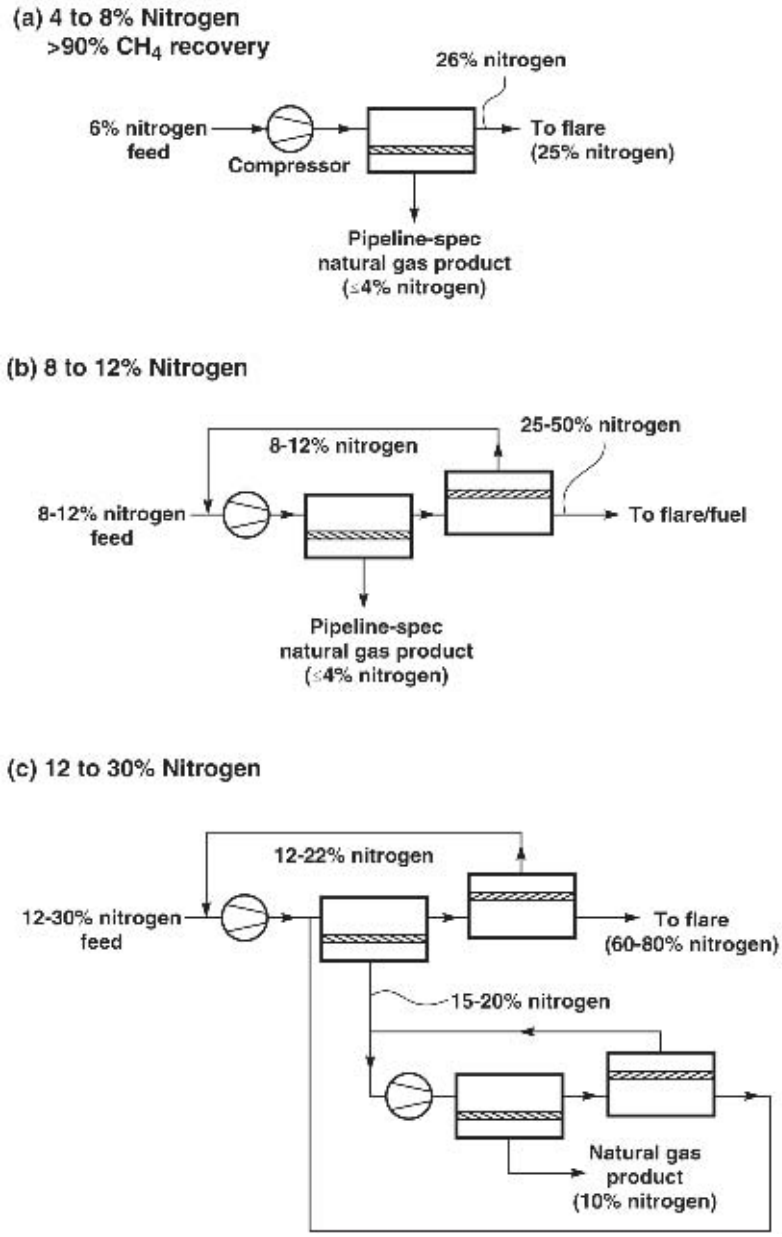

Figure 5. Membrane-based process designs for nitrogen removal from natural gas streams of varying nitrogen content.

MTR's first proof-of-concept system was designed to treat this type of gas. The gas was being used to power a fuel cell, but contained up to 6% nitrogen. High nitrogen was a problem because it produced small amounts of ammonia in the fuel cell reformer, which then degraded the fuel cell electrolyte. The customer purchased the membrane unit to reduce the nitrogen concentration to 3% in the permeate. The high- nitrogen residue gas was used as boiler fuel. This simple system has been in operation for two years and has demonstrated the overall reliability of the membranes. A photograph of the system at the fabricator's shop is shown in Figure 6.

Figure 6. Photograph of nitrogen removal membrane system that reduces nitrogen content of a fuel cell line stream from 6 mole% to 3 mole%.

If the natural gas stream being treated contains more than about 8% nitrogen, it is no longer possible (with today's membranes) to produce gas with ≤4% nitrogen and good hydrocarbon recovery in the product gas in a single-stage membrane process. For feed gas containing 8-12% nitrogen, the type of design shown in Figure 5(b) would be used. As in the Figure 5(a) design, the gas is passed across the first set of membrane modules to produce a permeate product gas containing ≤4% nitrogen. The nitrogen-rich residue then passes to a second set of modules, which produces a residue gas containing 25-50% nitrogen and a nitrogen-depleted permeate gas containing 6-10% nitrogen. The permeate gas contains too much nitrogen to be mixed with the product gas, so it is recycled and mixed with the incoming feed gas. A residue stream containing 25-50% nitrogen gas can be used as compressor fuel. As for the previous lower nitrogen content approach the process for treating 8-12% nitrogen streams achieves about 90% methane recovery in the product gas and typically close to 93-94% Btu recovery because of preferential permeation of the higher hydrocarbons.

Gas containing 12-30% nitrogen would be treated by a process of the type shown in Figure 5(c). The nitrogen content of the feed gas is too high for gas with ≤4% nitrogen to be produced in a single membrane unit, so two membrane separation units stages are linked. The first unit produces a residue stream containing 60-80% nitrogen to be flared and a low-pressure gas stream containing 12-22% nitrogen. This low-pressure stream is fed to a second membrane unit, which produces gas with ≤10% nitrogen content that can be blended with appropriate pipeline-quality natural gas to achieve the specified nitrogen content for an overall pipeline product gas. A residue gas from the second membrane unit (typically containing about 20% nitrogen) is recirculated to the first membrane process. Compressor fuel gas is obtained by fractionating a portion of the residue gas.

If the gas contains more than 30% nitrogen, processing with membranes to produce pipeline quality gas is usually not economically feasible. However, using the membrane process to fractionate a high nitrogen gas into a 10-20% nitrogen fuel gas and a 70-80% nitrogen gas to be flared or re-injected should be considered.

Economic Evaluation of the Membrane for Processing Nitrogen-Rich Blow Gas Produced in Nitrogen Foam Fracturing

Two cases have been considered: 1) for a high-volume horizontal well and 2) for a vertical well.

Nitrogen foam fracturing generates wellhead gas with nitrogen content varying over time from as high as 54 mol% to as low as 5-12 mol%. Our economic evaluation is based on transient-state nitrogen content. The reason to evaluate the economics on a transient basis is because as nitrogen content falls, the overall MMBtu recovery level increases and therefore net revenue also increases.

Right after fracturing and holding the well with nitrogen foam, the well pressure is reduced. The initial gas is predominantly nitrogen and over time, as the well is blown down, methane content starts to increase. Up to 3-8 days of blowdown are required to reduce the nitrogen content to levels where the gas can be piped for sale. This represents a transient condition on the wellhead with respect to nitrogen content, flow and pressure. During this period, however, a large amount of natural gas is also lost with the nitrogen. If the natural gas in the stream could be recovered effectively, it would be efficient not only for its economic value but the emission of the greenhouse gases would also be reduced. To date, no easy solutions have been available for processing this transient stream to provide pipeline-quality gas. However, with the recent availability of nitrogen separation membrane technology, this application is now feasible. Not only are membranes good in delivering suitable product under transient conditions of changing nitrogen content and so forth, but membrane systems are compact and lightweight. They can be mounted on flat bed trailers to produce the mobility required to bring the technology to any wellhead that can be reached by truck. Furthermore, this mobility means that membrane units can be moved from site to site to cover a broad area of wells that are being fractured sequentially.

The performance, capital and operating costs of the membrane systems illustrated in Figure 5(b) & (c) are shown in Table 3. The economic analysis of these membrane systems show simple payback times of less than a year at the current natural gas price of US $ 8.00 per MMBtu. MTR's nitrogen removal membrane systems require only a simple filter coalescer upstream to remove aerosols and particulates, which significantly reduces the pretreatment capital and operating expenditure required, when compared to other technologies. Typical membrane cartridge life is from 3-5 years of continuous operation.

The economics are obviously more attractive with US$8 per MMBtu natural gas prices, reducing the payback time to 9 months from 18 months for US$4 per MMBtu.

Table 3. Performance, Capital, and Operating Cost of Membrane Systems With Horizontal and Vertical Well Nitrogen Removal Membranes.

	Vertical Well High-Nitrogen Blowdown Processing	**Horizontal Well High-Nitrogen Blowdown Processing**
System Characteristics		
Feed Gas (MMSCFD)	0.5	3.5
Inlet Nitrogen Feed Gas (mole%)	15-8	31-12
Product Gas Nitrogen Content(mole%)	<4	<10
System Design Pressure(psig)	310	500
Capital Cost ($ thousand)		
Membrane System Price(Including Membrane Cartridges, Pressure vessels, Inlet Filter Coalescer, skid frame, Flat bed trailer) (US $)	350	650
Total Capital Cost	350	650
Operating Cost(per year)		
Compression Leasing, 20% of Total compression (310 psig @ US $ 600/hp & 500 psig @ US $ 900/hp)	35	220
Labor and Maintenance at 10% of Capital Cost	35	65
Capital and Depreciation at 20% of Capital Cost	70	130
Annualized Membrane Replacement Cost(@3-5 year life)	25	100
Total Operating Cost	165	515
Net Revenue @ $ 8/MMBTU	600	3550
Simple Payback Period	9 months	6 months
Net Revenue @ $ 4/MMBTU	300	1775
Simple Payback Period	18 months	13 months

Field Experience

MTR, together with ABB-Randall Gas Technologies, have been developing the process described in this article for the past four years. The first pilot-scale module test system was operated at a Butcher Energy high-nitrogen gas field for almost six months in 2000-2001. Later, a commercial proof-of-concept system was installed to fractionate a small gas stream containing up to 6% nitrogen into 3% nitrogen gas to be used in a fuel cell, and high-nitrogen residue gas to be used as boiler fuel. This unit has been operating without attention in a virtually maintenance-free mode for the past three years. In April 2004, the first full-scale demonstration system using the technology was installed at a North Texas Exploration well in North Texas. A photograph of the membrane skid during installation is shown in Figure 8.

Figure 8. Photograph of the first full-scale commercial system under installation for North Texas Exploration in 2004.

Conclusion

MTR has completed development, testing and demonstration of new membranes for nitrogen/methane separation. Commercial installations are now in place producing pipeline-quality gas for clients. MTR has been offering these systems for commercial installations with full guarantees and warranties since 2003.

Due to the specific requirements of the applications discussed in this paper, MTR believes our solution fulfills the various needs of producers for wellhead nitrogen/methane separation, including mobile units, transient feed gas conditions, simplicity of design and automatic unmanned operation. MTR's membrane process provides not only significant

economic benefits of recovering natural gas, but also greatly reduces on-site methane emissions to the air. This provides a win-win solution for the gas producer and for the environment.

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State Electronic Commerce Initiatives: Produce More Oil and Gas and Increase Environmental Protection.

Paul Jehn, The Ground Water Protection Council, Stan Belieu Nebraska Oil and Gas Conservation Commission, Mark Bohrer North Dakota Industrial Commission, and Tom Richmond Montana Board of Oil and Gas Conservation.

Abstract

Electronic Commerce (electronic reporting, permitting and data mining) has become a necessity rather than a luxury for regulators and the regulated community in the oil and gas industry. The Ground Water Protection Council (GWPC), State Oil and Gas Agency's, BLM, POSC and Industry have developed an XML schema needed for data sharing. To ensure seamless data sharing, each state will use the same XML schema for reporting and permitting. Entities which need a common XML schema to exchange data include: U.S. DOE, U.S. EPA, U.S. BLM, U.S. MMS, State Oil and Gas Agencies, oil and gas operators and explorations companies.

The identified goals of the electronic commerce initiative include: seamless data sharing, reducing the time it takes to issue permits, simplifying reporting requirements and make the environmental and technical data currently contained in disparate state and federal databases available to industry. The cost savings to industry with these activities help to increase production and increase environmental compliance by make information readily available to decision makers. Delays in coordinating permit approvals between federal and state agencies translate into increased operational costs and stresses for the oil and gas industry. Making federal lease stipulation and area restriction data available on state agency Web sites will streamline a potential lessors review of available leases, encourage more active bidding on unleased federal lands, and give third-party operators independent access to data who otherwise may not have access to lease restrictions and other environmental data.

In this project, GWPC and states are developing several ways to submit permits or electronic reports. Operators will be able to use the national XML schema for batch submittals or logon to agency web site, and enter an identification or API number. A Web-Form application will then populate the form with most recent data. The operator either completes form or downloads to computer to complete and submit electronically at a later date. Significant progress has been made in the electronic commerce initiative. Electronic data mining is operational in Alaska, North Dakota, Montana, Utah, New Mexico, Colorado, Kentucky, Nebraska and other states. Electronic reporting of production data using the national XML schema is now available in Utah, Nebraska, Montana, New York and Pennsylvania. Electronic permitting is being tested in California and will soon be available in Alaska, Kentucky and Alabama.

BACKGROUND

Before an oil and gas operator can drill a well on virtually any land within the continental US, including navigable waters and contiguous three-mile offshore areas, permission must be obtained from the appropriate state oil and gas regulatory agency. State permission is required on private, state, and federal lands, and, except for tribally operated wells on Indian lands and the Osage Mineral Reserve in Oklahoma, state permission is also required for wells drilled on Indian lands. On federal and Indian land, there is overlapping state and federal jurisdiction.

In most states, when drilling on federal and Indian lands, operators must submit separate applications to both the BLM and to the state oil and gas regulatory agency. While the application and supporting materials submitted by the operator to the state is similar to the application package submitted to the BLM, there are differences, and these differences vary from state to state, as each state has its own regulations and set of application forms.

With the advent of the Internet and electronic commerce, both the BLM and states realize the benefits of allowing operators to submit drilling applications and subsequent reports of drilling and completion operations electronically. The BLM and several states have already commenced the development and implementation of such e-permitting systems.

To further the acceptance of, and to reduce both governmental and private costs of electronic permitting, both the BLM and the states recognize the need to develop uniform data transfer standards. A common data transfer schema will greatly simplify electronic filing for operators who must submit applications to both the BLM and states agencies, and for operators who apply for well permits in multiple states. A common data transfer schema will also facilitate sharing of well data between state and federal agencies, and enable the states and the federal government to more easily share software designed to process and report on well application and completion data.

The task at hand is to define and reach agreement between industry and regulators on a comprehensive common set of data elements to be used for the electronic transfer of application, drilling, and completion data. The comprehensive set of data elements will include all data elements used in common and most unique data elements used by the BLM and state agencies. The plan will also allow for the transfer of exceptional data elements that are not included in the common set.

Ideally, industry and state and federal agencies would design their computer databases around the set of common standardized data elements. In actuality, the BLM, other federal agencies, most state agencies, and many oil and gas operators have made significant investments in developing existing computer systems and databases. While a great deal of comparable data is warehoused in these systems, identical information in each system may be referred to by different data element names and stored using different data types. Therefore, in addition to developing a common set of standard data elements for the data transfer schema, work must also be performed mapping the existing state, federal, and industry databases to the common data transfer schema.

While translating and mapping the various state, federal, and industry databases to the standard schema is a significant effort, each database needs to be only mapped once. Without a common well-data transfer schema, each database would need to be individually mapped to each disparate computer system with which it must communicate. If an operator drills in multiple states and has wells on federal land, the operator must report and map to multiple dissimilar

systems. With the standard data transfer schema under development, the operator would map once to the schema.

DISCUSSION

Representives of the oil and gas industry and the state and federal agencies have advocated the use of information technologies to create solutions. Since June of 2003, a work group representing state agencies, GWPC, BLM, MMS, POSC, and the American Petroleum Institute (API) (representing industry), has been actively advocating the overall development of a national e-commerce initiative. This group has already embraced a collaborative approach to e-permitting. The result of this group effort was the development of a working business case (http://12.173.158.190/Downloads/GWPC/business case epermit_feb04.pdf).

As stated in the business case, "There is a growing recognition among agencies and industry that the development of uniform data transfer procedures, reusable computing resources, and supporting standards can accelerate the acceptance and reduce the cost of moving to electronic permitting."

Thus, the associated business case sets out the tasks to accomplish this vision. These tasks involve defining and agreeing on a comprehensive and common set of data elements and definitions related to the electronic transfer of permitting, drilling, and completion data. These elements and definitions will include data used by the BLM and state agencies, from the common ones to those unique to a single agency. Based on the principle of maximizing consistency while respecting necessary differences, the proposed solution will allow for the transfer of exceptional data elements not defined in the common set. Moreover, where possible, the proposed solution will employ data definitions and transfer messages currently being standardized by industry for operational purposes. A common approach to permitting data transfers will greatly simplify electronic filing for operators who must submit applications to both the BLM and the states as well as for operators who apply for permits in multiple states. A common approach to permitting data transfers will also facilitate sharing of associated well technical data between state and federal agencies. This will enable the state and federal governments to more easily share solution software designed to process and report on drilling application and completion data[1].

Industry has indicated that they would like states and BLM/MMS to develop a system where they can transfer a batch submittal of permits to the regulatory agency for approval. Under the current proposal, industry would map their data elements to the RBDMS e-business XML schema which would then parser the data to the appropriate state and/or federal regulatory agency. Permit applications which do not meet the minimum data requirements would be rejected by the parser and returned to the applicant. Some states have indicated that for permits like a routine re-work, permit approval could be automated. Figure 1 represents an idealized data flow diagram for bulk permitting.

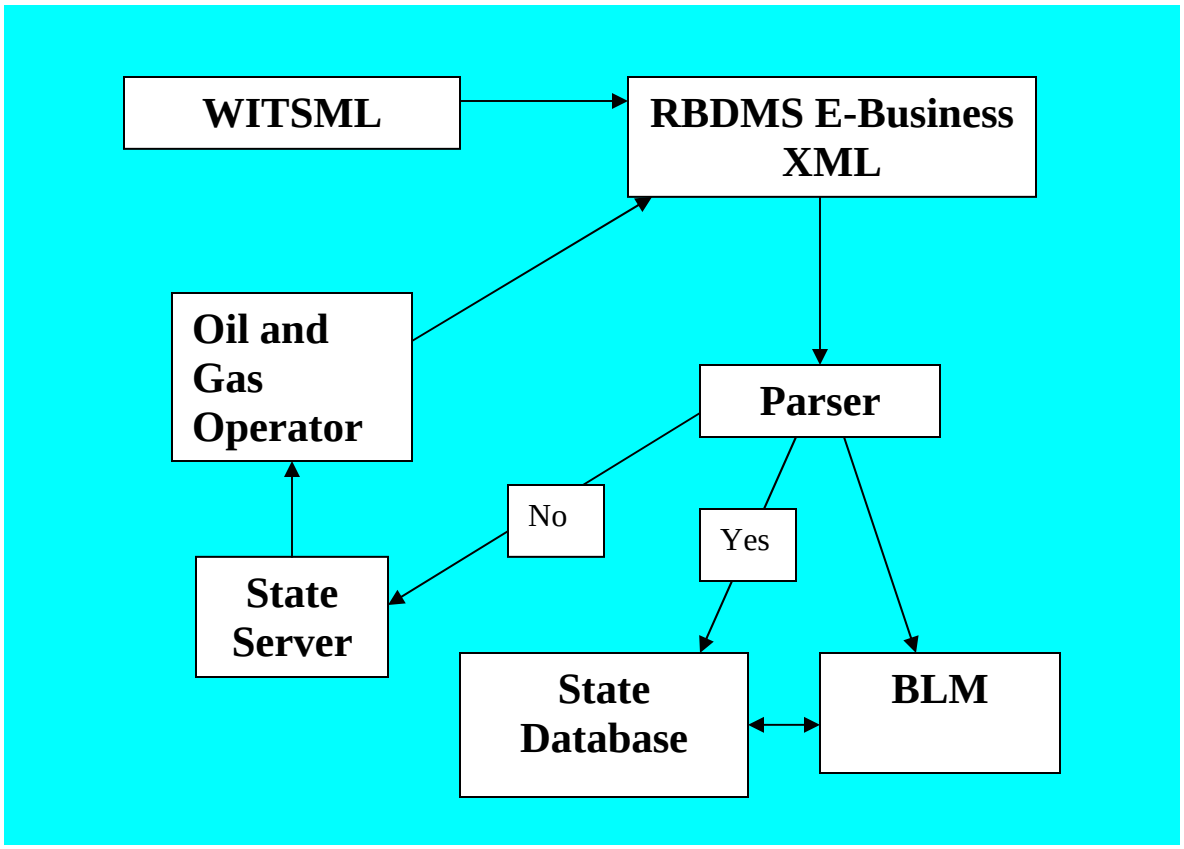

Figure 1 Generalized eCommerce Data Flow Model for bulk transfer of permit applications

An XML schema that conforms to the regulatory oversight process over the complete lifecycle of oil and gas wells is currently under development and is being tested in California. This schema will serve as a baseline for future applications that will open the way for streamlining any dual-permitting requirements, provide for bulk data transfer, and facilitate data exchange between government and industry.

Since 2002, major oil and gas industry service companies, such as BJ Hughes, Dowell Schlumberger, and Halliburton, have established industry-standard XML formats for well service activities for their oil and gas company clients. These schemas are used to transfer well information gathered on-site and with trading partners. These XML data exchange standards are supporting real-time drilling activities both on and off shore and are now being applied by the well service industry for well operations in major basins onshore. This body of work is known as the POSC WITSML, and GWPC will leverage this standard during this initiative through its interagency technical advisory committee (TAC) representatives.

The California Department of Conservation has stepped forward to pilot test the batch submittal of XML files needed for electronic permitting. In this initial project, a draft XML schema covering the permitting and sundry notices of intent for well workovers will be developed. This sub-set of XML schema is referred to as e-permit.

Representatives of POSC have presented to the developers of the RBDMS/CalWims project a draft schema that has been mapped to the necessary data elements within both the

California Department of Conservation and California BLM information systems. The XML schema referred to as e-permit was then mapped to Alaska's RBDMS database. The results of this effort demonstrate e-permit's compatibility with the Alaskan RBDMS database. Because of similarities of RBDMS systems throughout the country, individual modifications should be negligible.

This XML schema will allow operators to simultaneously submit electronic applications and reports to both state and federal agencies. To expand the XML schema for the entire well lifecycle, GWPC's contractor will conduct a schema literature review of existing schemas that may have relevance and applicability to this task.

The workgroup members have indicated that much of this existing work was developed for industry's use with other trading partners, not for regulatory purposes. Coordination with key personnel responsible for these individual bodies of work will be of critical importance, (1) to understand the primary drivers, (2) to identify potential leveraging points from these existing works to the development of a regulatory process schema, and (3) to prioritize the use of established tag names for the data fields.

XML data elements from the body of existing work that are suitable for re-use in the regulatory schema will be identified. This data will then be placed in a searchable database in which crawler data contents will be searchable by schema name, tag name, description, and data type. Existing element names in the Petroleum Industry Data Dictionary (PIDD) may be used, and work resulting from the use of the tag crawler will be offered to the PIDD maintenance staff.

From the literature review, GWPC will identify where the gaps are in the well lifecycle XML tags for state agency permitting needs. The team will then evaluate a suitable architecture for the well lifecycle schema. A hierarchical data structure for data elements in a permitting schema will then be drafted for TAC review.

GWPC will incorporate comments from the first review and develop draft tag definitions and attributes for the schema. A draft technical documentation and schema use guideline will then be prepared for broader review among the interested parties. At this point, a review of all state and federal oil and gas regulatory bodies will be conducted. GWPC will then incorporate changes from the plenary review. The schema and all documentation will be finalized for fatal flaw review and release. Additional briefings and technical presentations will be made to ensure the participation of existing stakeholders, other federal and state agencies, standards bodies, and industry associations.

ENVIRONMENTAL DATA

Many state oil and gas regulatory agencies also have primacy from the Environmental Protection Agency (EPA) for the Class II Underground Injection Control (UIC) Program.

GWPC proposes to create XML schema definitions for EPA's Form 7520, UIC measures reporting, and Class II well geospatial data. The information provided will originate from the data now stored in RBDMS.

The geospatial data that the GWPC and its partnering agencies envision providing to the Central Data eXchange (CDX) includes latitude and longitude for Class II wells. EPA and state agencies can then overlay this data on the source water protection area polygons collected to determine environmentally sensitive areas. Furthermore, as a part of this project effort,

GWPC and its partnering agencies propose to add a new national network node on the Exchange Network.

Once the GWPC node is installed and the transfer standards are in place for the UIC measures data, the partnering agencies propose to implement the UIC data flow on the Exchange Network to provide UIC and related spatial data to the EPA's CDX. Work in this later phase will include demonstrating the value of the Exchange Network and the UIC data flow between agencies in the form of ongoing technology transfer and education outreach through the GWPC's nationwide membership body.

RBDMS On-Line

GWPC member states have recognized the need to fully extend electronic data exchange. RBDMS needs to upgrade to an N-tier database technology. By using .net software, GWPC, and state agencies have the necessary software development tools to build electronic business applications that will optimize existing state data sources such as MS SQL server and deliver this data via the internet using XML Web services. **Fig 2**

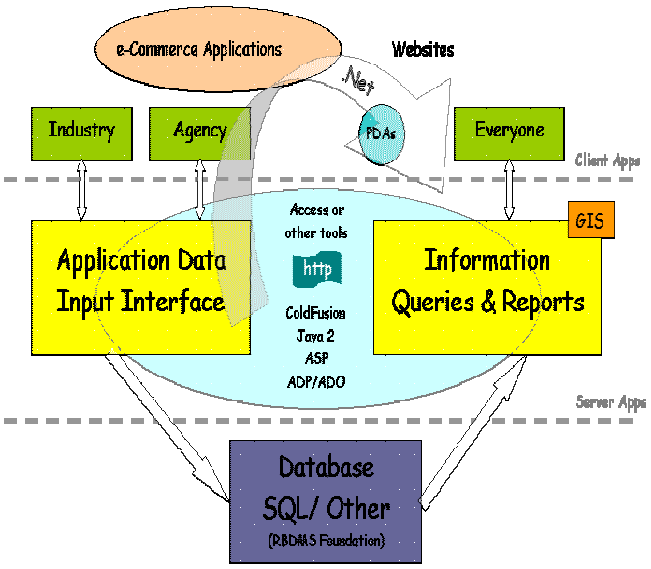

Fig 2 Flowchart showing N-tier database

This project is essential to simplify the e-commerce needs of the oil and gas industry. These needs include: automated regulatory reporting, permit notice review, and data mining.

Small independent operators, who often do not have sophisticated in-house databases, will be able to use a subset of the same RBDMS tools available on-line to file permit notices and production reports. Once the data passes automated quality control checks, the application will upload the data into the agency's RBDMS database. The operators will also have access to state agency datasets to focus exploration efforts and to perform production forecasting, economic evaluations, and risk assessments. With the ability to identify economically feasible oil and gas prospects (including unconventional plays) over the Internet, operators will minimize travel and other costs.

GWPC will coordinate these data sharing efforts with the BLM. This project will improve access to public lands and make strides towards reducing the duplicative reporting to which industry is now subject for leases that cross jurisdictions. The resulting regulatory

streamlining and improved access to agency data will make more domestic oil and gas available to the American public while continuing to safeguard environmental assets.

The 2005 RDBMS annual report *The Effects of the RDBMS/E-Commerce Initiative on Domestic Oil and Gas Production and Water Resource Protection* provides additional documentation on this exciting electronic commerce initiative. This report is available on-line at www.gwpc.org.

CONCLUSION

Because of technological innovations the past few years, an unparalleled opportunity for data sharing now exists. The deployment of these technologies will allow industry, regulatory agencies, and the public to access the data needed to facilitate and expedite the decision making process, benefiting all parties.

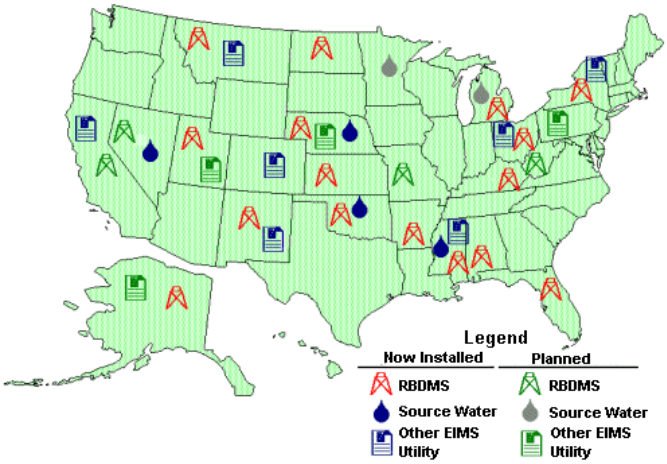

Fig. 3 Map showing states using RBDMS

Acknowledgements

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LNAPL Management: Moving Toward Site Specific Clean-up Goals

Jeffrey A. Johnson, Ph.D.

Abstract

Contamination from light non-aqueous phase liquids (LNAPLs) continues to pose one of the most significant problems faced by the petroleum industry. LNAPL contamination has historically been perceived as a significant environmental threat by the general public and the regulatory community, and as a result, LNAPL cleanup standards are extremely conservative. These conservative standards are primarily the result of regulatory guidance that was developed in the 1980's with limited technical and scientific understanding. More specifically, these regulatory standards produced clean-up levels based on very low apparent well product thicknesses. Research during the past decade has provided significant insight as to the distribution and movement of LNAPL and its impact in different environments. These findings indicate that the LNAPL paradigm from which the regulatory clean-up levels were based is incorrect and that the character and impact of LNAPL contamination is highly dependent upon specific site conditions.

LNAPL poses risk through various pathways; these include (1) direct dermal exposure as a separate phase, (2) as a source of vapors, and (3) as a source of dissolved contaminants. Screening level analyses can readily evaluate the impact of the LNAPL on these pathways. Mobility analyses can assess the potential for LNAPL movement, and vapor and dissolved transport models can predict mass transfer from the LNAPL to the air- and water-phases. These analyses enable the definition of site-specific clean-up goals at LNAPL sites. Although not widespread, the application of site-specific LNAPL goals is increasing and regulatory agencies are beginning to recognize that through appropriate characterization and reasonable analyses, reliable and prudent clean-up levels can be developed.

Introduction

A nonaqueous phase liquid results from the physical and chemical differences between liquid hydrocarbon and water, and these differences produce a distinct physical interface between the two liquids. As such, two distinct liquids exist in the subsurface. The acronym "NAPL" refers to the nonaqueous phase liquid. Fluids such as gasoline, diesel, heating oil and lubricants have a density less than water and are designated as LNAPLs – light nonaqueous phase liquids. Technically, the remediation of LNAPLs is difficult because the physical character of the product, the nature of the soil conditions, and the hydrologic setting affect the efficiency of extraction. As a result, the management of LNAPL contaminated sites is a scientific and an engineering challenge.

Regulations protecting groundwater resources were initiated in the United States in the 1970's and 1980's. Federal statutes that were implemented during this time period included the Resource Conservation and Recovery Act (RCRA) of 1976, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980, and the 1984 Hazardous and Solid Waste Amendments (HSWA) to RCRA. Although none of these regulations specifically address the management of nonaqueous phase liquids, LNAPLs were considered as a source of contamination and it was expected that they be eliminated or destroyed to mitigate the need for

long-term management. As a result, guidance documents were developed which defined expectations for the remediation of LNAPLs. A review of these guidance documents indicates that most regulatory agencies require LNAPL to be recovered to the "extent practicable." The definition of the term, "to the extent practicable" varies. For most states and provinces within North America, LNAPL is required to be remediated to low levels, such as 0.01 feet prior to evaluating risk and/or site closure.

The conceptual understanding of LNAPLs that was the basis for the guidance documents in the 1970's and 1980's was disproven by research in the 1990's. This advancement in technical understanding indicated that the distribution and movement of LNAPLs are dependent upon the complex interrelationship between the physical properties of the soil and NAPL, the site hydrology, and the volume of the release. In particular, the thickness of LNAPL that is measured in a well has meaning only with respect to the physical conditions (i.e., the capillary properties of the soil) in the vicinity of the well bore and the fluid type. Hence, site specific assessment is required to evaluate the potential impacts of the LNAPL.

LNAPL Risk

LNAPL contamination produces three general conditions that pose human health and environmental risks. These are (1) direct exposure, (2) a source of hydrocarbon vapors, and (3) a source of dissolved contaminants. The factors that control the risk posed by the potential conditions vary spatially and transiently. As such, it is important that site specific assessments be conducted to develop site specific clean-up goals.

Direct exposure to LNAPLs is rare since these fluids are present on the groundwater table. Potential conditions that may result in direct exposure include excavations and seepage along surface water interfaces, such as a river. Engineering controls are generally implemented to mitigate the risk posed by exposure.

Vapors may be produced from LNAPL in the subsurface. Due to density and buoyancy effects, LNAPLs occur on the water table – the interface between the saturated and unsaturated zones. As such vapors may migrate upward through the unsaturated zone toward the surface. The potential risk posed by the vapors is site-specific. In particular, the impact of vapors is highly dependent on the composition of the LNAPL, the soil conditions, and presence of structures on the surface. For example, an the vapor concentrations will be higher from an LNAPL composed of gasoline than an LNAPL composed of heating oil. Soil conditions control the transport of vapors in the unsaturated zone. Sands, which are more permeable and have greater air saturation, will readily transfer vapors to the surface whereas clay-rich soils mitigate the transport of vapors. The primary concern of vapors in the subsurface is their collection beneath and within buildings. Where buildings are not present, the potential risk resulting from hydrocarbon vapors is low. Hence, site specific assessment is required to evaluate the potential impacts of vapors.

The presence of LNAPL in the subsurface acts as a continuing source of potential contamination to groundwater. For example, one gallon of gasoline contains approximately 500,000 milligrams (mg) of BTEX (benzene, toluene, ethylbenzene, and xylenes). If dissolved at a concentration of 50 milligrams per liter, this mass would contaminate over 2,500 gallons of groundwater. The potential impact from dissolved contamination, although significant in many cases, is a site-specific problem and influenced by many factors. Conditions that affect the development of dissolved plumes include the composition, volume and age of the LNAPL, the hydrogeologic setting, and biodegradation. The transfer of mass from the LNAPL phase to the

water phase is dependent upon the composition of the LNAPL and the chemical and physical character of the aqueous phase. More soluble LNAPLs such as fresh gasoline can produce significantly greater impacts that aged bunker fuels. In addition, the velocity of the groundwater and how the LNAPL is distributed vertically within the aquifer can significantly influence the mass transfer to the aqueous phase. At many sites, biodegradation is an active process and dissolved plumes become stable within a few hundred feet of the LNAPL source. Over time as the mass transfer decreases from the NAPL, the dissolved plumes will shrink and their potential to pose a risk diminishes. Hence, the impact of NAPL to produce dissolved contaminants is dependent upon site specific conditions.

Site Specific Assessments

The application of a defined apparent well thickness level as a regulatory standard is meaningless in terms of assessing environmental impact and risk from LNAPL. Proper LNAPL management requires a thorough understanding of many chemical and physical factors. Appropriate data must be collected in the field and laboratory to enable this understanding. More specifically, this data should include the LNAPL composition, density, viscosity, and interfacial tensions and measurements of the capillary properties of the soil as well as commonly collected information on the groundwater flow conditions. From this data, LNAPL mobility can be calculated such that realistic clean-up goals can be defined. Various groups such as the American Petroleum Institute and American Society for Testing and Materials (ASTM) have developed guidance documents to address proper characterization and analytical methods for LNAPLs. These methods need greater attention by industry and regulators such that site specific assessments can replace the out-dated and unscientific application of apparent well thickness measurements as clean-up goals for LNAPL.

Conclusions

LNAPL contamination has historically been perceived as a significant environmental threat by the general public and the regulatory community, and as a result, LNAPL cleanup standards are extremely conservative. These conservative standards are primarily the result of regulatory guidance that was developed in the 1980’s with limited technical and scientific understanding. Research indicates that the risk posed by NAPL is highly dependent upon site specific conditions. As a result, regulatory guidelines implementing apparent well product thickness levels as clean-up goals are unrealistic standards in evaluating impacts to human health and the environment. Site specific assessments are needed to provide the critical information necessary to evaluate and define clean-up goals for LNAPL.

Cementing Additives for Use in Environmentally Sensitive Regions

Sam Lewis, Mike Szymanski, and Mike Wilson, Halliburton

ABSTRACT

Environmental sensitivity is an ever-increasing concern, especially in the oil and gas industry. As standards grow more stringent around the world, the industry is taking steps to help ensure that the ecological impact of oil and gas production is as benign as possible. To this end, a strategy has been adopted to assist in adherence to environmental regulations for North Sea wells. These regulations are the most proactive of the current regulations in force.

Typically, additives for use in primary cementing have been made very robust to withstand the often extreme conditions of an oil well. This robustness, however, can lead to many of these materials not being environmentally acceptable due to the resulting lack of biodegradability, their biopersistence, or possible toxicity concerns.

This paper briefly describes the current North Sea regulations and how typical cementing additives perform in relation to these regulations. Additionally, the paper presents comparative studies of some typical additives for oil-well cementing and the results of ongoing research into developing more environmentally acceptable alternatives. Data are provided concerning the performance of additives at various temperatures, additive performance in several cement slurries, and some selected field studies to verify performance characteristics. Ecotoxicological data for these additives are presented to exemplify the authors' work in adhering to the environmental requirements of the North Sea.

INTRODUCTION

In recent years, the global awareness and response to environmental issues has dramatically increased. Environmental concerns have become a major issue in most industrialized countries. These concerns are particularly apparent in the oil and gas or petrochemical industries. Environmental regulations are becoming very stringent in all sectors of the oil and gas industry, especially for offshore oil wells where the effect of chemical processes on the aquatic environment is of great concern. These concerns profoundly impact oilfield service companies.

EFFECTS OF ENVIRONMENTAL REGULATIONS

Oslo-Paris Commission (OSPARCOM)

One of the most proactive areas in environmental regulation is the North East Atlantic—primarily Norway and the European Union. Within this region, the Oslo-Paris Commission (OSPARCOM) was inaugurated in 1992 and ratified in 1998. The OSPARCOM mainly focuses on protection of the marine aquatic environment. The 1992 OSPAR Convention is the current instrument guiding international cooperation on the protection of the marine environment of the North East Atlantic. Specifically, the commission sets forth the guidelines by which chemicals are evaluated for offshore use. To help evaluate chemicals for offshore use, the Harmonized Offshore Chemical Notification Format (HOCNF) was introduced in 1995 (1). The HOCNF is a mandatory form that a company must complete before applying for a discharge permit in any area governed by the OSPARCOM. The company must include data on biodegradation, bioaccumulation, and toxicity (typically four specific organisms). The only exception to this data requirement is a substance that is given a PLONOR rating (2). Materials with a PLONOR rating have been deemed by the OSPARCOM members to "Pose Little Or No Risk" to the environment and do not require further testing. Conversely, materials that appear on Annex 5 (previous Annex 2) of the OSPAR strategy are known Mutagens, Carcinogens, Reprotoxins, etc., and are essentially denied use (3).

Harmonized Mandatory Control System (HMCS)

In 2001, the Harmonized Mandatory Control System (HMCS) was implemented primarily to maintain at least a baseline of rigor for the move to more environmentally responsible chemicals (4). The HMCS is comprised of four aspects. First, environmental data of the product has to be generated. Second, this data must be reported in the HOCNF. This document is the basis of the assessment from the authorities as to whether a chemical can be introduced in the North Sea. Third, based on the data in the HOCNF, the product will be assessed according to the new pre-screening scheme. This step has several outcomes. Finally, when the chemical passes the pre-screening scheme, it will be subject to a Chemical Hazard Assessment and Risk Management (CHARM) assessment.

The prescreening requires two of the three following conditions to be met for a chemical to be initially ranked with the CHARM model (5):

1) Biodegradation >60% tested with OECD 306 marine saltwater testing
2) $Log(P_{ow}) < 3$
3) LC_{50} or EC_{50} >10 mg/l for all test organisms

Additionally, all substances must pass the initial criteria of >20% biodegradation (6). Figure 1 illustrates the prescreening process and provides guidelines for determining initially whether a chemical's use is to be permitted, refused, granted temporary permission, substituted, or ranked for evaluation with the CHARM model.

Norwegian Authority

Beyond the criteria set forth by the HMCS, individual country authorities will evaluate the HOCNF data to determine priorities for chemicals on the phase-out plan. A first example is the Norwegian regulatory body. They currently have the most stringent environmental requirements in the OSPARCOM region. A general breakdown of the Norwegian interpretation of the HOCNF is shown in Figure 2 (7). Any chemical that falls into a "black" category is not permitted; "red" category chemicals are generally permitted but placed on a phase-out plan, which means that alternatives must be located; and with a "yellow" ranking, the most favorable, permission to use a chemical is almost always granted.

United Kingdom

A second example is that of the United Kingdom. The UK utilizes the Hazard Quotient generated by the CHARM assessment to assign a ranking which is summarized in Figure 3. The UK assessment is of particular interest due to the fact that all registered products are listed publicly along with their ranking at http://www.cefas.co.uk/ocns/index.htm. The Offshore Chemical Notification Scheme (OCNS) is a useful tool for general environmental information about current offshore products.

Development Goals

Because Norwegian standards are particularly stringent, our objective is for all new products that are destined for environmentally sensitive regions to meet these criteria. This goal is particularly challenging with regards to cementing fluid loss agents, dispersants, and foaming agents. The remainder of this paper discusses recent efforts to achieve these goals and presents the findings of this research.

ENVIRONMENTAL PRODUCT DEVELOPMENT

Previously, the development of environmentally competent fluid-loss materials for cementing applications suffers primarily due to poor biodegradation. To be useful cementing materials, fluid-loss agents must be primarily soluble in water, which provides a favorable bioaccumulation in almost all cases. Due to the high molecular weight of these materials, they are typically poorly absorbed by aquatic organisms as a result of poor transport across the cell wall membrane. This property leads to low toxicity toward aquatic organisms. This same property, however, prevents the material from being biodegraded by the microorganisms in the environment. Because the toxicity, biodegradability, and performance are directly, and often oppositely, related, maintaining all of the desired properties can be a challenging goal to achieve.

Cement dispersants are often polymeric, although not as high in molecular weight as the aforementioned fluid-loss agents. The polymeric nature gives dispersants the same general problems associated with fluid-loss agents. The lower molecular weight tends to help the biodegradability aspect but in order to avoid performance side effects, sulfur-based ionic groups that are not easily metabolized by most aerobic microorganisms are often used. This places dispersing agents in the same difficult category as fluid loss agents in terms of maintaining all the desired performance and environmental properties.

Foaming agents for cementing suffer from different difficulties related to environmental compliance. Foaming agents (for cementing and in general) are surfactants or mixtures of surfactants. Surfactants have potential issues primarily in regards to biopersistence and toxicity. Surfactants by definition are surface active and partition at the interface of any largely immiscible substances (primarily liquid/liquid or liquid/gas). It is this property that causes experimental measurement of the bioaccumulation to be difficult to achieve. Bioaccumulation is measured by the amount of a material that dissolves in a layer of octanol and the amount in a layer of water. Surfactants are often present in the interface of both layers at the same time making measurement very difficult by the standard OECD 117 or 107 methods. Surfactants are also well known for their capability to adsorb onto a surface such as a cell wall, gill membrane, etc. This property often leads to high toxicity to many aquatic organisms. The toxicity often has the side effect of lowering the biodegradation potential, adding another difficulty to obtaining an acceptable foaming agent.

Current Materials

The importance of achieving good biodegradation in environmentally sensitive areas has driven the continued research in fluid-loss agents and dispersing agents. Fluid Loss A and Dispersant A are agents that have been recently used and were due for phase out. The ecotoxicological data for these products is presented in Figure 4. These materials are not deemed highly bioaccumulating, which is shown by the fact that the $Log(P_{ow})$ is significantly less than 3 in both cases. Similarly, these products are nontoxic to the aquatic test species. However, they also have biodegradation values of 9 and 5%, respectively. As shown in Figure 2, these materials both end up with a “red” ranking because of the lack of toxicity, but they still required placement on the phase-out plan.

As mentioned previously, foaming agents have difficulties in all three environmental categories but particularly in toxicity and bioaccumulation. These reasons have led to intense searching for materials that meet performance and environmental requirements. Foaming Agent A is a current cement foaming agent and its ecotoxicological profile is shown in Figure 5. This material was determined not to be bioaccumulating but it does suffer from low biodegradability and poor toxicity results. This data places Foaming Agent A in the red category at best and needed to be replaced.

Results of Product Development

Recently there have been many new materials developed to satisfy the goals set out above. Two new fluid loss agents, Fluid Loss B and Fluid Loss C have been developed and their ecotoxicological profiles are shown in Figure 6 in comparison to Fluid Loss A. Fluid Loss B and C are also deemed nonbioaccumulating and nontoxic, but have biodegradation values of 24.7% and 29% respectively, which is higher than Fluid Loss A and is above the 20% mark required in the HMCS process. These materials thus fall one rank higher than Fluid Loss A. Because of the lack of aquatic toxicity, a “yellow” rating is now given by the prescreen interpretation, making Fluid Loss B and C the most environmentally sound synthetic materials for fluid-loss control.

Similarly two new dispersing agents, Dispersant B and C have been developed and their ecotoxicological profiles are shown in Figure 7 in comparison to Dispersant A. Dispersant B was deemed to be acceptable as PLONOR and Dispersant C is deemed nonbioaccumulating and nontoxic, but has a biodegradation value of 38%, which is higher than Dispersant A. Therefore Dispersant B is acceptable without further analysis and Dispersant C gains a ‘yellow’ rating. This allows for both a ‘yellow’ dispersing agent as well as a ‘green’ alternative.

Development of compliant foaming agents is somewhat more complicated but two new compliant foaming agents, Foaming Agent B and C, have been developed and their ecotoxicological profiles are shown in Figure 8. Foaming Agent B is readily biodegradable (>60%) and non-toxic, while also being non-bioaccumulating which leads to a ‘yellow’ ranking. Foaming Agent B however suffers from somewhat poor performance. Foaming Agent C is a high performing foaming agent and is also readily biodegradable and non-bioaccumulating but it is rated as toxic. Thus Foaming Agent C also gets a ‘yellow’ ranking. This allows for two ‘yellow’ options with different properties dependent upon the particular situation. Development of an environmentally competent material is a difficult task, but developing a responsible chemical that displays good technical performance is even more difficult.

Performance Comparison of New Material

The ultimate goal of developing an environmentally responsible additive is to achieve a “yellow” ranking and at least equal or surpass the technical performance of the material to which the additive is an alternative. All of the newly developed materials that have been discussed achieve the ‘yellow’ ranking, and comparisons of products A and C for each class are shown in Figures 9 through 11 to illustrate the performance characteristics of these alternative materials. Ultimately, Fluid Loss C was proven to be salt-tolerant and effective at temperatures up to 400°F, verifying that it is robust enough to be satisfactorily used in cementing applications. Dispersant C is proven to be almost an exact performance equivalent to Dispersant A and effective through the same temperature range and shows equivalent performance with other cements and additives.

Foaming Agent C displays virtually the same ability to foam cement slurries as Foaming Agent A, often requiring less material to achieve stability.

CONCLUSIONS

The expanding impact of environmental regulations has put great demands on new product development. The newly established criteria for acceptable materials have made balancing the technical and environmental performance complex in many cases. This demanding task, however, has not deterred the development of environmentally responsible materials. This paper has described recent developments in fluid loss, dispersing, and foaming agents for oil-well cementing applications that have been developed that meet the stringent requirements of the Norwegian sector of the North Sea. These new products have ecotoxicological properties that help them all achieve the favorable “yellow” rating after prescreening, unless PLONOR. Additionally, the effort focused on these products has led to technically competent materials that outperform the current materials in many cases. The success of these product developments strengthens the idea that doing business in an “environmentally responsible” way is not only the right thing to do, but it does not necessarily require that the performance suffer to achieve this commendable goal.

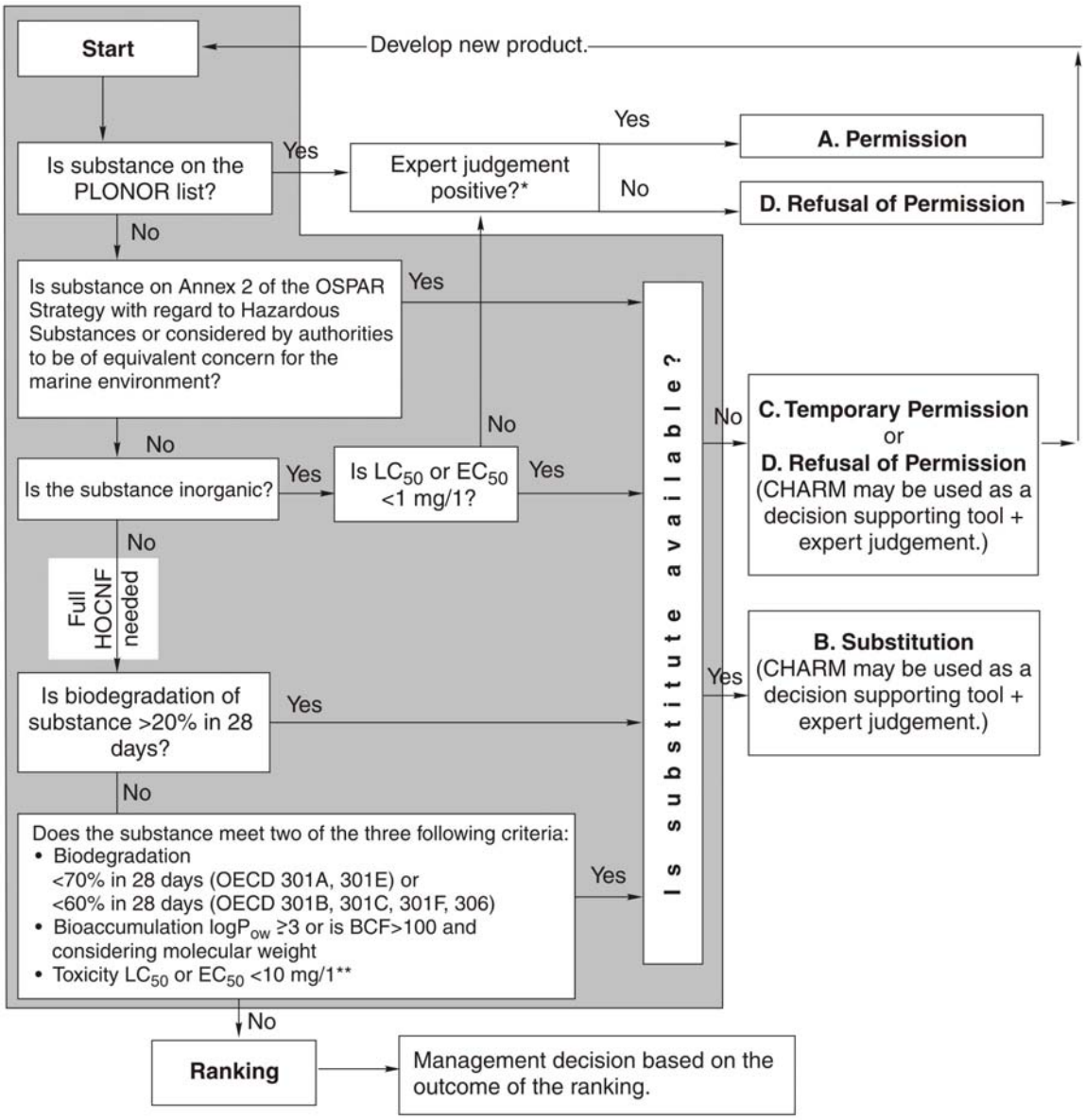
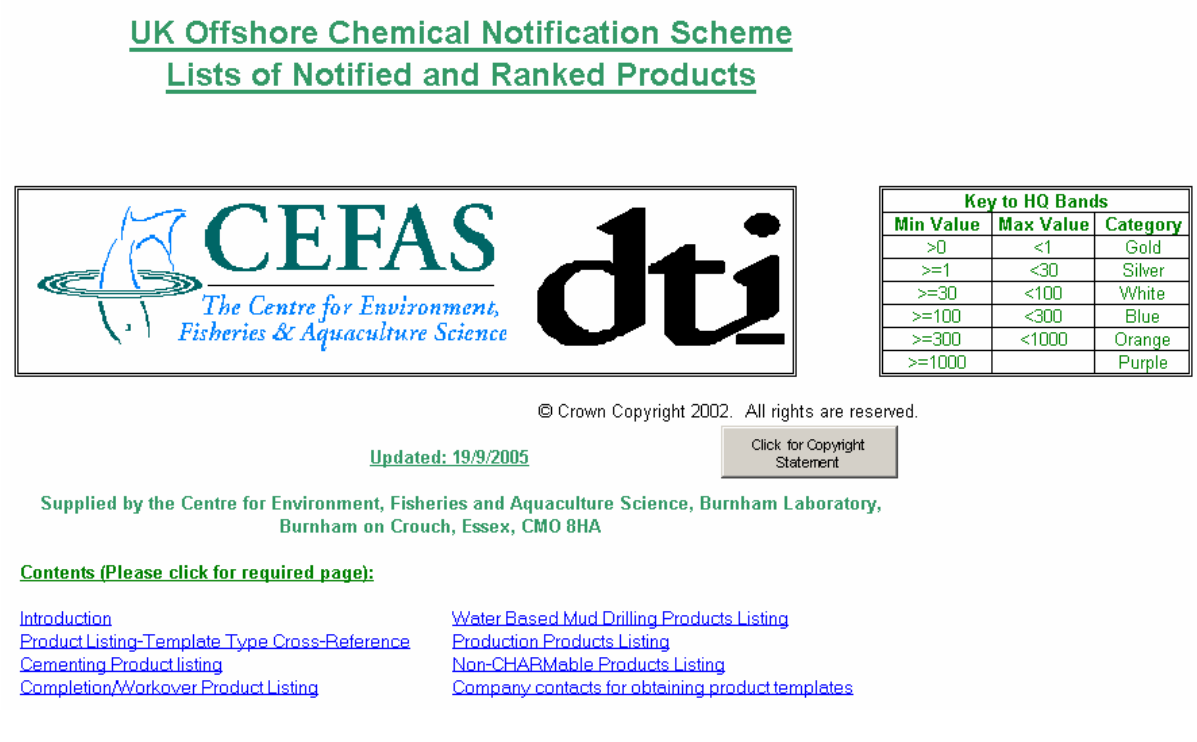


Figure 1. Flowchart used by the HMCS for prescreening (shaded area).

BOD ≥60%	If toxic => red	If toxic => red	
BOD <60%			If toxic => red
BOD <20%		If toxic => black	If toxic => black
	$\log P_{ow}>5$	$\log P_{ow}>3$	$\log P_{ow}\leq 3$

Figure 2. Prescreening interpretation by the Norwegian authorities.



UK Offshore Chemical Notification Scheme
Lists of Notified and Ranked Products

CEFAS
The Centre for Environment, Fisheries & Aquaculture Science
dti

Key to HQ Bands		
Min Value	Max Value	Category
>0	<1	Gold
>=1	<30	Silver
>=30	<100	White
>=100	<300	Blue
>=300	<1000	Orange
>=1000		Purple

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Contents (Please click for required page):

Introduction
Product Listing-Template Type Cross-Reference
Cementing Product listing
Completion/Workover Product Listing
Water Based Mud Drilling Products Listing
Production Products Listing
Non-CHARMable Products Listing
Company contacts for obtaining product templates

Figure 3. UK Ranking Scheme Based on HQ Values.

	Fluid Loss A	Dispersant A
Biodegradation	9%	5%
Bioaccumulation	<0	<0
Toxicity	non-toxic	non-toxic

Figure 4. Ecotoxicological profile of Fluid Loss A and Dispersant A.

	Foaming Agent A
Biodegradation	<60%
Bioaccumulation	<3
Toxicity	toxic

Figure 5. Ecotoxicological profiles of Foaming Agent A.

	Fluid Loss A	Fluid Loss B	Fluid Loss C
Biodegradation	9%	34.70%	29%
Bioaccumulation	<0	<0	<0
Toxicity	non-toxic	non-toxic	non-toxic

Figure 6. Ecotoxicological profile of Fluid Loss A, B, and C.

	Dispersant A	Dispersant B	Dispersant C
Biodegradation	5%	PLONOR	38%
Bioaccumulation	<0	PLONOR	<0
Toxicity	non-toxic	PLONOR	non-toxic

Figure 7. Ecotoxicological profile of Dispersant A, B, and C.

	Foaming Agent A	Foaming Agent B	Foaming Agent C
Biodegradation	<60%	69.90%	>60%
Bioaccumulation	<3	<3	<3
Toxicity	toxic	non-toxic	toxic

Figure 8. Ecotoxicological profile of Foaming Agent A, B, and C.

Temp (F)	Fluid Loss (ml/30 min)	Fluid Loss A (%)	Fluid Loss C (%)
100	52		0.66
100	88	0.66	
104	74		0.22
104	30		0.55
122	12		1.00
140	98		0.22
140	62	1.5	
149	34		0.66
149	30		1.10
149	26		1.32
149	160	1.5	
180	84		0.77
180	54	2.5	
190	107	0.5	
190	70	1.5	
190	42		0.88
190	40		0.77
400	32		1.07
400	40	1.5	

Figure 9. Performance comparison of Fluid Loss A and C.

	Solution	Shear Stress at Given RPM							
Additive	% NaCl	600	300	200	100	60	30	6	3
–	18	183	105	82	60	49	41	25	18
Dispersant A	18	120	57	37	18	10	5	0	0
Dispersant C	18	127	62	40	19	11	4	0	0
Additive	% NaCl	600	300	200	100	60	30	6	3
–	37	105	59	45	31	26	21	16	14
Dispersant A	37	95	50	31	15	10	5	1	0
Dispersant C	37	81	44	28	14	8	3	0	0
Additive	% CaCl2	600	300	200	100	60	30	6	3
–	2	227	117	95	70	59	49	25	18
Dispersant A	2	150	72	46	22	12	6	1	0
Dispersant C	2	185	92	59	27	15	7	1	0

Figure 10. Performance Comparison of Dispersant A and C.

Additive	% NaCl	Foaming Time (sec)	Base Density (lb/gal)	Foam Density (lb/gal)
Foaming Agent A	0	<10	15.8	11.2
Foaming Agent C	0	<10	15.8	11.1
Foaming Agent A	5	<10	15.9	11.0
Foaming Agent C	5	<10	15.9	10.2
Foaming Agent A	18	10	16.5	11.5
Foaming Agent C	18	<10	16.5	11.3
Foaming Agent A	37	10	17.0	11.2
Foaming Agent C	37	10	17.0	11.2

Figure 11. Performance Comparison of Foaming Agents A and C.

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Modeling of LNAPL Distribution and Recovery at a Former Refinery Site

Tie Li[1], PhD, PE and Xiaomin Yang[2], PhD,
[1]URS Corporation, Houston, Texas
[2]BP Remediation Management, Warrenville, Illinois

ABSTRACT

The American Petroleum Institute (API) Model for Design of Free-Product Recovery was used to model the distribution of light non-aqueous phase liquid (LNAPL) in the subsurface and to predict LNAPL recovery rate from dual pumping systems at a former refinery site. The modeling efforts were divided into two phases: LNAPL distribution and LNAPL recovery.

Soil boring samples were first collected at nine locations within the LNAPL plume for geotechnical analyses, including fluid properties, Dean-Stark fluid saturations, and air/water capillary drainage curves. A RETC program also was used to calculate the van Genuchten parameters N and α from the air/water drainage data. The measured fluid property data and calculated N and α data were input into the API spreadsheet model to estimate the vertical LNAPL distributions in the soil formations below and above the water table at the nine boring locations. The model-estimated LANPL saturations in the formations were compared with the measured ones, and the results indicated good fits between the two sets of data at five of the nine boring locations.

Two additional dual-pumping wells were proposed to be installed at the site. The API model was used to predict LNAPL recovery rates over time from those wells. Major findings of the LNAPL recovery estimation are: 1) only a fraction of LNAPL are recoverable; 2) LNAPL recovery rate decreases rapidly as recovery progresses, and reaches asymptotic plateau after a period of time (~five to 10 years), which in turn causes the cost per unit volume of LNAPL recovered increase over time; 3) and reasonable recovery end point should be determined by LNAPL thickness in the monitoring wells, soil type and recovery cost considerations; and 4) Initial LNAPL recovery rate increases proportionally with groundwater pumping rate.

The results of LNAPL recovery modeling will be used in the selection of new recovery well locations at the site, the determination of recovery well spacing, and the establishment of recovery end goals.

INTRODUCTION

The American Petroleum Institute (API) Model for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids (1) was used to model the distribution of light non-aqueous phase liquid (LNAPL) in the subsurface and to predict LNAPL recovery at a former refinery site. The modeling efforts were divided into two phases: LNAPL distribution and LNAPL recovery.

The objective of the first phase modeling is to evaluate the distribution of LNAPL in the soil formations below and above the water table and to estimate the total volume of LNAPL within the smear zone. The objective of the second phase modeling is to predict LNAPL recovery performances over time. The results of LNAPL recovery modeling will be used in the selection of new recovery well locations, the determination of recovery well spacing, and the establishment of recovery end goals.

As part of API modeling input requirements, a series of geotechnical analyses were performed on soil samples collected at several boring locations within the LNAPL plume. The geotechnical analyses include fluid properties, Dean-Stark fluid saturations, air/water capillary drainage curves, grain size analysis, and fractional organic carbon (FOC). Some of these geotechnical results were used directly as model input parameters (i.e. fluid properties) or indirectly to estimate model input parameters (i.e. van Genuchten parameters). Other geotechnical results (i.e. Dean-Stark fluid saturations) were used to evaluate the performance of LNAPL distribution modeling.

This paper presents the approaches and results of the first phase LNAPL and second phase LNAPL recovery modeling.

OVERVIEW OF API MODEL FOR FREE-PRODUCT RECOVERY

The API Model for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids (1) is a spreadsheet software developed by Charbeneau and coworkers at University of Texas at Austin. The spreadsheet model can be used to predict vertical distribution of LNAPL in the formation based on LNAPL thickness in a monitoring well and to predict LNAPL recovery performance during pumping. Refer to the model guidance document (1) for the details of this spreadsheet software.

The use of this API spreadsheet model for LNAPL distribution has several general assumptions: homogeneous soil media, LNAPL spreading laterally on water table, no vertical source directly above modeled area, and no water level fluctuations. In modeling LNAPL recovery, the API spreadsheet model assumes a uniform LNAPL layer saturation and effective layer relative permeability within the radius of capture.

There are also three assumptions that provide basis for calculating the vertical equilibrium liquid distribution. First, the air and water soil characteristic curve provides sufficient information describing the pore size distribution for the soil. Second, the characteristic curve for a different fluid system may be estimated from the air and water curve using scaling parameters that depend only on properties of the fluids involved. Third, in a three-phase system, the capillary pressure

between the LNAPL and water phase is a function of the water saturation, while the air and LNAPL capillary pressure is a function of the total liquid saturation.

There are two separate and standalone spreadsheets available for the use of LNAPL modeling. The Burdine version uses the Burdine model for calculation of the relative permeability and is more applicable to sandy soil conditions. The Mualem version uses the Mualem model for calculation of the relative permeability and is more applicable to fine grain soil conditions. The Burdine version of the API spreadsheet was selected for LNAPL modeling at the Wood River site due to sandy soil conditions in the uppermost aquifer at the Site.

LNAPL DISTRIBUTION MODELING

In the first phase of this modeling effort, the API spreadsheet model was used to model LNAPL distribution and to estimate LNAPL volume in soil formations. LNAPL distribution modeling was performed for nine boring locations at the Site. Geotechnical data and fluid properties were used directly in the model or used indirectly to determine model parameters. This section presents the determination of model input parameters and results of LNAPL distribution modeling.

Model Input Parameters

The API spreadsheet model input parameters include soil characteristics (i.e. porosity, van Genuchten parameters alpha and N, irreducible water saturation, and residual LNAPL saturations in the vadose and saturated zones), fluid properties (i.e. density, viscosity, and interfacial tensions), and LNAPL thickness in the monitoring well.

Van Genuchten parameters alpha and N are two important input parameters of the API spreadsheet model. They are dependent on soil characteristics such as grain size analysis and pore size distributions. The alpha and N values determine the model predicted LNAPL and water behaviors in pore spaces and thus vertical distributions of LNAPL in the formation. The USEPA RETC Program (Version 6.0, 2000) was used to calculate the van Genuchten parameters alpha and N and irreducible water saturation from the air/water capillary drainage data obtained from soil samples at nine boring locations. Table 1 presents the calculated alpha, N, and irreducible water saturation values at theses different boring locations.

Table 2 provides a summary of other model input parameters used for these boring locations. Soil porosity values used in the model are average values of analyses near the water table. Fluid properties (density, viscosity, air/water surface tension, air/NAPL surface tension, and NAPL/water interfacial tension) were based on analytical results from product at wells in the vicinity of these boring locations. Residual LNAPL saturations in the vadose and saturated zones are estimated based on a table provided by Mercer and Cohen (2) and soil and product types at the site. LNAPL thickness in the nearest monitoring well(s) of each boring location measured in October 2003 was used in the model. October 2003 was a relative low water table event and was representative likely of maximum potentially mobile and recoverable product condition, as product thickness generally tends to increase as water level drops.

Model Predicted LNAPL Distribution versus Field Measured Saturation

At each modeled boring location, the API spreadsheet model generated an LNAPL saturation profile at depths above and below groundwater table. Dean-Stark analyses were also performed from measure LNAPL saturation of samples collected from different depths. Field measured saturations were then compared with model predicted saturation profile to evaluate model performance. Comparison of field results and model predicted results indicates that there are relatively good fits between model predicted LNAPL saturations and field measured saturations at boring locations RST-3, RST-4, RST-6, RST-7, and RST-8. Greater discrepancies exist between model predicted LNAPL saturations and field saturation data at locations RST-1, RST-2, RST-5, and RST-9.

Figures 1 and 2 present model predicted LNAPL distributions at boring locations RST-5 and RST-6, respectively. Field measured LNAPL saturations were also plotted in the corresponding figures. Figure 1 shows greater discrepancies between model predicted LNAPL saturations and field measured saturation at boring RST-5. The maximum field saturation for boring RST-5 was measured to be only 3.2 percent at 0.76 feet below water table. It is much lower than the model predicted saturation of 23.7 percent at 0.67 feet above the water table. Potential reasons for the discrepancies between model predicted LNAPL saturations and field saturations include water level fluctuations, hydraulic influence from gradient control wells, and changes in fluid property (i.e. viscosity).

Figure 2 shows relative good fit between field measured LNAPL saturations and model predicted saturations at RST-6. Model predicted maximum LNAPL saturation for boring RST-6 is 11.6 percent at 0.53 feet above water table, which is consistent with the maximum field saturation of 11.4 percent at 0.14 feet below water table.

LNAPL RECOVERY MODELING

In the second phase of this modeling effort, the API spreadsheet model was used to model LNAPL recovery performance at two proposed well locations. Prior to LNAPL recovery modeling, specific recoverable volumes were evaluated for a series of well locations/points. This section presents the results of and recoverable volume evaluation and LNAPL recovery modeling.

Specific Recoverable LNAPL Volume

At each well location, the specific recoverable LNAPL volume can be calculated from (1):

$$D_0 - \gamma b_o$$

where D_o is model calculated specific LNAPL volume in the formation, b_o is field measured LNAPL thickness in the monitoring well. The parameter γ plays the same role in continuity for the LNAPL layer as the specific retention plays in continuity at the water table of an unconfined aquifer. It can be calculated as

$$\left[(1-\rho_r)nS_{orv} + \rho_r nS_{ors}\right]$$

where ρ_r is LNAPL/water density ratio, n is porosity, S_{orv} is the residual LNAPL saturation in the vadose zone, and S_{ors} is the residual LNAPL saturation in the saturated zone.

Table 3 shows the calculated specific recoverable LNAPL volume at different well locations based on gauging data in October 2003. Figure 3 shows a specific recoverable LNAPL volume contour generated with the Surfer program. As shown in Figure 3, there are two "bulls eye" around wells W026 and W027, which have higher specific recoverable LNAPL volumes. These areas can be considered as preferred locations for installing new recovery wells.

Modeling of LNAPL Recovery Performance

Based on the contour map in Figure 3, two recovery wells A-1 and A-2 were proposed to be installed near wells W026 and W027, respectively. The API spreadsheet model was used to predict LNAPL recovery at these two locations. For illustration purpose, this paper presents the results of LNAPL recovery modeling at the proposed recovery well A-1.

The input parameters of well A-1 LNAPL recovery modeling are provided in Table 4. The determination of these parameters was based on available site data and is not discussed in this paper. The well A-1 will be a one-foot recovery well with a total fluid pumping rate of 40 gallons per minute (gpm). The radius of capture (ROC) of well A-1 is assumed to be 400 feet. Model predicted LNAPL recovery performance by well A-1 is discussed below.

Figure 4 shows the model predicted LNAPL thickness in recovery well A-1. It was predicted that LNAPL thickness in well A-1 would decrease from 4.19 feet to 2.85 feet after 10 years of total fluid recovery at 40 gpm.

As shown in Figure 5, the model predicted that the total volume of LNAPL recovery in well A-1 would be approximately 1.23 million gallons in 10 years of recovery. The dashed line in Figure 5 shows a model predicted total LNAPL volume of 3.1 million gallons within the ROC of 400 feet. This suggests that LNAPL recovery volume of 1.23 million gallons in 10 years is less than 40 percent of total LNAPL volume within the ROC of well A-1.

Figure 6 presents model predicted LNAPL recovery rate during the 10 years of recovery. LNAPL recovery rate is predicted to be approximately 550 gallons per day (gpd) at the start of LNAPL recovery and would gradually decrease to approximately 200 gpd after 10 years.

LNAPL recovery was modeled for different durations, and the predicted LNAPL recovery volumes were divided by the total LNAPL volume within the ROC to calculate the percent of LNAPL recovery. Figure 7 shows the model predicted percent LNAPL recovery after years of recovery. As shown in Figure 7, it would take well A-1 approximately 60 years to recover 80 percent of total LNAPL volume within the ROC of 400 feet. The percent of LNAPL recovery is predicted to reach asymmetric plateau after a significant period of time. This is due to decreasing LNAPL recovery rate as LNAPL in soil formation depletes by recovery. At the end of LNAPL recovery operation, it may take tens of years to recover an additional one percent of LNAL, which would not be cost effective and practical. This suggests that an appropriate LNAPL recovery end points need to be established for recovery systems at the site based on model predicted and observed recovery performance, risk analysis and consideration of other factors. Once the appropriate end point is reached, any additional LNAPL recovery will not be necessary.

In order to evaluate the effect of groundwater pumping rate on LNAPL recovery, total LNAPL recovery volumes at well A-1 were modeled for different pumping rates and the results are

presented in Figure 8. As shown in Figure 8, LNAPL recovery volume from well A-1 in a ten-year period increases with increasing pumping rate.

SUMMARY AND CONCLUSIONS

The API spreadsheet model proves to be a simple analytical model readily applicable to the former refinery site. It was used to estimate LNAPL distributions at nine different boring locations of the Site. There are relatively good fits between model predicted LNAPL saturations and field saturations at five of the nine boring locations. Potential reasons for the discrepancies between model predicted LNAPL saturations and field saturations include water level fluctuations, hydraulic influence from gradient control wells, and changes in fluid property (i.e. viscosity).

Specific recoverable LNAPL volumes were calculated using the API model for different well and boring locations. A specific recoverable LNAPL volume contour map was generated and used to determine the locations of new recovery wells. The API model was then used to predict LNAPL recovery performance at one of the proposed new recovery well locations. The following summarizes major findings of LNAPL recovery modeling that can be used to manage LNAPL recovery system at the site:

- Only a fraction of LNAPL can be recovered even after years of operation;
- LNAPL thickness in well decreases as recovery progresses;
- LNAPL recovery rate decreases rapidly as recovery progresses;
- LNAPL recovery rate increases with groundwater pumping rate;
- The percent of LNAPL recovery is predicted to reach asymmetric plateau after a significant period of time due to decreasing LNAPL recovery rate as LNAPL in soil formation depletes by recovery; and
- Reasonable recovery end point should be established based on LNAPL volume, site condition, and recovery performance.

In summary, the API spreadsheet model was successfully used to model LNAPL distribution and recovery at the site. Modeling results can be used in decision-making process of LNAPL management at the site. The model will also be modified based on future LNAPL recovery performance observed in the field.

REFERENCES CITED

1. Charbeneau, R.J., Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids, American Petroleum Institute, Publication Number 4729, (2003).

2. Mercer, J.W. and Cohen, R.M.; "A Review of Immiscible Fluids in the Subsurface," *J. Contam. Hydrol.*, **6**, 107-163 (1990)

Table 1. RETC calculated van Genuchten parameters and irreducible water saturation

Boring location	Depth (ft)	Alpha (ft^{-1})	N	Irreducible water saturation
RST-1	34.0	1.37	2.15	0.105
RST-2	33.0	1.08	2.26	0.107
RST-3	30.6	0.15	2.58	0.15
RST-4	34.3	0.28	2.71	0.05
RST-5	42.3	0.47	2.53	0.103
RST-6	33.0	0.22	1.89	0.1
RST-7	32.5	0.53	2.31	0.132
RST-8	32.2	0.42	2.27	0.108
RST-9	38.5	0.72	2.14	0.087

Table 2. Summary of other model input parameters

Soil Boring	LNAPL Density (gm/ml)	LNAPL Viscosity (cP)	Surface Tension Air/Water (dynes/cm)	Interfacial Tension LNAPL/Water (dynes/cm)	Surface Tension Air/LNAPL (dynes/cm)	Soil Porosity	Residual Saturation (Vadose)	Residual Saturation (Saturated)	NAPL Thickness in Well (ft)
RST-1	0.793	1.13	54.5	11.3	22.4	0.367	0.026	0.036	0.92
RST-2	0.8126	1.6	55.4	16.2	23.9	0.401	0.026	0.036	1.67
RST-3	0.8126	1.6	55.4	16.2	23.9	0.499	0.026	0.036	3.24
RST-4	0.8126	1.6	55.4	16.2	23.9	0.416	0.026	0.036	1.72
RST-5	0.7504	0.58	63.7	17.0	20.6	0.452	0.026	0.036	1.64
RST-6	0.793	0.98	59.7	17.0	22.4	0.4	0.026	0.036	2.03
RST-7	0.803	1.26	55.0	22.7	12.3	0.412	0.026	0.036	2.49
RST-8	0.8044	1.33	55.2	13.5	22.5	0.395	0.026	0.036	2.71
RST-9	0.793	0.98	59.7	17.0	22.4	0.406	0.03	0.036	1.5

Table 3. Calculated Specific Recoverable LNAPL Volume from Measured LNAPL Thicknesses in October 2003

Well ID	Measured LNAPL Thickness (ft)	Specific Recoverable Volume (ft^3/ft^2)
W001	3.24	0.1309
W002	1.67	0.1651
W003	3.24	0.1309
W004	0.89	0.0129
W005	1.60	0.0268
W006	1.91	0.0359
W007	1.15	0.0147
W008	2.83	0.0978
W009	0.01	0.0059
W010	0.85	0.0099
W011	1.72	0.0286
W012	0.06	0.0041
W013	1.83	0.1634
W014	6.65	1.4342
W015	0.02	0.0037
W016	1.24	0.0404
W017	1.07	0.0174
W018	2.03	0.0624
W019	2.01	0.0617
W020	2.57	0.2965
W021	2.71	0.2357
W022	1.91	0.1756
W023	2.89	0.2693
W024	1.08	0.0529
W025	2.36	0.2830
W026	3.35	0.4484
W027	4.19	0.7693
W028	1.46	0.0991
W029	0.92	0.1215
W030	0.45	0.0314

Table 4. Summary of LNAPL recovery modeling input parameters for Well A-1

Parameter	Value	Unit
Apparent LNAPL Thickness	4.19	ft
Soil Porosity	0.41	NA
Alpha	0.53	NA
N	2.31	NA
Irreducible Water Saturation	0.13	NA
Residual LNAPL Saturation (vadose)	0.026	NA
Residual LNAPL Saturation (saturated)	0.036	NA
LNAPL Density	0.803	gm/cc
Air/Water Surface Tension	55	dynes/cm
LNAPL/Air Surface Tension	22.7	dynes/cm
LNAPL/Water Interfacial Tension	12.3	dynes/cm
LNAPL Viscosity	1.13	centipoise
Hydraulic Conductivity	26	ft/day
Groundwater Pumping Rate	40	gpm
Radius of Capture	400	ft
Radius of Recovery Well	0.5	ft

Notes:
ft – feet, ft/day – feet per day, NA – Not Applicable, gm/cc – gram per cubic centimeter, dynes/cm – dynes per centimeter, gpm – gallons per minute

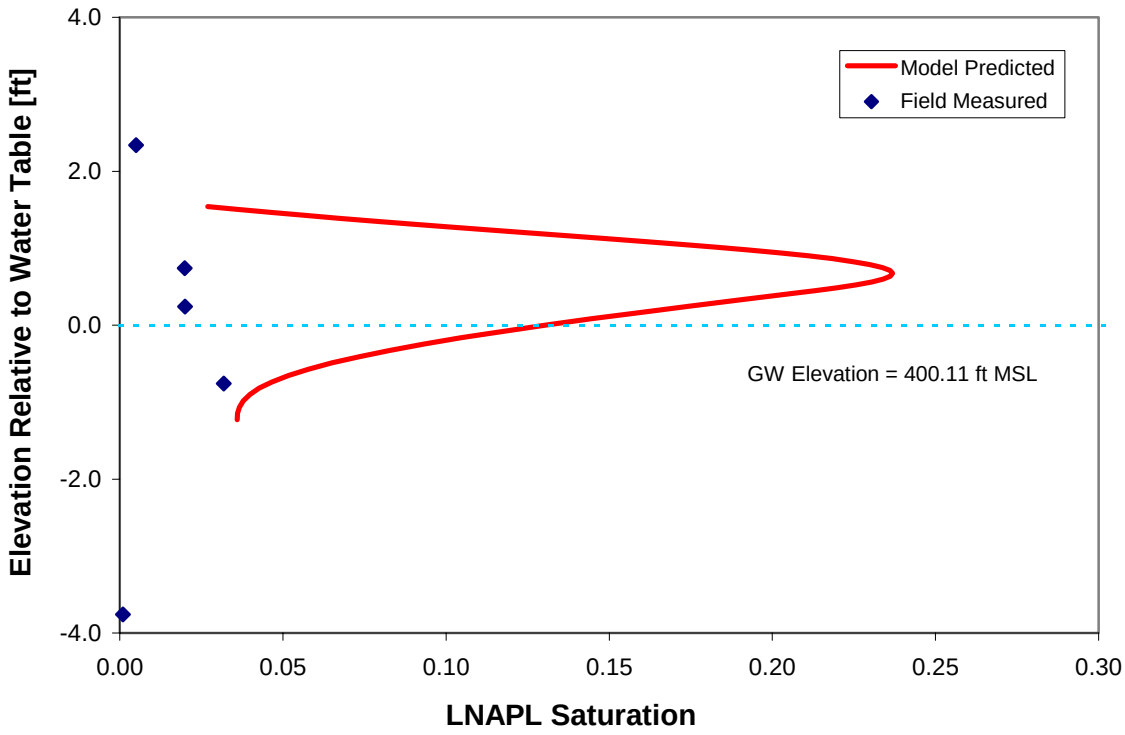


Figure 1. Field measured and model predicted LNAPL saturation profiles at RST-5

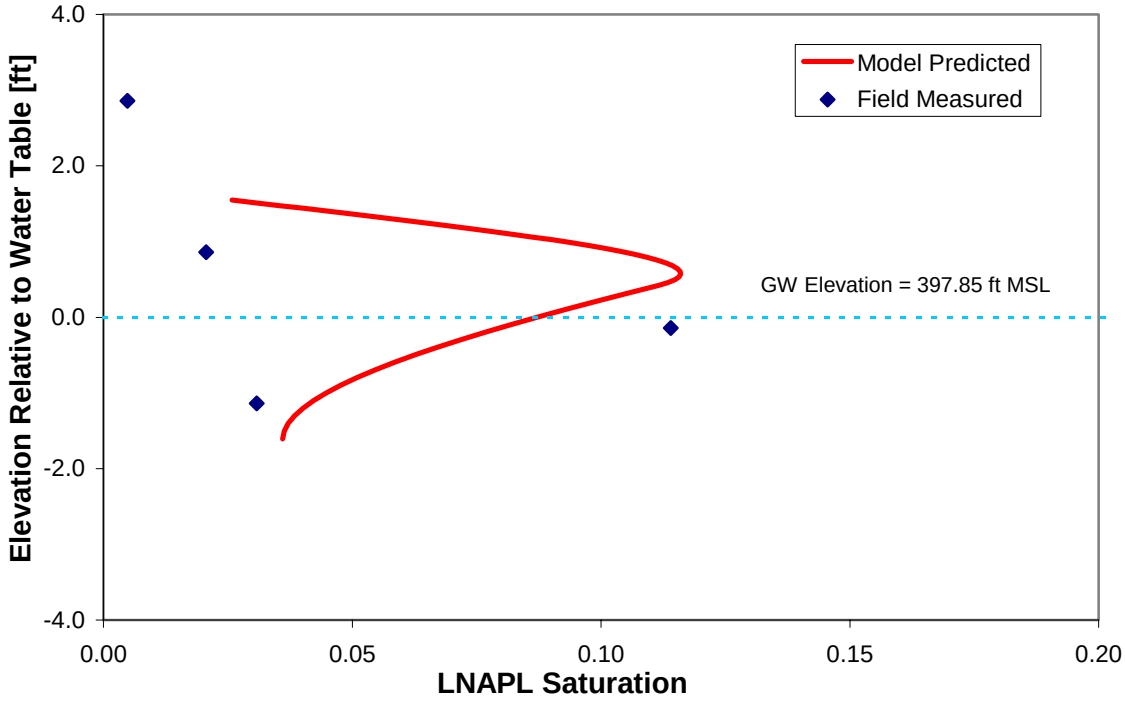


Figure 2. Field measured and model predicted LNAPL saturation profiles at RST-6

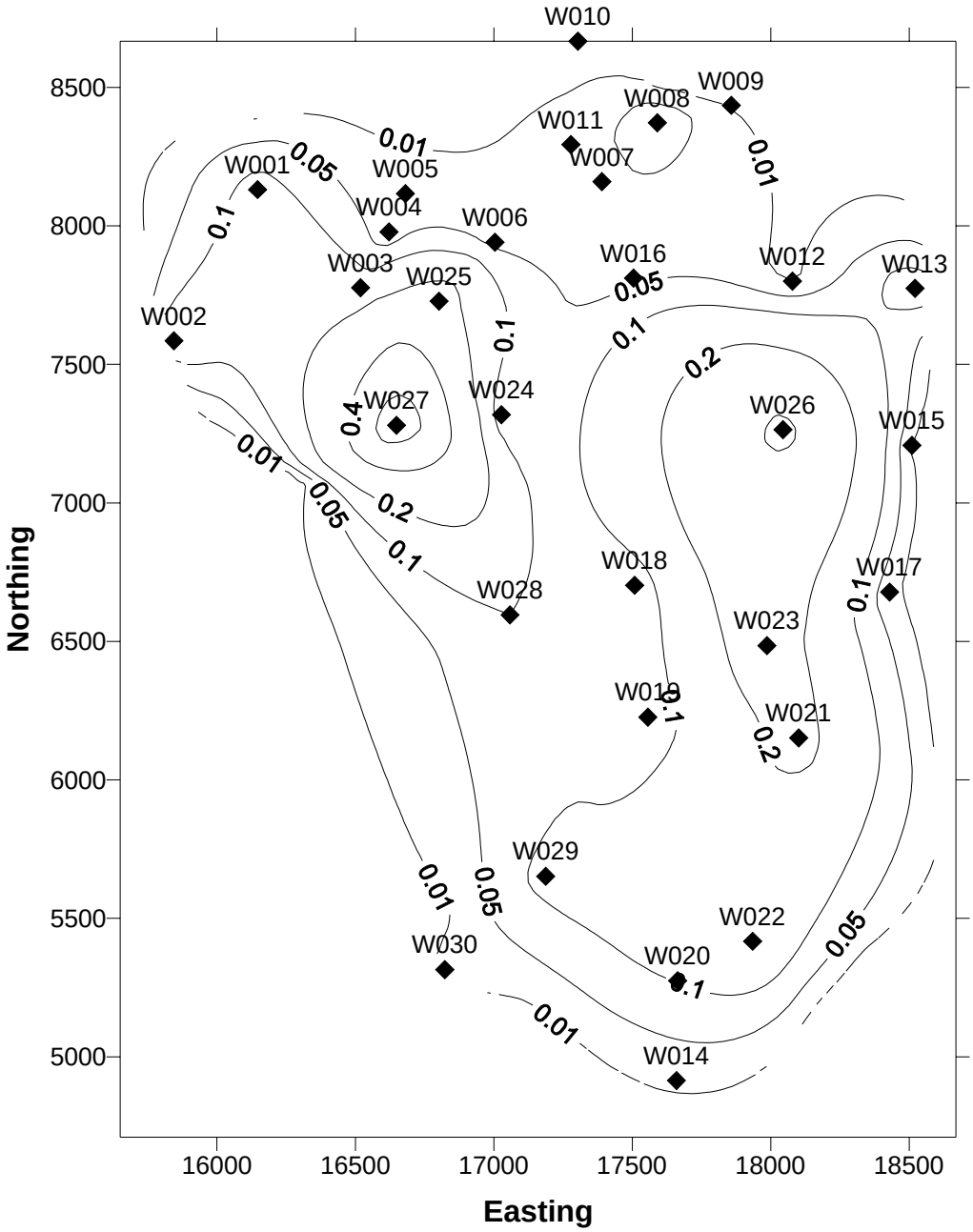


Figure 3. Contour Map of Specific Recoverable LNAPL Volume Calculated from Measured LNAPL Thicknesses in October 2003

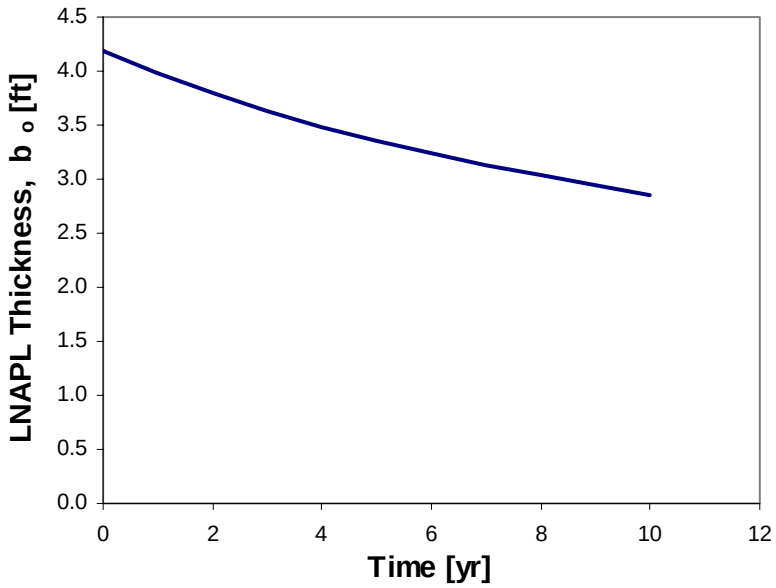


Figure 4. Model Predicted LNAPL Thicknesses after Ten Years of Recovery at Well A-1

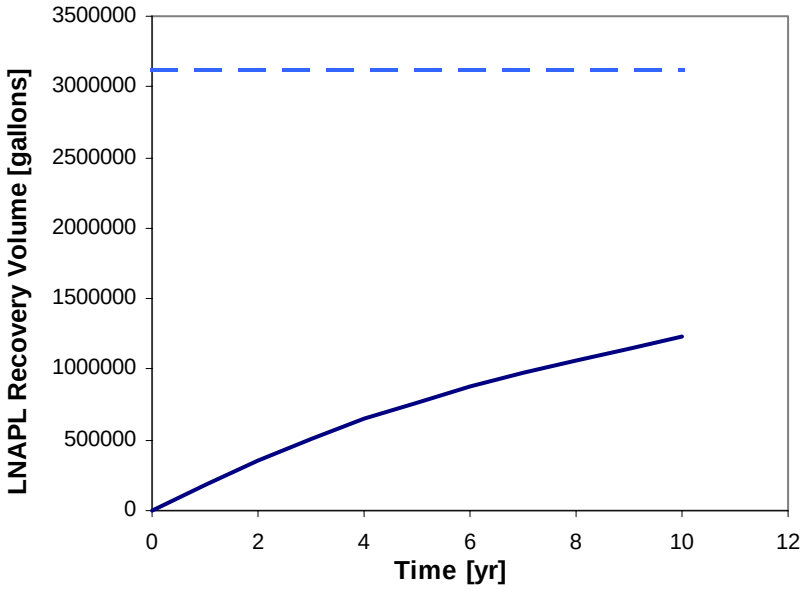


Figure 5. Model Predicted LNAPL Recovery Volume after Ten Years of Recovery at Well A-1

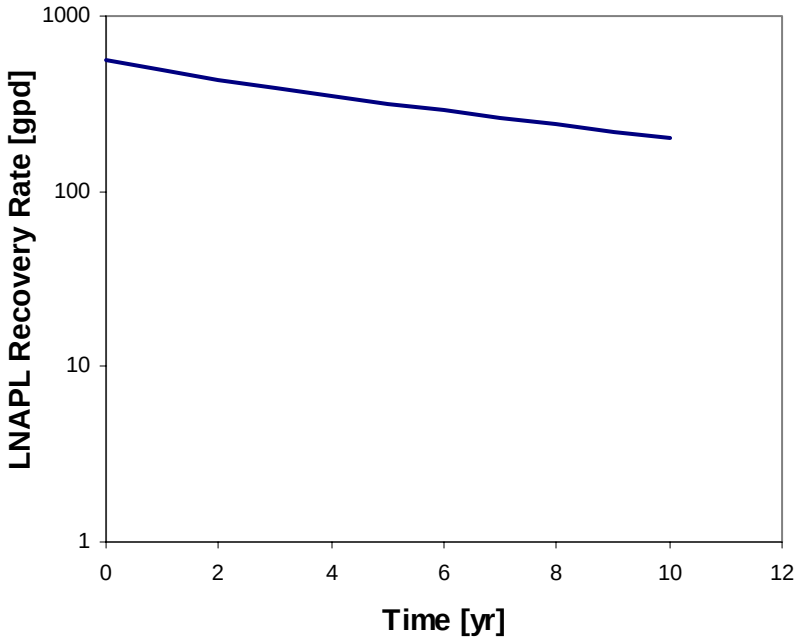


Figure 6. Model Predicted LNAPL Recovery Rate Over Time, Well A-1

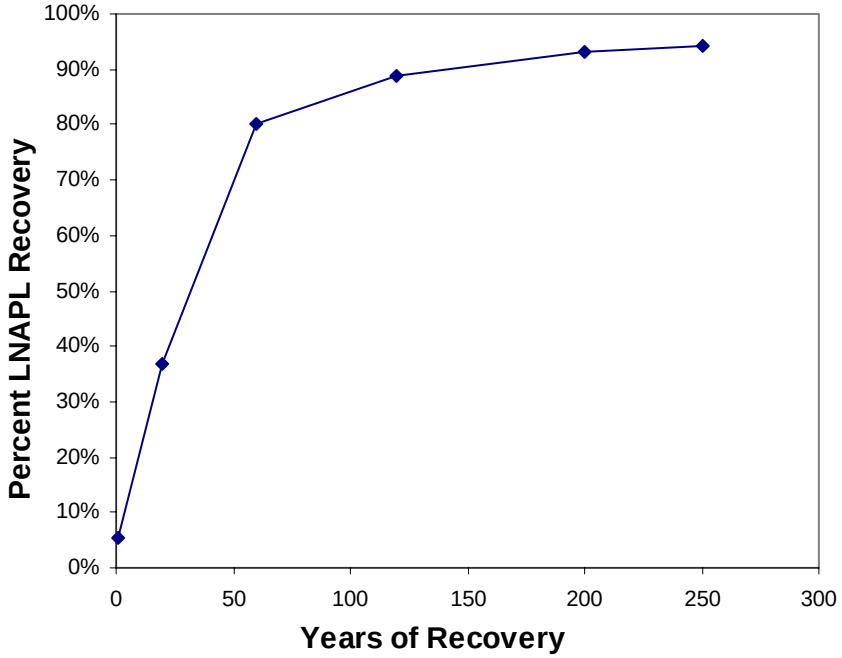


Figure 7. Model Predicted Percent LNAPL Recovery Over Time, Well A-1

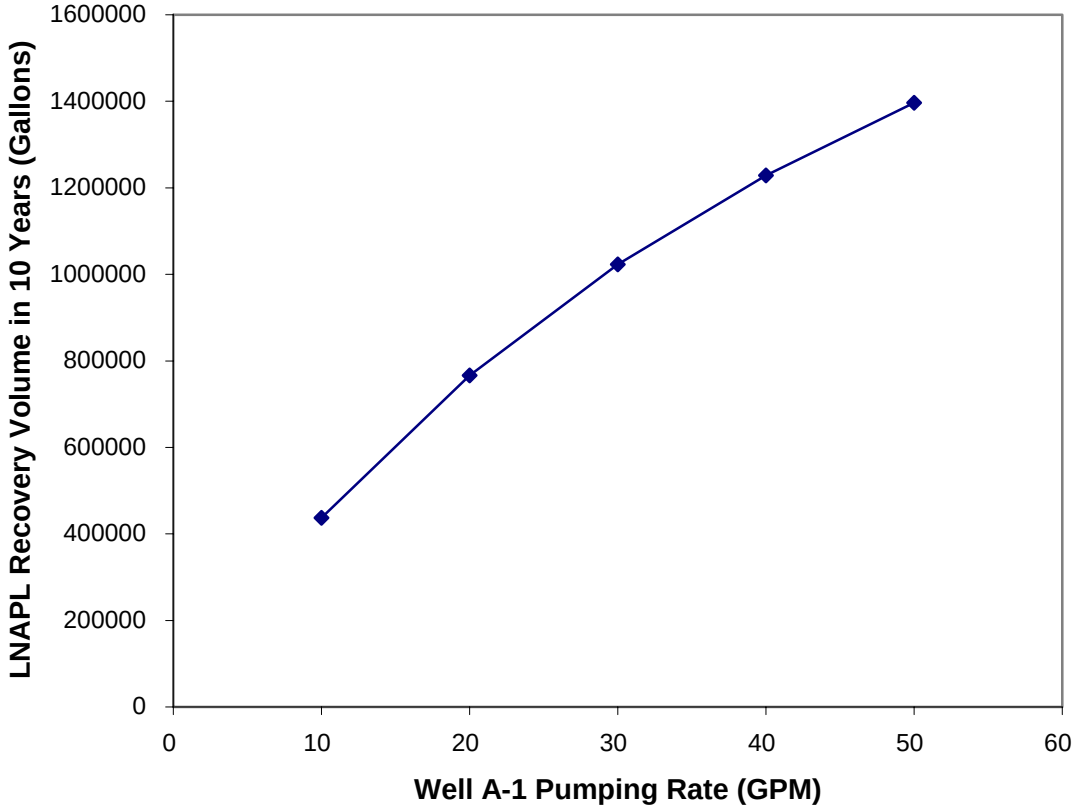


Figure 8. Model Predicted LNAPL Recovery Volumes at Different Pumping Rates

Improve Hydrocarbon Contamination Assessment and Conceptualization Using Visual Imagery Technology and LIF Data

Meng Ling, Ph.D., The RETEC Group, Inc.
Jeffrey A. Johnson, Ph.D., The RETEC Group, Inc.

ABSTRACT

Accurate conceptualization of the distribution of hydrocarbon contamination in the subsurface is critical to the development of appropriate remedial responses. Recent advances in Laser Induced Fluorescence (LIF) investigation and computer visual imagery technologies have enabled the site assessment and conceptualization to be conducted in an accurate and timely manner. The LIF-ROST system, an in-situ hydrocarbon contamination detection system, is able to provide vertically a high resolution of response data rapidly and at low cost. Utilizing the cutting-edge applications in 3-D computer visual imagery, these LIF data can be readily interpreted with the complex hydrogeologic settings of the subsurface to derive a dependable conceptual model of the site and contamination distribution. The visual imagery technology also facilitates technical understanding and communication of the assessment data.

This paper documents the 3-D visual imagery application to LIF data for site conceptualization and presents several examples of its use at various sites. In particular, the paper presents how the technology was utilized to visualize the LIF data, interpret the spatial distribution of the hydrocarbon contamination, and determine the potential migration pathways of the light non-aqueous phase liquid (LNAPL) in the complex subsurface settings.

INTRODUCTION

Since its introduction into the environmental industry in the last decade, laser induced fluorescence-based technology (LIF) has been widely applied for detecting petroleum hydrocarbon contamination in the subsurface. This application is based on the mechanism that certain compounds of petroleum-based fuels (e.g., gasoline, diesel, and kerosene), when excited by ultraviolet light, will fluoresce. The fluorescence intensity of a subsurface sample, which is proportional to the contaminant concentration, can then be analyzed to assess the existence and distribution of petroleum hydrocarbon contamination.

The Rapid Optical Screening Tool (ROST™), or ROST™ LIF, is such a tool for the in-situ detection of petroleum hydrocarbons in the subsurface. The ROST™ LIF is a wavelength tunable dye laser induced fluorescence system designed as a field screening tool. It uses a pulsed laser coupled with an optical detector to make fluorescence measurements via optical fibers. The measurement is made through a sapphire window on a probe that is pushed into the ground with a truck mounted cone penetrometer (CPT). As an in-situ field screening technique, its biggest advantage is to determine the presence/absence and characterize the subsurface distribution of petroleum hydrocarbon contamination before installing any monitoring wells or soil borings. And the immediate availability of the LIF data makes the investigation a time wise and cost-effective process. With such information, further site investigation can be focused on areas of concern with a limited number of borings or wells, resulting in the optimal use of remediation resources.

Difficulty in LIF Data Assessment & Interpretation

LIF data come in the form of fluorescence intensity of individual wavelengths and their summation. The intensity is usually expressed as percent of response. Because the vertical resolution of ROST™ LIF are usually less than 0.2 feet, the whole set of LIF data could have thousands of records on average. For instance for a CPT bore that is 30 feet deep with a vertical resolution of 0.1 feet, 300 LIF records will be produced. If there are 40 CPT bores at this site, a total of 12,000 LIF records will be produced. Although plots for individual bores are readily available and can be interpreted easily, examining all the data collectively and understanding their relationships presents a challenge. More specifically, the three dimensional (3-D) nature of the data makes its effective presentation, communication, and interpretation with traditional mapping tools (GIS, CAD) a difficult or even impossible task. These traditional tools can be used for generating 2-D plots, which can be LIF intensity for a single bore or several bores along a cross section. However, it is very difficult to mentally synthesize these 2-D plots or results and make accurate and effective interpretation. In addition, presenting such plots to an audience of different backgrounds tends to generate confusions and cause communication difficulties.

A Solution with 3-D Visual Imagery

Visualizing and interpreting LIF data using 3-D visual imagery tools provides a solution to the above problems. Using such tools, LIF data can be visualized as 3-D interactive images and/or animations, and their spatial distribution (at a certain intensity) can be interpreted and visualized via 3-D interpolation routines. The 3-D interactive images can be viewed from any angle at any scale to provide a real 3-D depiction of all LIF data and their interrelations with subsurface hydrogeologic conditions. Animation files can be played as a movie so that the site conditions and LIF data and/or interpretation can be effectively communicated in a matter of minutes. With the advances in computer technology in recent years, 3-D visual imagery has evolved from a costly and resources-intensive technique to one that is affordable and accessible to

average practitioners nowadays. Applying visual imagery to LIF data analysis allows straightforward presentation of LIF data, facilitates interpretation and site conceptualization, and is proven to be a very effective tool. Three example applications are presented later in this paper to illustrate their uses.

VISUAL IMAGERY TECHNOLOGY

Visual imagery is a computer-based technology that creates 3-D electronic images and animation files. It is an effective tool to document complex hydrogeologic settings and contaminant distributions in the subsurface. Because mental understanding is inseparable from visual perception, the ability to illustrate the relationships of geologic, hydrologic, and contaminant conditions is extremely valuable in environmental investigations. In particular, visual imagery technology as a tool provide several key functions: (1) it enables large volumes of data to be synthesized and organized in a simple, easy-to-use visual format; (2) it enables data to be interpreted in true 3-D; (3) it documents site activities and physical conditions through time; (4) it allows information to be readily communicated. Some key functions are described in more detail below.

3-D Data Synthesizing

Visual imagery technique is capable of transferring site information into a simple 3-D interactive image. In many cases, the image is a compilation of a large volume of information related to various site features such as boring logs, fluid levels, chemical data, site maps, and aerial photographs. As a result, visual technology acts as a data management tool that collates, organizes, and displays large volumes of site information. Therefore, the results that are normally presented in large and cumbersome reports can be archived and displayed as visual images.

Visual imagery can be used to readily document many types of site data. Commonly illustrated features include site topography, well construction (well screens and casings), geologic strata, and fluid surfaces (water or NAPL), and soil and groundwater chemical data. In particular, visual imagery can effectively document any specific set of data. For example, if groundwater concentrations above a certain level are of concern, images can be developed to only illustrate those well screens where concentrations exceed the specified level. The concentration data can be interpolated to develop a 3-D plume at or above the specified level. And its volume and mass can be easily calculated. By loading the geologic strata and/or fluid surfaces into the image, the contamination distribution relative to the subsurface conditions can be evaluated.

Excellent Communication Tool

As most environmental problems are both transient and 3-D in nature, flat 2-D, snap-shot representations are limited in their capability to transfer information. A 3-D image that allows interactive viewing greatly clarifies understanding among technical as well as non-technical individuals. Once understanding is maximized through visual perception, improved information transfer can be achieved. For example, environmental problems at a refinery generally require individuals from different disciplines to interact in order to effectively comprehend, analyze and remediate subsurface contamination. Such a technical team is commonly composed of hydrogeologists, engineers, chemists, and regulatory specialists. With a clear understanding of the site conditions delivered by the visual imagery, the technical team can quickly reach consensus on an accurate conceptual model. Because physical and chemical interrelationships can be readily

represented with visual imagery, team members are more effective and efficient working together to achieve an effective and efficient solution.

Visual imagery is also a favorable technique for use in court presentations and exhibits. The interactive 3-D images and movies provide quick understanding of technical information to the non-technical professional and the general public. As such, visual imagery technology clarifies critical site conceptual features and facilitates understanding of physical and chemical interrelationships, aiding in decision making.

EXAMPLE APPLICATIONS

Three example applications with LIF data are presented in this section. The first application illustrates the direct visualization of LIF data from which an overall understanding of potential contamination can be developed. In the second application, the data from first application were interpolated to generate 3-D "plumes" of LIF to investigate the spatial distribution of the contamination. The third application illustrates using LIF data to identify potential LNAPL migration pathways underneath a petroleum refinery.

Visualize LIF Data Directly

At a petroleum hydrocarbon contaminated site, 37 CPT bores were pushed into the subsurface for ROST™ LIF investigation. These CPT bores range in depth from 25 to 35 feet below ground surface (bgs). The vertical resolution of the LIF data is less than 0.1 feet and this generated more than 13,600 records in total. The total fluorescence from these 13,600+ records was visualized as color spheres to indicate the intensity or percent response (Figure 1). The magnitude of the total fluorescence was used to identify the presence or absence of potential contamination. Figure 2 is a snapshot of the generated 3-D interactive image, in which red color stands for high total fluorescence while blue color represents low total fluorescence. This 3-D interactive image, when rotated and rescaled, allows LIF intensity to be readily illustrated both horizontally and vertically, and from any angle. Also illustrated in this image are ground surface and facility map. It can be seen from Figure 2 that the hot spots are in the central portion of the sites at a depth of 10 to 25 feet bgs. When zoomed in, the full resolution of the LIF data become available (Figure 3). The advantage of visual imagery is obvious: a single image is capable of visualizing such a large volume of data and delivering the information in a straightforward way.

Interpret the Distribution of Contamination

The LIF data shown in Figure 2 are horizontally discrete in space, i.e., there are no data between the CPT bores. As a result, it is desirable to derive a continuous spatial distribution of the LIF intensity exceeding a certain level, similar to developing concentration contours from discrete samples. Such a distribution is useful for delineating the impact area and estimating a volume of the potentially contaminated soil, proving the direction for site remediation and further characterization.

The data presented in the first application were interpreted via 3-D interpolation methods to derive the spatial distribution of the LIF "plume". In this case, kriging was used for building the 3-D plume. Variogram model was first fitted and its validity was checked. Kriging was then applied to the 3-D LIF data to estimate the intensity at unsampled locations represented by grid nodes. The 3-D grid is pre-specified which has a horizontal resolution of 10 feet and vertical

resolution of approximately 0.33 feet (different resolution can be specified if needed). Figures 4a and 4b illustrate the LIF "plume" at or above the intensity of 50 percent and 100 percent, respectively. The image as shown by Figure 4 was generated assuming that the horizontal and vertical anisotropy are equivalent, i.e., horizontal correlation is same as vertical correlation. Figure 5 illustrates the same LIF "plumes" except that the ratio of horizontal to vertical anisotropy was adjusted to 10, that is, horizontal correlation is considered 10 times higher than vertical correlation. These images provide slightly different spatial distributions of the potential contamination but the hot spots remain essentially the same. The apparent layering of the "plume" is partly due to the horizontal resolution of the grid. If the horizontal resolution of the grid is increased to 5 feet, for example, the "plume" layering will be less obvious and the "plume" surface will look smoother.

Assess Potential LNAPL Migration Pathway

ROST™ LIF data were collected from a number of CPT bores beneath a petroleum refinery to investigate the potential LNAPL migration pathways. These CPT bores were placed around an area where LNAPL was consistently observed in monitoring wells. Figure 6 is a snapshot of the 3-D image generated to show the interrelations of LIF data (total fluorescence) and geologic surfaces. The geologic surfaces were generated through 3-D kriging of lithologic data from soil borings. It is seen that most of the high intensity LIF data are inside the sand formation, bounded by the mud (silt or clay) surface on top and the sand surface at bottom. This is consistent with the hydrologic settings of the aquifer that LNAPL tend to reside in the permeable layer.

But there are several bores beneath the mud surface (Figure 7), indicating LNAPL has migrated into a deeper stratum. This can be further illustrated by showing the lithologic data side by side with the LIF data (Figure 8). The image as shown by Figure 8 was generated by posting the borehole lithology as color tubes. The deeper CPT bore on the right has some high responses in a sandy formation beneath a mud layer. Therefore, it was concluded that a possible window might be present in that area. Another conclusion from this analysis is that the source of the LNAPL release may be around or close to the CPT bore in the center of Figure 8, which shows high LIF intensity throughout most of the bore length. These findings provide important information to the site managers for conducting further investigation and characterization at the site.

CONCLUSIONS

In recent years, ROST™ LIF technology has been widely used for detecting petroleum hydrocarbon contamination in the subsurface. As an in-situ field screening technique, its advantage lies in the immediate availability of the results and its cost-effectiveness. However, the large volume of data produced from ROST™ LIF investigation and its 3-D nature presents a challenge for effective presentation, interpretation, and communication. Computer visual imagery is an effective tool in presenting and interpreting LIF investigation results.

New applications in 3-D visual imagery have enabled LIF data as well as complex subsurface settings to be readily illustrated. This technology facilitates technical understanding and communication of site data. Using this technology, LIF data can be visualized as 3-D interactive images and/or animations, and their spatial distribution can be interpreted. When studied with other subsurface conditions, LIF data visualization can provide important

information for site investigation and conceptualization. Three example applications were presented to illustrate its viability. The first illustrates the direct visualization of LIF data from which an overall understanding of potential contamination was developed. The second generated 3-D “plumes” of the LIF data to assess the spatial distribution of the contamination. The third application illustrates LIF data visualization in identifying potential LNAPL migration pathways underneath a petroleum refinery.

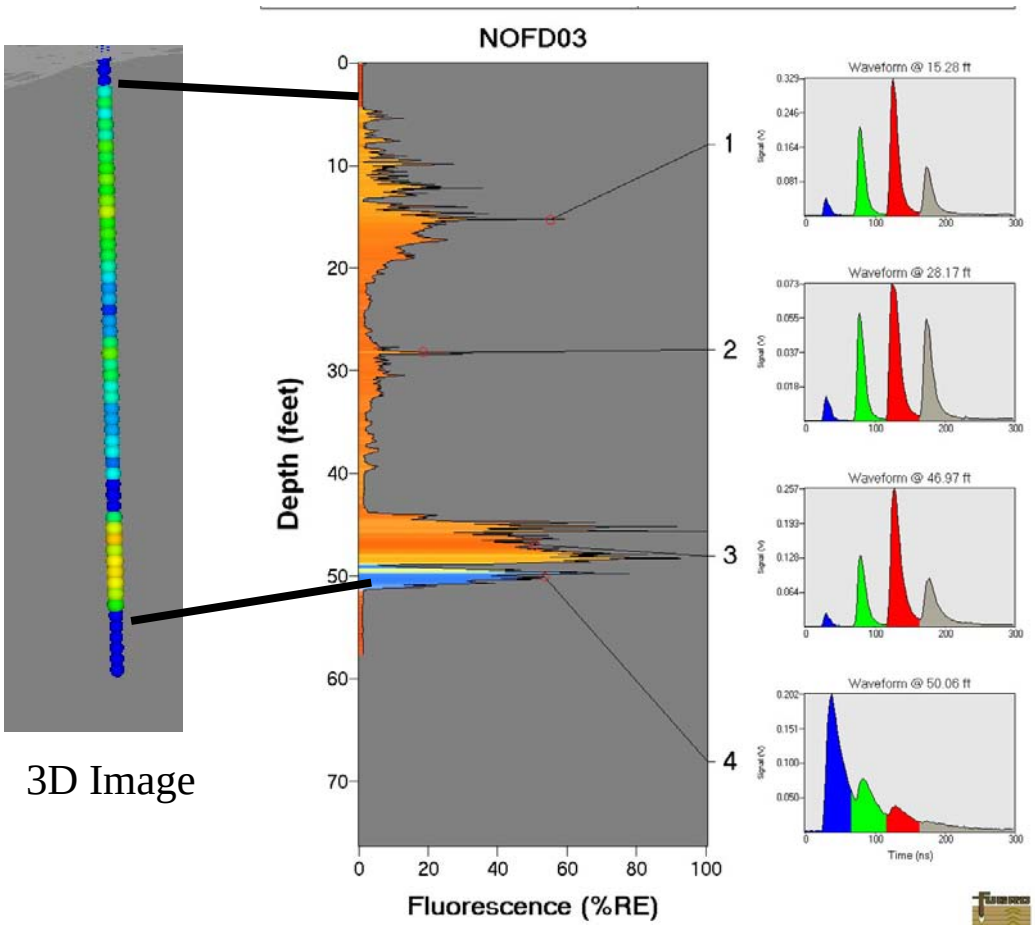


Figure 1. Visualization of LIF total fluorescence as color spheres in a 3-D image.

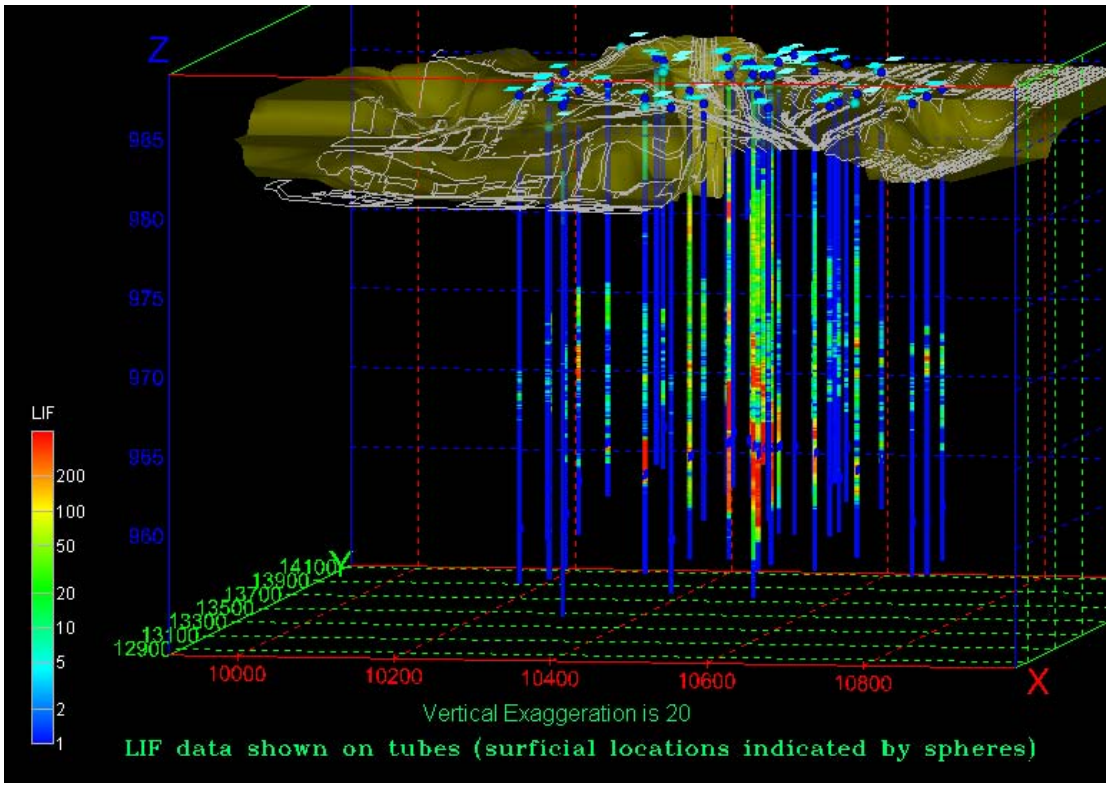


Figure 2. Direct visualization of LIF data as color spheres.

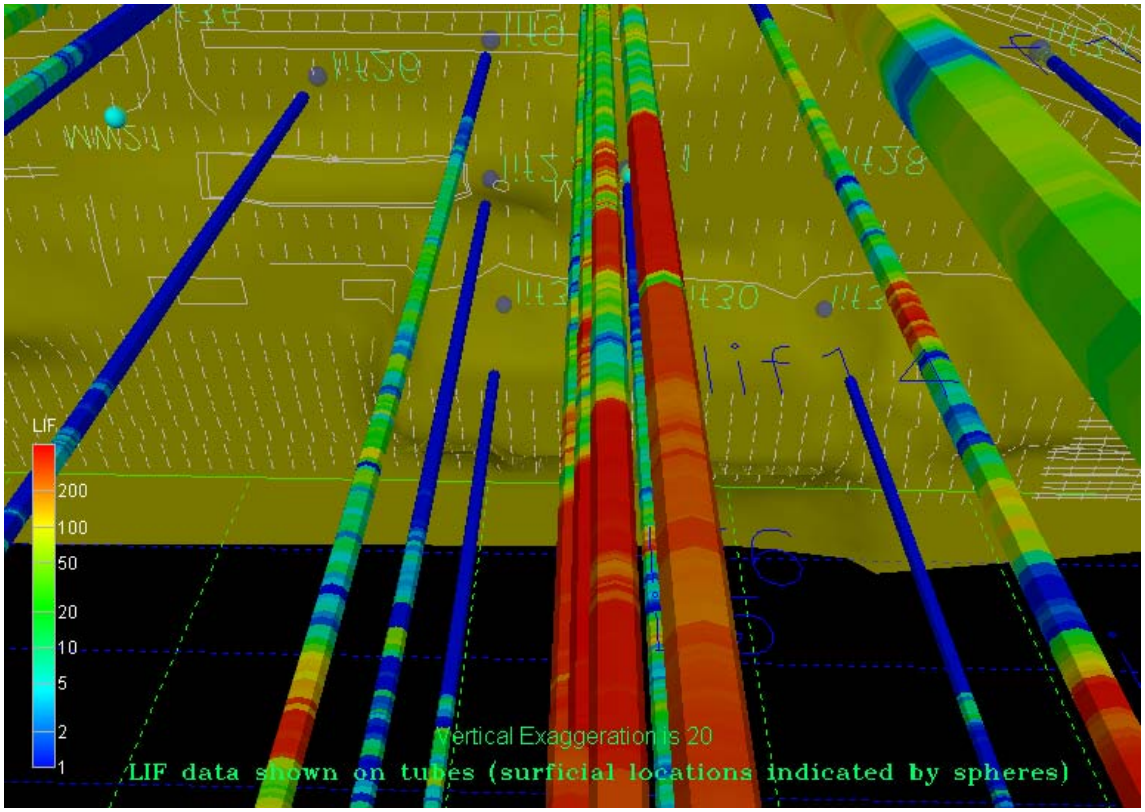
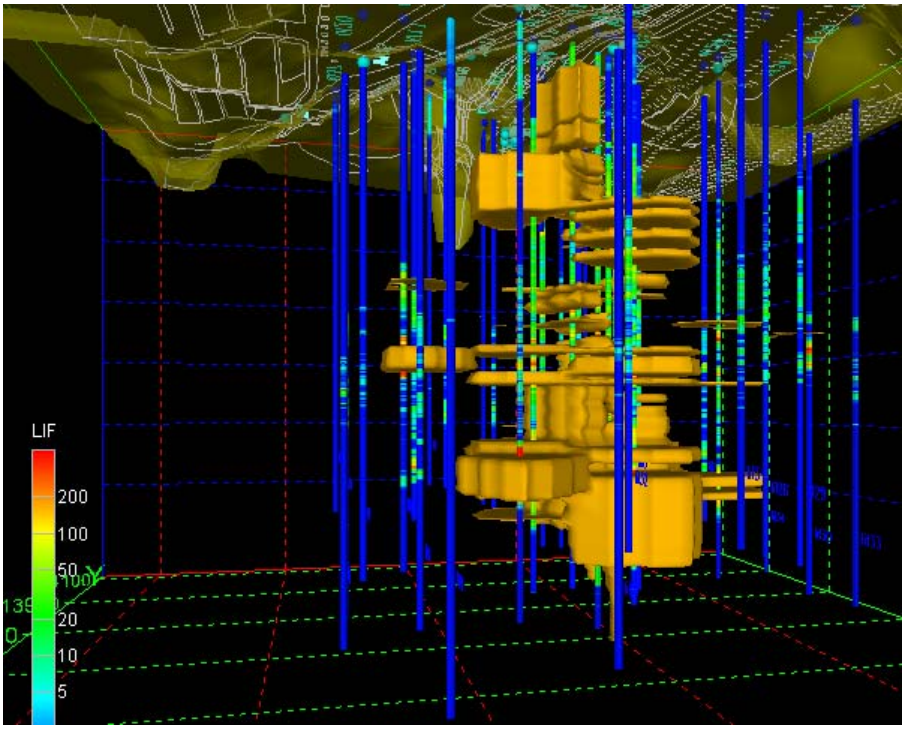
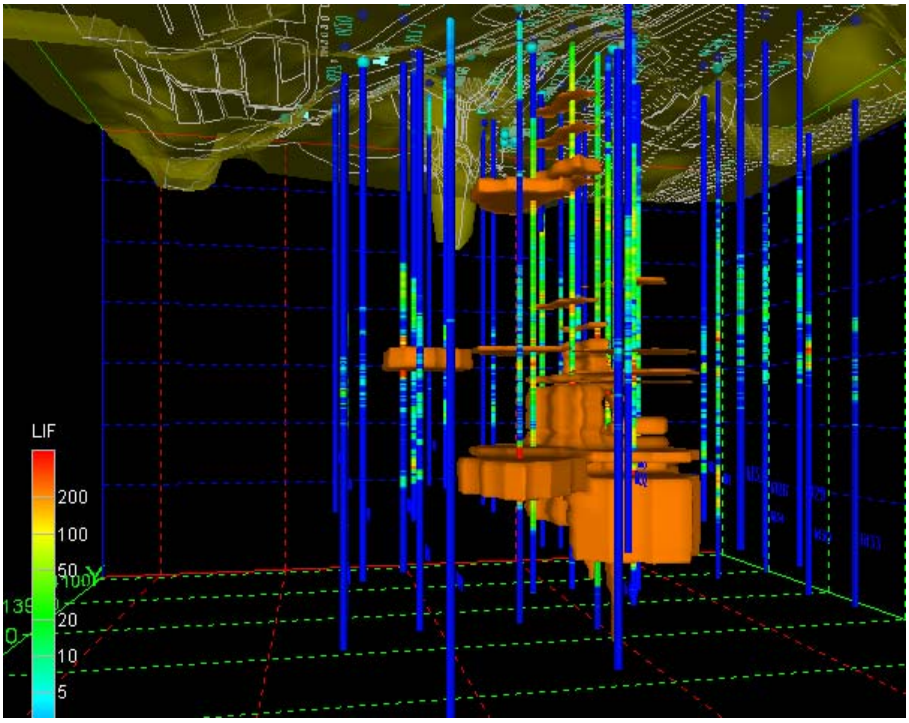


Figure 3. A closer look at the LIF data in a 3-D image.

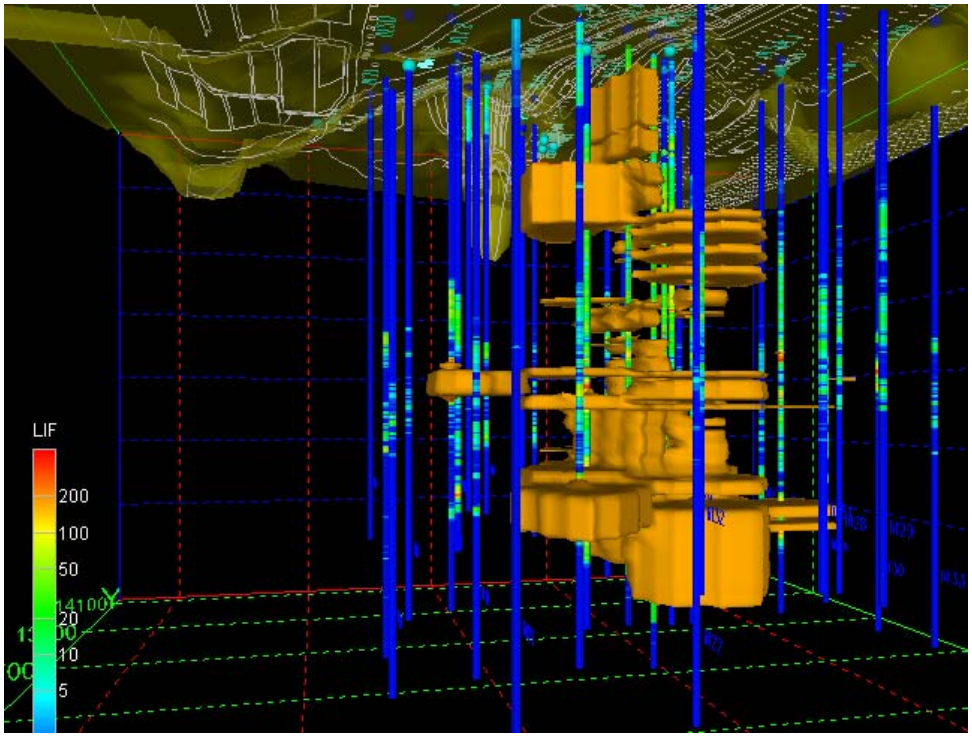


a)

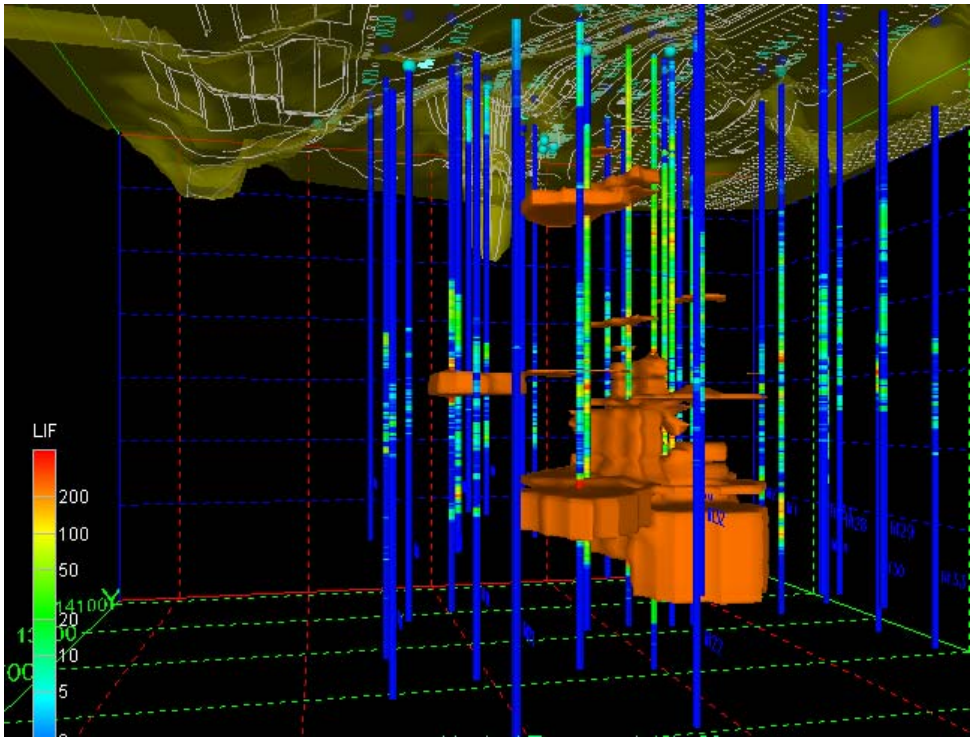


b)

Figure 4. LIF "plumes" at **a)** total fluorescence of 50 and **b)** total fluorescence of 100. Ratio of horizontal to vertical anisotropy is 1.



a)



b)

Figure 5. LIF "plumes" at **a)** total fluorescence of 50 and **b)** total fluorescence of 100. Ratio of horizontal to vertical anisotropy is 10.

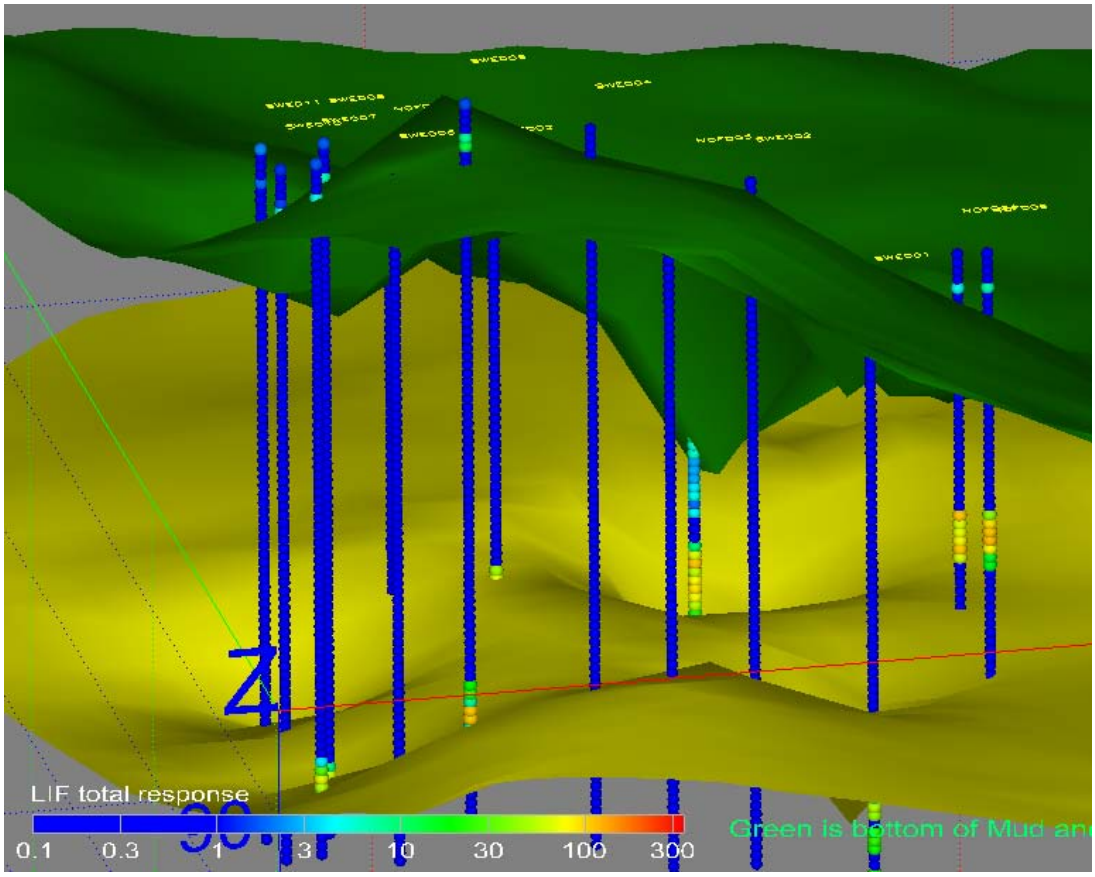


Figure 6. LIF data and geologic surfaces visualized. Green surface is the bottom of mud (silt or clay) formation and yellow surface is the bottom of sand formation.

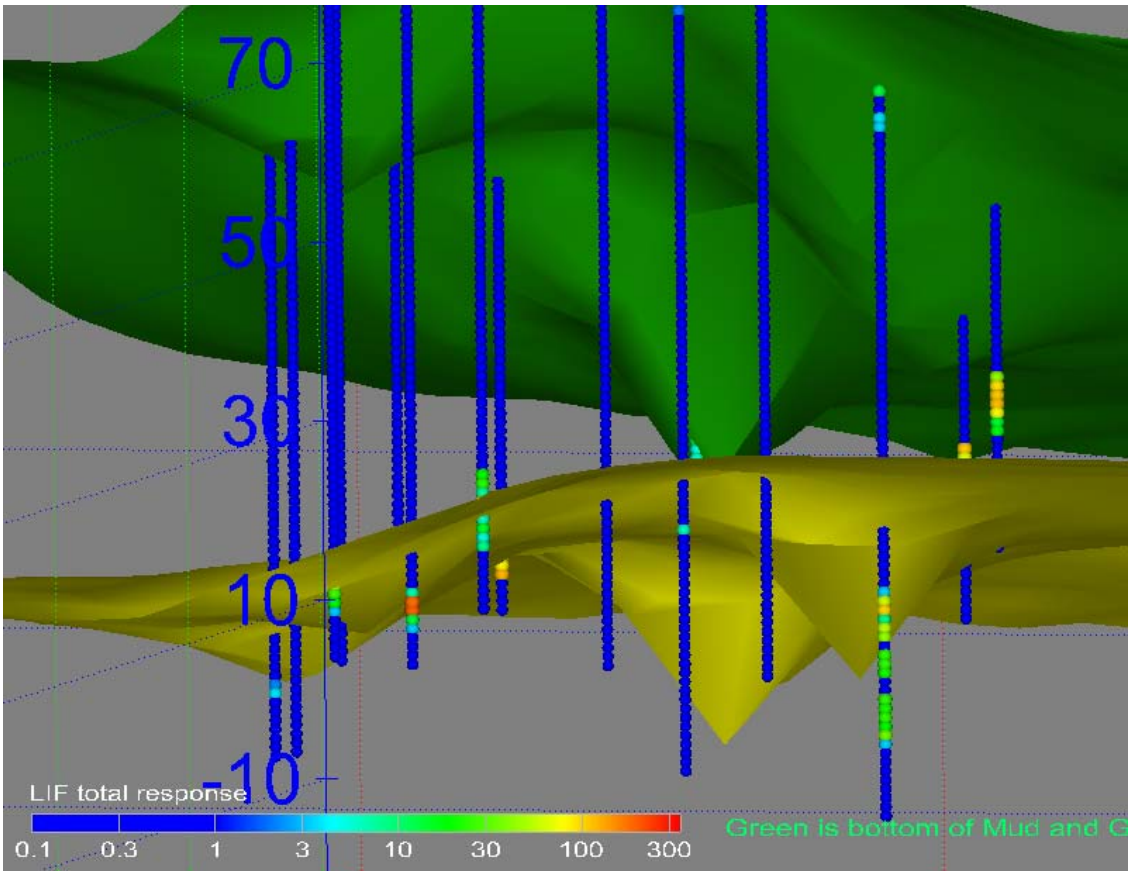


Figure 7. High LIF responses below the bottom of sand formation (yellow).

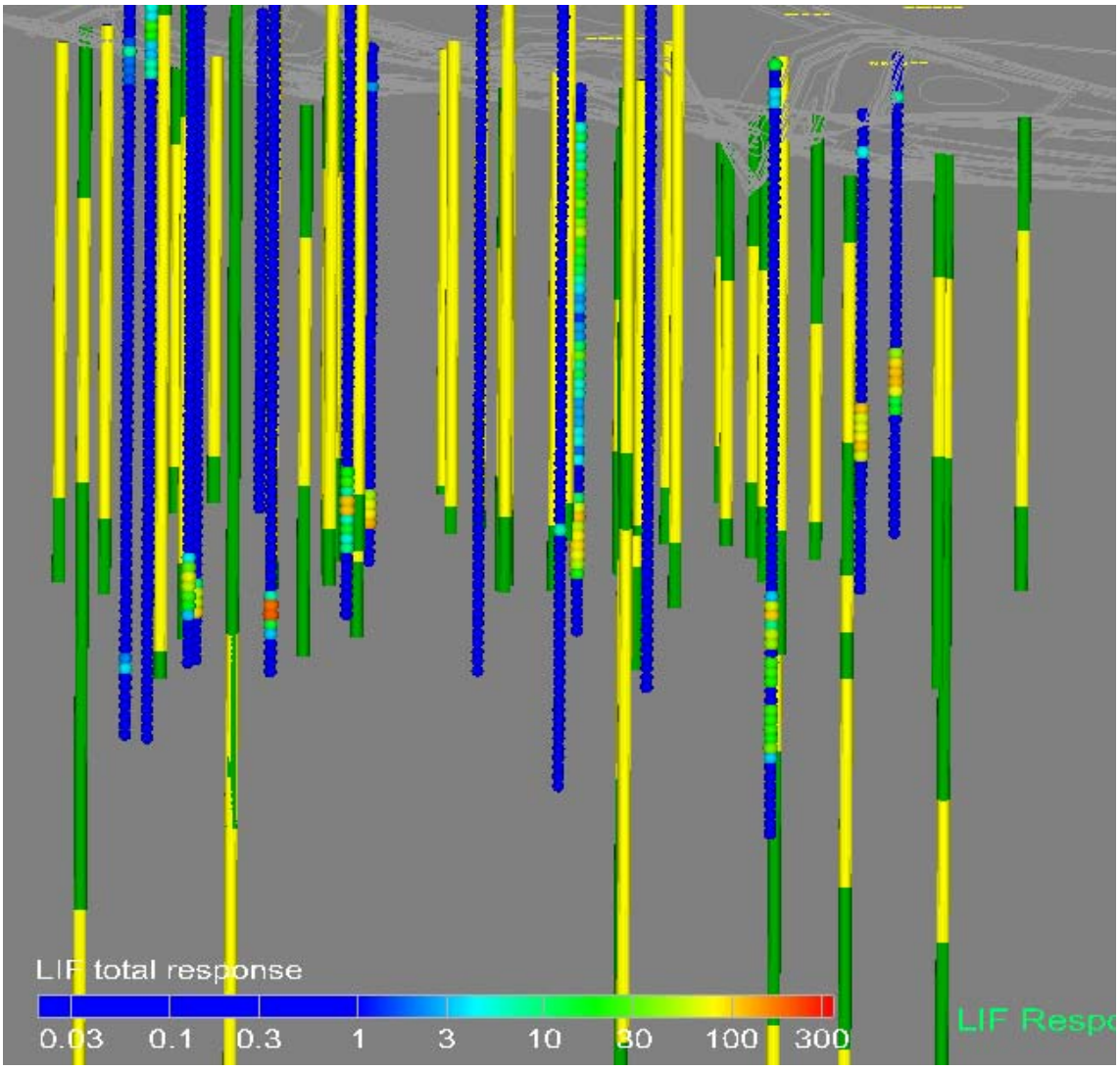


Figure 8. LIF data side by side with bore hole lithology. Green tubes represent mud (silt or clay) and yellow tubes represent sand.

NPDES Storm Water Permitting
Oil & Gas Construction Activities

Legal and Regulatory Overview

Janet McQuaid
12th Annual International Petroleum Environmental Conference, Houston, Texas
November 9, 2005

FULBRIGHT & Jaworski L.L.P.
Attorneys at Law

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EPA Semi-Annual Agenda
70 Fed. Reg. at 65,345 (10/31/05)

"On Monday, August 8, President Bush signed into law The Energy Policy Act of 2005 (H.R. 6, "the Energy Bill"). . . .

EPA Semi-Annual Agenda
70 Fed. Reg. at 65,345 (10/31/05)

"Section 323 of the legislation modifies section 502 of the Federal Water Pollution Control Act to define the term *'oil and gas exploration, production, processing, or treatment operations, or transmission facilities'* to mean . . .'

EPA Semi-Annual Agenda
70 Fed. Reg. at 65,345 (10/31/05)

"'All field activities or transmission facilities, including activities necessary to prepare a site for drilling and for the movement and placement of drilling equipment, *whether or not such field activities or operations may be considered to be construction activities*.' . . . "

EPA Semi-Annual Agenda
70 Fed. Reg. at 65,345 (10/31/05)

"EPA interprets this statutory language change as *excluding all construction activities associated with oil and gas exploration and production operations* from NPDES storm water permit requirements."

EPA Semi-Annual Agenda
70 Fed. Reg. at 65,345 (10/31/05)

"Reflecting the changes in the new law, EPA expects to *propose modifications to its current regulations* governing construction site storm water discharges for oil and gas activities regulated by the *Phase I and Phase II* storm water rules."

EPA Semi-Annual Agenda
70 Fed. Reg. at 65,345 (10/31/05)

- NPRM — December 2005
- Final Action — To Be Determined

Existing Statute
CWA §§ 402(p)(1)-(2) (1987)

- 2/87 – Congress tells EPA to require permits for storm water discharges from "industrial activities" by 1992
- 2/87 – Congress exempts storm water discharges from oil and gas activities

Existing Statute
CWA §§ 402(*l*)(2) (1987)

"The Administrator *shall not require a permit* under this section [402], nor shall the Administrator directly or indirectly require any State to require a permit . . .

Existing Statute
CWA §§ 402(*l*)(2) (1987)

"For *discharges* of stormwater runoff from mining operations or *oil and gas exploration, production, processing, or treatment operations or transmission facilities*, . . .

Existing Statute
CWA §§ 402(*l*)(2) (1987)

" *Composed entirely of* flows which are from conveyances or systems of conveyances (including but not limited to pipes, conduits, ditches, and channels) used for collecting and conveying *precipitation runoff* and . . .

Existing Statute
CWA §§ 402(*l*)(2) (1987)

"Which are *not contaminated by contact with*, or do not come into contact with, * any overburden, *raw material, intermediate products, finished product, byproduct, or waste products located on the site of such operations."*

* Mining Standard. 40 C.F.R. § 122.26(c)(1)(ii); *NRDC v. EPA,* 966 F.2d 1292, 1305-06 (9th Cir. 1992)

"Industrial Activity"
40 C.F.R. § 122.26(b)(14)(x) (1990)

"*Construction activity* including clearing, grading and excavation, *except* operations that result in the disturbance of *less than five acres* of total land area.

"Industrial Activity"
40 C.F.R. § 122.26(b)(14)(x) (1990)

Construction activity also includes the disturbance of less than five acres of total land area that is a part of a larger *common plan of development or sale* if the larger common plan will *ultimately disturb five acres or more*.

O&G Exempt Unless Contaminated 40 C.F.R. 122.26(c)(1)(iii) (1990)

- Reportable quantity of *hazardous substance* for which notification is or was required;
- Reportable quantity of *oil* for which notification is or was required; or
- Contributes to a *water quality standard violation*.

EPA Response to Comments Pages 86-87 (11/16/1990)

Industry: "Construction activities related to exempt oil and gas operations are exempt."

EPA: "To the extent that the construction activity is related to those activities exempted under the Act, and there is no contamination requiring a permit application, the Agency agrees."

1992 EPA Memorandum
33 F.3d 319, 320 n.1 (4th Cir. 1994)

Permit required for:

"Storm water discharges from *construction activities involving oil and gas facilities* (*e.g.*, access roads, drilling pads, pipelines, etc.) . . . ."

1992 EPA Memorandum
33 F.3d 319, 320 n.1 (4th Cir. 1994)

"The exemption afforded to *oil and gas operations* . . . applies *only to the oil and gas operation itself, not associated activities* that may fall under different parts of the definition of storm water discharge associated with industrial activity."

2001 EPA Letter to IOGA-PA
www.epa.gov/npdes/pubs/ioga802.pdf

"The Agency does *not* interpret the statutory exclusion . . . to refer to the clearing, grading, and excavation of land surfaces, i.e., *construction, that precedes such operational activities*.

2001 EPA Letter to IOGA-PA
www.epa.gov/npdes/pubs/ioga802.pdf

Therefore, the statutory references to *uncontaminated* and non-contact runoff *do not constrain EPA's interpretation.*"

"Deferral" Rule
40 C.F.R. § 122.26(e)(8) (2003)

With respect to small oil and gas construction activity:

"Discharges associated with small construction activity at such *oil and gas sites require permit authorization by March 10, 2005*."*

*Delayed to June 10, 2006. 70 FR 11,560 (9/9/05)

Storm Water Litigation

- *Appalachian Energy Group v. EPA*, 33 F.3d 319 (4th Cir. 1994) (dismissing appeal as not final agency action)
- *TIPRO et al. v EPA*, 410 F.3d 479 (5th Cir. 6/16/05) (dismissing appeal as not ripe), petition for rehearing pending
- *TIPRO et al. v. EPA*, 410 F.3d 964 (7th Cir. 6/13/05) (staying decision), supplemental briefs filed 11/7/05

Why The Fuss?

- Endangered Species Act Consultation
- Historic Preservation Consultation (res.)
- TMDL Consultation
- Site-specific SWPPP paperwork
- BMPs beyond industry standards
- Inspections and recordkeeping
- NOI's

New Statute*
CWA §§ 502(24) (2005)

"The *term 'oil and gas exploration, production, processing or treatment operations or transmission facilities'* means . . .

* H.R. 6, 109th Congress, 1st Sess. § 323

New Statute
CWA §§ 502(24) (2005)

[A]ll field activities or operations associated with exploration, production, processing, or treatment operations, or transmission facilities,

New Statute
CWA §§ 502(24) (2005)

[I]ncluding activities necessary to prepare a site for drilling and for the movement and placement of drilling equipment, *whether or not such field activities or operations may be considered to be construction activities*.

New Statute
CWA §§ 502(24) (2005)

[I]ncluding activities necessary to prepare a site for drilling and for the and placement of drilling equipment, movement and placement of drilling equipment, whether or not such field activities or operations may be considered to be construction activities.

EPA Semi-Annual Agenda
70 Fed. Reg. at 65,345 (10/31/05)

"EPA interprets this statutory language change as *excluding all construction activities associated with oil and gas exploration and production operations* from NPDES storm water permit requirements."

What Does CWA § 502(24) Mean? In Non-Delegated States for O&G[1]

- All field activities and operations
- "Associated With" O&G Activities [2]
- Unless site's discharge is contaminated[3]
- No five-acre limit on exemption

[1] *E.g.*, AK, AZ, ID, NM, OK, TX

[2] 68 Fed. Reg. 11,325 (3/10/05) (pipelines)

[3] 40 C.F.R. § 122.26(c)(1)(iii)

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Opportunities and Limitations of CBNG Produced Water Management Alternatives in the Powder River Basin

Thomas J. Osborne
Joel E. Adams
HydroSolutions Inc

ABSTRACT

The range of options utilized for CBNG produced water management in the Powder River Basin is changing in response to water quality and environmental issues. Direct discharge has been limited by the salinity and SAR of produced water in the western and northern portions of the basin where irrigation and fisheries occur. Favorable settings for off-channel unlined pits have become difficult to find in the highly layered Wasatch and Fort Union formations, and in areas with higher quality shallow groundwater. Opportunities for off-channel pits exist, however, thorough site evaluations of groundwater quality and migration pathways are becoming the rule. On-channel reservoir opportunities are limited by shortages of favorable sites, prior water rights, greater engineering design requirements, and permitting of incidental discharges in high quality watersheds. Larger, carefully screened sites and engineering controls provide some opportunities. Managed irrigation of un-treated water on amended soils, and treated water on partially amended soils using center pivots has been gaining popularity. Injection has had limited success since blanket sandstone or limestone receivers are thousands of feet deep, and shallow receivers have unpredictable performance. Centralized treatment using ion-exchange methods are gaining popularity where discharge to perennial streams is possible.

THE CBNG RESOURCE

Increased demand for natural gas and commensurate higher prices in North America have boosted the exploration and production of coalbed natural gas (CBNG) resources nationwide. The in-place coalbed methane resources of the United States are estimated to be more than 700 trillion cubic feet (Tcf), of which an estimated 100 Tcf may be economically recoverable, equivalent to a five-year U.S. supply at present consumption rates (1). Accompanying the CBNG gas production is over 14 billion barrels (Bbbls) (~1.8 million ac-ft) per year of produced water, according to a 2002 Argonne National Laboratory study. The Powder River Basin (PRB) of Wyoming and Montana (see Figure 1) contains an abundance of CBNG due to the thickness and number of coal beds in the Tertiary Fort Union Formation. However, it also results in some of the highest water/gas production ratios of any fields currently produced.

CBNG AND GROUNDWATER

Most gas in coal is stored on the internal surfaces of organic matter. Gas content generally increases with coal rank, depth of burial of the coal bed, and reservoir pressure. Fractures that permeate coal beds are usually filled with water; the deeper the coal bed, the less water is present, but the more saline it generally becomes. For gas to be released from the coal, its partial pressure must be reduced. This is accomplished by pumping water from the coal beds through a well field. Wells are typically spaced on 80 or 160-acre grid patterns. Unlike conventional oil and gas operations, which typically produce more water as the field ages, peak water rates from CBNG production occur at the outset (see Figure 2).

Water production falls markedly over time as the wells create overlapping cones of depression in the producing area. CBNG production depressurizes, but does not dewater the coalbed aquifers, since some hydrostatic pressure is desirable to maintain formation permeability. Once the fluid pressure is lowered in the coal seam, the methane is released and becomes available for production through the same wells (see Figure 3).

CBNG in the PRB is considered a “shallow” gas play, with production occurring from as many as 20 coal seams at depths of 250 to 2,500 feet. Ranchers and landowners rely on alluvial groundwater and the uppermost coal and sandstone aquifers and are concerned with effects of drawdown and aquifer depletion. However, economic supplies of CBNG are not likely to exist in the shallow groundwater system since the pressures required to confine the gas over a geologic time frame do not exist. Aquitards of claystone or siltstone usually overlie and separate the coalbed aquifers.

Regional groundwater studies by the USGS (2) and (3) have documented two relatively distinct groundwater systems; a shallow system which includes alluvial aquifers and bedrock aquifers shallow enough to be hydraulically connected to the alluvium; and deeper confined aquifers not having a direct hydraulic connection to nearby surface recharge sources or to the stream alluvium. Observations of paired monitoring wells along with modeling studies have shown CBNG-induced drawdown of overlying aquifers to range from 1% to 6% of that in the produced coal beds. Evaluation of well depths in Montana’s CBNG play indicates that 90 percent of private wells are less than 300 feet deep, while the same percentage of CBNG wells are deeper than 300 feet. In some areas, faults that offset the coal beds against other strata occur with regularity, limiting the zone of influence from CBNG drawdown.

PRODUCTION TRENDS IN THE POWDER RIVER BASIN

Monthly trends in CBNG and water production rates for Wyoming are depicted in Figure 4. Cumulative CBNG gas production in Wyoming through June 2005 was 1.685 Tcf with cumulative water production of 3.15 Bbbls (~400,000 ac-ft), from a total of over 14,000 wells. Montana's production has been much less, with cumulative CBNG production of about 0.04 Tcf and cumulative water production of 0.102 Bbbls (~13,000 ac-ft) from 495 wells through 2004 (4 and 5). Over the past 10 years water production rates have averaged 2.2 bbls water per MCF of gas, whereas the San Juan average is about 0.031 bbls water per MCF.

The CBNG production rate in Wyoming has leveled off since 2002. Figure 4 indicates that the rate of well drilling has slowed, likely due in part to the increased water quality regulation, such as Montana's electrical conductivity (EC) and sodium adsorption ratio (SAR) standards on the Tongue and Powder River, and Wyoming's regulation of impoundments.

PRODUCED-WATER MANAGEMENT ISSUES IN THE PRB

Issues surrounding the production and management of CBNG water are clearly among the most controversial of many regional water resource topics. Based on the most active current subjects of environmental regulation, proposed legislation and litigation, the hydrologic issues receiving the most attention in the PRB are:

- aquifer drawdown and concern for potential effects to springs, wells, and long-term groundwater availability;
- potential effects of direct or indirect discharge of CBNG-produced waters on the quality of irrigation water available from the Tongue and Powder rivers;
- interstate and tribal-state water quality regulations and allocation of assimilative capacity relative to salinity and sodium adsorption ratio (SAR);
- potential effects of seepage from unlined produced-water impoundments on groundwater and surface waters.

The approach to these issues varies significantly between Wyoming and Montana. Although an in-depth treatment of the regulatory programs governing CBNG produced water is beyond the scope of this paper, the principal regulatory tools used in the two states which address key issues of importance to CBNG water management are summarized in Table 1.

Going beyond the ordinary administration of water right law, the Montana DNRC in 1999 adopted the "Powder River Basin Controlled Groundwater Area" which sets forth additional requirements on CBNG production. Coal bed methane operators must offer water mitigation agreements to owners of water wells or natural springs within one-half mile of a CBM field proposed or within the area that the operator reasonably believes may be impacted by a CBM production operation, whichever is greater. This area will be automatically extended one-half mile beyond any well adversely affected. The mitigation agreement must provide for prompt supplementation or replacement of water from any natural spring or water well adversely affected by the CBM project, and subject to conditions as the parties mutually agree upon. The CGWA also specifies that hydrologic conditions in produced coal beds must be assessed by operators prior to field development to establish baseline conditions. Groundwater pressure monitoring in appropriate locations using dedicated monitoring wells is required. Data collected from testing and production

of CBM wells and any groundwater monitoring wells and springs will be available to the public and provided to the Montana Bureau of Mines and Geology.

The Wyoming DEQ has primacy for administration of the Class V underground injection control (UIC) well program for CBNG wells. Wyoming has adopted General Permits under this program which may be used by producers to facilitate injection of produced water. In Montana, the Class V UIC program is administered by the EPA, and there are no General Permits.

Wyoming has adopted policies specifically designed to protect the class of use of state groundwater resources. The Groundwater Pollution Control Division of the Wyoming DEQ has taken a regulatory approach similar to that used at leaking underground storage tank sites, requiring baseline characterization of shallow aquifers and groundwater quality, generally three monitoring wells around impoundments, a defined monitoring and reporting schedule, and a compliance plan if adverse impacts are observed. Montana's regulation of CBNG impoundments is through permitting by the BOGC and the MPDES program for all impoundments connected to a discharge point. Impoundments designed for infiltration could be subject to the state's Ground Water Pollution Control Discharge Permit.

Going beyond the pre-existing Clean Water Act regulatory program administered by the Montana DEQ, Montana adopted numeric standards for EC (electrical conductivity) and SAR (sodium adsorption ratio) for the drainages of Rosebud Creek, Tongue River, Powder River and Little Powder River, specifically in response to CBNG development. Wyoming chose not to adopt numeric standards after a review by a Technical committee. The standards vary by drainage basin and by season. The most restrictive values are for Rosebud Creek and the Tongue River, where the irrigation season monthly average standard for EC is 1000 µS/cm, and no sample may exceed an EC of 1500 µS/cm. The monthly average numeric water quality standard for SAR is 3.0 and no sample may exceed an SAR value of 4.5. These standards are currently the most pervasive limiting factor governing the assimilative capacity for CBNG discharges in Montana and also in the portion of the Wyoming PRB in these watersheds. The Northern Cheyenne Indian Tribe has also promulgated salinity and SAR water quality standards for the Tongue River which are both more and less stringent than Montana standards, depending on the parameter and season. Application of these standards by the Tribe and agencies is pending the Tribe's attaining, "recognition as a state" status under the Clean Water Act.

CBNG production from federal minerals is covered by the rules of the respective state, plus Bureau of Land Management (BLM) administration of applicable federal rules. Water produced by oil and gas wells located on federal or Indian leased/owned lands, and its subsequent disposal, is regulated by BLM under 43 CFR Part 3160, Onshore Oil and Gas Operations. This statute requires operators to comply with all applicable BLM standards for pits. The same requirements are established when approval is requested for removing water that is produced from wells on leased federal or Indian lands and is to be disposed of into a lined or unlined pit. BLM also has authority over design, construction, reporting, maintenance, and reclamation requirements for pits, which will vary depending on project specific parameters, and water analysis. BLM requires water analysis be taken at the current discharge point. A reclamation plan detailing the procedures expected to be followed for closure of the pit and the contouring and re-vegetating is required prior to pit abandonment (6).

PRODUCED WATER MANAGEMENT OPTIONS

Produced water management in the PRB has responded principally to water quality concerns and the regulations and policies that have followed. The principal water management options used in the PRB, along with their opportunities and limitations are summarized in Table 2. The options are generally listed in order of historical practice by the industry.

Direct Discharge

Direct discharge of untreated produced water has been the most common management practice in the eastern and southern portions of the PRB where the TDS and SAR of produced water is generally similar to or lower than the surface waters. It has become much more difficult to discharge untreated waters within the Tongue and Powder river basins since the salinity and SAR of the streams is generally less than that of the produced water. It has generally been the practice of the Wyoming DEQ to permit produced water discharges to these basins only when it can be demonstrated that the discharge will meet the quality of the Class II receiving water, i.e., the Tongue and/or Powder River main stems. Since Montana adopted EC and SAR standards for these streams, Wyoming has also reviewed permits for conformance to those standards, while accounting for any assimilative capacity.

Permits for direct discharge to the Tongue and Powder River drainages in Wyoming have been limited to tributaries where discharge is unlikely to reach the main stem channels. As the number of direct and indirect discharges has increased, however, some ephemeral tributaries have begun to show signs of intermittent or perennial flow. The Wyoming DEQ has increased monitoring requirements for new or renewal permits, and has required mitigation measures or contingency plans to avoid discharge to main stems. In Montana, only one untreated water discharge has been permitted; that being to the Tongue River between the Wyoming state line and the Tongue River Reservoir, in the total amount of 1600 gpm. This permit is currently up for renewal but has not yet been approved.

Interest in treating produced water to lower TDS and SAR has increased due to Montana's EC and SAR standards and limited assimilative capacity. The most popular treatment methods have been ion-exchange (IX) and reverse osmosis (RO). Various ion-exchange systems have been tested or applied in the PRB, including conventional, Higgins Loop (EMIT Technologies, Inc) and HYDRO (patented). These systems are generally designed to remove cations and bicarbonate alkalinity and will require additional treatment components if other anions require removal. Application of IX technology depends on site-specific conditions, including feed water chemistry, treatment objectives, proximity to a disposal well and cost (7). Water is treated to meet specific levels of SAR and EC, with reductions of up to 92 to 98% possible. Typically, treated and untreated water is blended to meet discharge requirements. RO treatment systems typically remove TDS from wastewater in two passes. Wastewater influent may require pretreatment to remove TSS, iron, and bacteria to prevent membrane fouling. Because contaminants are removed in proportion, SAR is changed little as the TDS is removed. Removal rates of up to 95% can be achieved, however, post treatment of SAR in the treated water is likely needed prior to discharge. Typically 5% to 8% of the influent flow from the treatment process must be disposed via commercial vendors or deep well injection. Treatment costs vary with the degree of ion loading and removal specified, but for RO are reported to range from $0.51 to $0.73 per BBL, and $0.35 to $0.63 per BBL for IX (7), inclusive of brine disposal costs. Another system based on natural zeolites is very similar to IX, capable of removing cations and bicarbonate alkalinity. These systems have lower capacities and require more vessel volume and retention time than conventional IX systems, but are suitable for some waters present in the basin.

Treating produced water is not always a panacea. It is an attractive option if the treated water can be discharged to and mixed with that of a perennial stream at levels which meet water quality standards. Discharging treated water to ephemeral or intermittent drainages requires that the discharge meet all water quality standards directly from the pipe, including trace elements which may not be removed by the treatment method. Treated water discharged to dry channels will, in most cases, result in the effluent quickly dissolving natural salts in the channel and soils, potentially resulting in salinity levels which could be greater than that of the initial produced water.

Absent the opportunity to discharge to perennial streams, treated water could be used for other beneficial purposes such as irrigation or other off-site use.

In some situations, treated water may be too clean to discharge. When the Wyoming Department of Environmental Quality recently planned to issue a discharge permit for 100 cubic feet per second (cfs) from a series of proposed ion-exchange treatment system, the state's Game and Fish Department objected that too much clean water could adversely affect the unique aquatic ecology of the sediment-rich Powder River. As a result, the permit was scaled back to 20 cfs.

Impoundments

Off-channel and on-channel impoundments have proven popular with industry in the PRB because they provide water storage capacity important in the early stages of production, and in many areas, landowners have been receptive to the new water sources. In Wyoming, the DEQ has defined "Off channel impoundments" as those receiving CBNG produced water and not sited within 500 feet of a designated water feature as defined on a United States Geologic Survey (USGS) 1:24,000 scale topographic map, or mapped alluvium or floodplains of stream systems. These water features include perennial and intermittent streams, dry washes, lakes, among others etc. "On channel" impoundments are those receiving CBNG produced water sited within a designated water feature or within the floodplain or alluvium of a stream system. The Montana DEQ has not specifically defined on- or off-channel sites.

The locations and designs of impoundments may be chosen to maximize storage and minimize infiltration, or vice versa, depending upon the overall water management strategy, permitting approach, and environmental factors. Impoundments may be on-channel or off-channel as dictated by the available sites, relative water qualities of the discharge and receiving waters, and the above-described rules. The highly layered stratigraphy of the Wasatch and Fort Union formations along with dissected terrain promotes horizontal seepage migration and makes for difficulties in locating suitable off-channel impoundment sites on ridge tops and in upland areas that avoid surface discharges. Valley-margin settings over bedrock or colluvium may be favorable if shallow groundwater is not high quality and seepage does not migrate to surface drainages. Site-specific hydrogeologic investigations have become commonplace in evaluating potential impoundment locations.

Use of existing stock reservoirs and new on-channel impoundments are often favored by landowners since these features have a value that will succeed the life of CBNG development. On-channel reservoirs fall into two categories under the Wyoming SEO rules: 1) those with a capacity of 20 acre-feet or less and dam crest height of 20 feet or less, and, 2) those exceeding these criteria, which are subject to special regulations. All on-channel impoundments must be equipped with a controllable low-level outlet and a self-regulating runoff control bypass facility to prevent runoff from up to and including the average annual flow from being stored. On-channel impoundments are subject to the same groundwater compliance monitoring provisions as off-channel impoundments. On-channel impoundments in Wyoming have been designed and permitted for controlled CBNG water discharge to downstream drainages from runoff events ranging from the 2-year 24-hour storm to the 100-year 24-hour storm. In each case however, the applicant must demonstrate that the event-related discharge will comply with the water quality standards on that drainage. This generally entails development of design discharge hydrographs and mixing calculations for water quality parameters of concern.

Water balances performed on small off-channel CBNG produced water pits indicate that seepage typically accounts for over 90% of the total annual water budget, with evaporation and consumptive uses responsible for the remainder. Infiltration rates typically range from 0.05 to 0.3 feet per day for new construction, to 0.01 to 0.05 feet per day for older on-channel reservoirs with sediment accumulation. Although CBNG water is often of better quality than that of the shallow

groundwater system, soils and surface sediments of the semi-arid PRB often contain abundant soluble salts which can drive TDS of infiltrating produced water to high levels. Groundwater monitoring beneath one CBNG reservoir revealed TDS levels in excess of 70,000 mg/l (8). Seepage quality beneath some sites has meet existing groundwater standards if site lithology and salt content are favorable.

Managed Irrigation

For the CBNG industry in Wyoming and Montana, "managed irrigation" with CBNG produced water has been defined as: *the application of applied soil science, water chemistry, and agronomic principles to utilize CBNG produced water in a beneficial manner to produce forage for livestock and wildlife while protecting soil physical and chemical properties* (9, 10, 11). Its suitability as a water management alternative depends on many factors, including produced water chemistry, site and soil characteristics, landowner objectives, and project economics. The sodium bicarbonate water produced with CBNG is inherently problematic for irrigation. The primary physical processes associated with high sodium concentrations are soil dispersion and clay platelet and aggregate swelling. The forces that bind clay particles together are disrupted by excessive sodium, causing swelling and soil dispersion, resulting in reduced infiltration, reduced hydraulic conductivity, and surface crusting (12). High levels of bicarbonate in alkaline soils exacerbate sodium effects by precipitating calcium carbonate, making calcium unavailable in the soil solution, and raising SAR. The adverse effects of the elevated sodium and bicarbonate levels in CBNG produced water are typically managed by land-spreading gypsum to add calcium and elemental sulfur to lower soil pH. Alternatively, produced water may be treated before application, however soil amendments may still be necessary.

CBNG produced water has been effectively utilized by managed irrigation projects on approximately 2,000 acres in the PRB (7). Some PRB operators have applied CBNG-produced water as irrigation using center pivots and atomizers. The design of the irrigation system depends on the quantity of water, SAR, and the characteristics of the land being irrigated. Irrigation with CBNG is not regulated by the CWA, and a NPDES permit is not required if the water is applied in an agronomic manner and if there is no direct communication (i.e., saturated flow) between applied water, shallow groundwater and surface water. In Wyoming, CBNG operators are required to obtain a permit from the State Engineer's Office and a permit to construct from the DEQ. In Montana, the DEQ would likely require that the irrigation plan be reviewed for potential need for a discharge permit prior to irrigation. Operators must manage agronomic practices to prevent impacts to soils due to the elevated SAR if clay-rich soils are present.

Managed irrigation may be a good option where the landowner desires more forage production on existing agricultural land, or where rangeland with suitable soils can be developed. Generally, suitable soils would be those of moderate clay content, salinity and sodicity.

Injection

Injection wells are regulated under the EPA Underground Injection Control, or UIC program. In Wyoming, the UIC program is administered by the Department of Environmental Quality. Injection wells for CBNG Produced Water will fall under either a Class II or Class V UIC permit. The State of Wyoming has Class V General Permits for injection of CBNG produced water into the Wasatch, Fort Union and Fox Hills formations. In Montana, the UIC program is administered by the EPA. There are no general UIC permits in place in Montana.

Injection of CBNG water has met only limited success to date. According to WDEQ (13), a total of 308 CBNG Class V injection wells have been permitted in Wyoming through mid-2005. Of this total, 60 were still active and injecting a combined 14,592,692 BBLS/yr. This amounted to approximately 3% of the total water produced. A study (7) of 21 CBNG injection wells in the Fort

Union formation of Wyoming found that the average total depth of injection wells was 1,441 feet, the average injection rate per well was 36.7 gpm, and that about one in two injection wells were failures. The duration that successful wells operated varied widely, from less than one month to over 12 years. Four injection wells averaging 4,191 feet deep targeted the Lance and Fox Hill formations, however, only one of these was successful.

The inherent geologic and hydrologic properties of the Fort Union Formation limit injection potential. Rock units below the level of the nearest perennial stream are usually already saturated with water, and have very little available porosity in which to store additional water. Confined coal or sandstone units in the Fort Union formation are naturally under pressure, and the total volume of those units capable of storing injected water is very small, often less than 1% by volume. The rate and amount of injection is limited by EPA regulations requiring that the injection pressure must remain less than the "fracture gradient", which, at higher pressures would result in artificially fracturing the overlying rock, possibly creating pathways to other aquifers or the surface.

Re-injecting into producing or depleted coal beds offers limited opportunities at this stage in the play, so as not to interfere with existing gas production. Sandstone units offer potential as receivers, however unlike the coal beds, they are a discontinuous and often "shoestring" shaped, making their location and extent unpredictable. Shallow injection (300 ft or less) into the Wasatch or Fort Union formations is constrained by differing water quality, potential connections to surface waters, existing wells and springs, restrictions on the allowable injection pressures, and accordingly the injection rates, and permitting difficulty where any of these factors are indicated or exceeded.

Water Marketing

Some operators have found opportunities to sell or provide gratis produced CBNG water for other beneficial uses. Some of these uses have included dust control for roads and mines, drilling makeup water, livestock watering, irrigation, and flow augmentation. The opportunity to market produced water is often a function of proximity to source of demand. As the industry has expanded, discussion has begun regarding potential collaboration to market water outside the immediate area of the PRB play to high demand industrial or commercial users via pipelines. Predicting the long-term availability of CBNG produced water may be one of the major hurdles to successful off-site water marketing.

Perspective

In the early years of CBNG production in the PRB, produced-water management of was driven by traditional economics and practices. More recently, challenging basin-wide water quality issues, environmental regulations which transcend state borders, and an array of complex socio-political forces have squeezed out some practices and stimulated innovations. A dichotomy has developed concerning CBNG-produced water in the PRB. In the ground, the water is regulated and regarded as an essential resource for livestock and domestic use. But when co-produced to the surface with CBNG, the water becomes a contaminant under the Clean Water Act, requiring a permit for any discharge to waters of the states. Further complicating water management issues, the Tongue and Powder rivers flow from Wyoming, with one set of regulations, into Montana, with a different set. The "water as a resource" versus "water as a pollutant" dichotomy has posed unique water management challenges for gas producers and regulatory agencies. The outlook for sustained higher gas prices is driving development of new, but costlier methods of water management, such as treatment, managed irrigation, deep injection and water re-use/marketing. The intensity surrounding regulation and management of CBNG produced water is likely to affect many aspects of water resource management throughout the West.

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Table 1. Regulatory Tools Used In CBNG Produced Water Management.

Issue	Wyoming	Montana
Aquifer Drawdown & Protection of Water Rights	Water Rights Administration (SEO); General Permit for Class V CBNG injection wells (DEQ)	Water Rights Administration plus Controlled Ground Water Area (DNRC); Class V injection wells (EPA) (no General Permit)
Irrigation Water Quality	WYPDES Permit process and TMDLs (DEQ)	MPDES permit process And TMDLs (DEQ)
Unlined impoundments	Groundwater quality "Compliance Monitoring Plans" attached to 14A OGCC pit permits, and WYPDES permits (OGCC & DEQ GWPCD)	MPDES permit covering all components of the water management system (BOGC & DEQ)
Assimilative capacity	Review of Individual and General WPDES discharge permits (DEQ); Timetable to implement 'Watershed-Based' permitting	Review of Individual MPDES discharge permits; application of EC & SAR standards (DEQ)

Abbreviations: WSEO- Wyoming State Engineer's Office; DNRC- Montana Department of Natural Resources and Conservation; TMDLs- Total Maximum Daily Loads; DEQ (Wyoming and Montana, Department of Environmental Quality; OGCC- Wyoming Oil and Gas Conservation Commission; GWPCD- Wyoming DEQ Ground Water Pollution Control Division; BOGC- Montana Board of Oil and Gas Conservation; EC- Electrical Conductivity; SAR- Sodium Adsorption Ratio.

Table 2. Summary of Main Produced Water Management Options Used in the PRB**.**

Options	Opportunities	Limitations
Untreated discharge to stream channels	• Where CBNG water is as good or better than surface water quality • Where streams have sufficient assimilative capacity • Where discharge all infiltrates prior to reaching perennial streams	• Difficult where CBNG water is poorer quality than surface water • Natural salts in ephemeral channels may degrade discharge in short distance
Off-channel impoundments	• Remote sites with favorable topography • Provides distributed water for livestock • Provides recharge to shallow aquifers	• Rough terrain provides few sites • Ridgetop sites may lead to seepage breakout • Seepage dissolves salts in soils leading to excessive TDS and impacts to groundwater quality
On-channel impoundments	• Uses existing stock ponds • Takes advantage of natural mixing • Leaves facility useable by landowner	• Must accommodate water rights • Greater design requirements • Mixing analysis must show compliance with standards • More regulatory permitting
Misters (untreated water)	• Takes advantage of high summer ET rates • Minimal permitting	• Seasonal limitations • Salts precipitate over down-wind area • Post-use reclamation less predictable
Injection wells	• If present, thick Ft. Union sand bodies and under-pressurized coal beds offer targets • Deep regional aquifers may be more predictable • Wyoming's Class V General Permit facilitates CBNG injection	• Wasatch & Ft. Union sands are un-predictable in extent and performance • Thin overburden (<300 ft) limits the allowable injection pressures, and accordingly the injection rates • More reliable receivers are often too deep for landowners to tap
Managed irrigation	• Produces valuable crop for landowner • Takes advantage of high ET rate	• Must either amend the soils or treat the water to counteract high SAR • Most producers don't own land, so leasing must be arranged • Producers must learn to become farmers • Post-irrigation reclamation must be addressed
Treatment and discharge	• Design can meet variety of water quality standards • Blend with un-treated water • Greater public acceptance	• Designing for high initial water rates may lead to oversizing • Cost and commitment limits other options • Natural salts in ephemeral channels may degrade discharge in short distance • Could be too clean for native prairie streams
Water marketing; Off-site beneficial uses	• Capitalize on chronic water shortages in region • Turn liability into asset	• Difficult to customize treatment if end-use not well defined • Declining rates of produced water may limit long term investments • Lack of nearby customer base

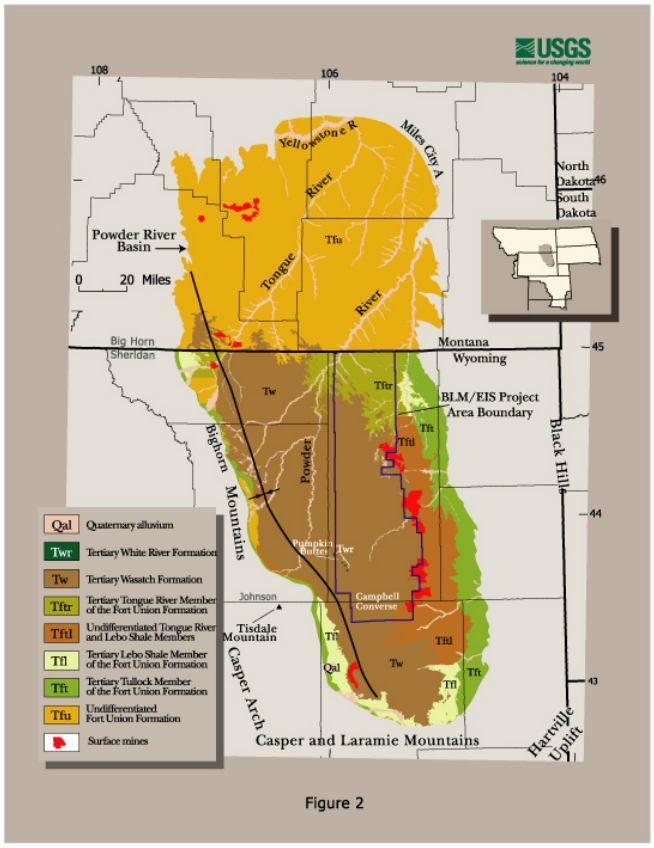
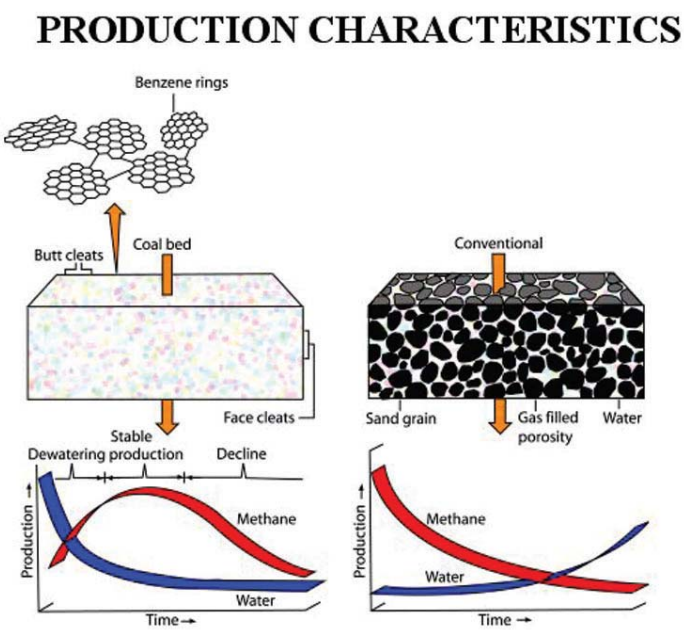
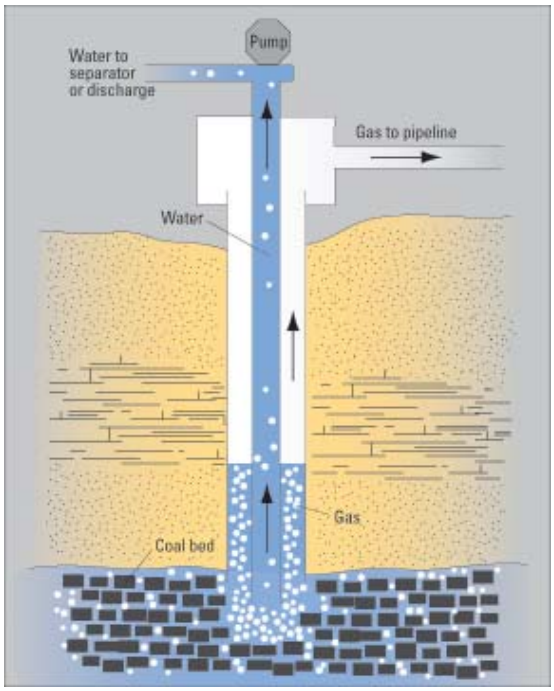


Figure 1. Tertiary geological map of the Powder River Basin, Wyoming and Montana (14)

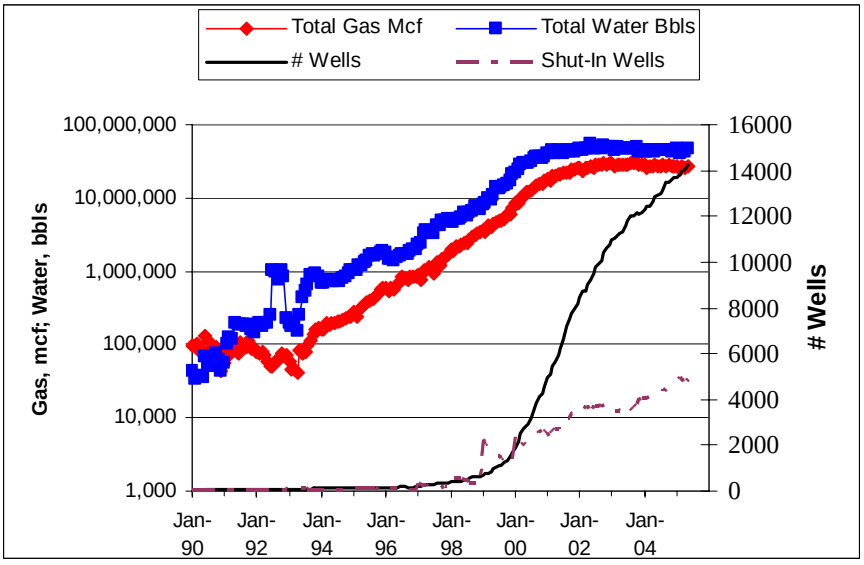


Source: (15)

Figure 2. Produced Water versus Gas Trends: CBNG and Conventional Gas



Source: (16)
Figure 3. Schematic of Coalbed Methane Well.



Source: (17)
Figure 4. Monthly CBNG and Water Production Rates in Wyoming's Powder River Basin

OVERVIEW OF REGULATIONS FOR POTENTIAL BENEFICIAL USE OF OILFIELD PRODUCED WATER IN CALIFORNIA

Raymond Ouellette, Rajagopalan Ganesh, and Lawrence Y.C. Leong

Kennedy/Jenks Consultants

ABSTRACT

Produced water generated during oil production by thermal (steam) recovery processes is often disposed by Class II deep well injection within the oil production zones. Such in-field injection may increase the water to oil ratio and reservoir pressure, resulting in decreased oil production. Reducing Class II injection through alternative disposition of the produced water may enhance oil field development and crude oil production.

The use of produced water involves treatment to meet specified water quality goals, delivery and storage of treated water and safe disposal of the residuals. Each of these activities is or may be subject to regulation by Federal, State and local agencies. A focus of this project, jointly funded by USDOE, Aera Energy LLC and Kennedy/Jenks Consultants, is to identify alternate end uses for produced water in the immediate vicinity of the San Ardo oilfield, located in the Salinas Valley near the Central Coast of California. This paper presents an overview of regulatory requirements and issues related to treatment, delivery, storage and waste stream management to potentially use produced water in the San Ardo area and concludes that the regulatory obstacles are, in some respects, significant. The regulatory agencies include United States Army Corps of Engineers; the California Regional Water Quality Control Board; California Department of Water Resources; California Department of Fish and Game, and Monterey County Water Resources Agency. The types of permits required vary with mode of treated water delivery and location of treated water storage facilities.

Background

Production of crude oil through enhanced steam recovery is typically associated with a large amount of produced water. Although the quality of the water produced varies, these waters typically have salinity concentrations from 1000 mg/l to more than 350,000 mg/l. The waters are generally high temperature (150 to 200 ^{o}F), and usually contain elevated levels of silica, boron, ammonia and dissolved organics. These waters are often injected into Class II wells. Such in-field injection may increase the produced water-to-oil ratio and reservoir pressure, resulting in lower oil production and higher oil production costs. Reducing Class II injection through alternative disposition or use of treated produced water may enhance oil production and increase recoverable reserves in an oilfield.

Limited water resources and increases in population have put a strain on California's water supply. Several reports indicate that the overall water demand for California will exceed supply after the year 2020. The effective and efficient treatment and use of the produced water could create a win-win situation for both oil producers and water users by increasing oil recovery while increasing much needed water resources.

This DOE funded (No.DE-FC26-02NT15463) study evaluates the potential for treatment and use of produced water from an oilfield near San Ardo in Monterey County, CA. Around San Ardo, the Salinas Valley groundwater basin provides most of the water supply needs. Due to high water demands from population growth and agriculture, groundwater extraction exceeds the sustainable yield of this basin. The dependence on groundwater has resulted in a long-term average overdraft of 19,000 acre-feetfeet per year (AFY) in the Salinas Valley basin. The overdraft conditions have resulted in seawater intrusion for about six miles into the northern Salinas Valley, before the Salinas River empties into the Pacific Ocean. A successful produced water treatment process could make available more than 4,000 AFY of water from the San Ardo oilfield. This is about one-fifth of the annual overdraft.

This paper describes the Federal, State and local regulations related to delivery, storage and use for possible end uses of the treated oilfield produced water in the project area. It must be emphasized that the uses identified in this paper are based on initial screening of potential alternatives.

Alternative Use and Water Delivery Options

In this section, the possible uses for the treated water, based on preliminary evaluations, are presented. These possible uses, however, must satisfy stringent regulatory, economic, user-perception, and long-term reliability criteria prior to actual implementation. Furthermore, depending on the type of use, implementation may also require complex water trade arrangements with one or more water agencies. Finally, large storage facilities (hundreds of million gallons capacity) would be needed if there is a large seasonal variation in water demand for the identified end use. Such limitations may increase the overall costs of the project significantly and render the use non-viable. These uses are presented in this section only to facilitate a discussion on regulatory requirements for various alternatives in the following sections.

The potential users of treated oilfield-produced water in the San Ardo area are limited because, among other things, there are no regional conveyance facilities in the Salinas Valley other than the Salinas River. Potential uses of the treated water in the project area could include the following:

- Agricultural applications in nearby farms, including those that currently utilize groundwater, and those landowners who desire to bring land into agricultural production
- Agencies at downstream locations
- Industrial applications
- Creation of wetlands in the Salinas Basin

Agriculture

A report by Monterey County Water Resources Agency (MCWRA, 2000) indicates that approximately 48,000 acres of farmland are available in the upper Salinas Valley Basin (San

Ardo area). About 3,500 acres of farmland are located within five miles of the oilfield, downstream of the Salinas River. The key crops cultivated in these farms include broccoli, lettuce, spinach, carrots, potato, cabbage and chile peppers. Data from MCWRA indicate that the average amount of water applied for irrigation in 1995 in the Upper Salinas Valley was about 2.75 AF/acre (MCWRA, 1998). Hence, all of the treated produced water generated from this project could, theoretically, be used on less than 2,000 acres of farmland. Treated water from the oilfield might be delivered through the Salinas River or by direct pipeline.

The limitations in the use of oilfield water for agriculture include i) efforts required to convince farmers to use recycled water for irrigation; ii) need for a large storage system/alternate use arrangement during the low demand season (September – May) since the oilfield produced water is generated throughout the year; and iii) transportation / conveyance of the water to farmers.

Agencies at Downstream Locations

The MCWRA is a public agency that has been charged with the long-term management and preservation of water resources in Monterey County. In order to prevent seawater intrusion into the Salinas Valley Basin and protect agricultural water use, MCWRA has undertaken two major projects: 1) the Salinas Valley Water Project (SVWP), and 2) the Castroville Seawater Intrusion Project (CSIP). The key components of these projects are to identify alternate sources of water for agricultural use in the Salinas Valley Basin and prevent seawater intrusion by reducing groundwater drawdown at the lower Salinas Valley Basin. The main objective of the SVWP is to increase the capacity of the Nacimiento Dam reservoir by i) modifying the Nacimiento Dam spillway; and ii) constructing a diversion facility to divert part of Salinas River water for the CSIP. Under the CSIP, the excess water from the Salinas River diversion would be diverted to the Castroville service area for agricultural use. This would replace the groundwater that is currently pumped for agricultural irrigation in this area, and would help prevent seawater intrusion into drinking water aquifers. The operational objective of the project is to stop seawater intrusion into the Salinas Basin and provide up to 1000 AFY net groundwater outflow to Monterey Bay. In addition, the average annual Salinas River diversion capacity is about 12,000 AFY. By comparison, the amount of water that would be generated by treatment of produced water at the San Ardo oilfield is about 4,000 AFY. However, one of the key limitations in this use is the loss of added water during transport due to evaporation and percolation, particularly in dry weather conditions.

Industrial Use

A power plant located at King City, California was initially considered as a candidate for using treated produced water for its cooling water needs. This plant is located about 30 miles north of San Ardo, downstream of the Salinas River. For this application, delivery of water through the Salinas River is not possible due to the beneficial use requirements in 40 CFR 435.30 (discussed below). In addition, delivery of water by a new, unsubsidized 30-mile pipeline appears to be cost prohibitive. Hence, this option is no longer under consideration.

Wetlands Development and Other Applications

The treated produced water could conceivably be used to create wetlands in the Salinas Basin. Such an end use would require a biodiversity study to identify potential benefits to animal and plant species in the project area. However, potential use of treated produced water for wetlands development may require long-term reliability of water supply from the oilfield. This may be a concern if the oilfield operations are curtailed for any reason or terminated at the end of the economic life of the oilfield or for other reasons.

Water Trade/Water Delivery Issues

The following water trade/delivery scenarios were considered for alternative disposition of the treated water:

- Convey the treated water directly (through hard pipe) to agricultural growers in the vicinity of the project area and allow a partnering water agency to obtain the agricultural end-user's unused groundwater. This groundwater would be discharged into the Salinas River, which would provide the conveyance system for downstream diversion to areas impacted by seawater intrusion and declining water levels.
- Provide treated produced water to a water agency that would discharge it directly to the Salinas River for downstream diversion to areas impacted by seawater intrusion.

Regulations for Delivery, Use and Storage of Treated Produced Water

Water quality requirements vary with the use and the mode of delivery. In addition, delivery of treated water through the Salinas River must address water rights issues for downstream users. Finally, permits related to the structural integrity of the containment basin and water quality must be obtained if the water is stored during periods of low demand. This section describes the agencies and regulations related to the above activities.

Table 1. Activities regulated and responsible agencies for potential delivery, use and storage of treated produced water

Agency	Activities Regulated
Central Coast Regional Water Quality Control Board	Water/waste quality issues related to treatment, delivery, storage and end use
California Water Resources Control Board – Water Rights Division	Water rights/water allocation issues if treated water is discharged into the Salinas River
California Department of Water Resources –Division of Safety of Dams	Storage of treated water near surface waters
US Army Corps of Engineers	Storage facilities near surface waters, if federal funding is involved

Monterey County Planning and Building Inspection Department	Grading permits for storage of treated produced water
California Department of Fish and Game	Activities which alter stream flows (e.g. construction of discharge structures in the river bank)

Regulations Related to Water Quality

Central Coast Regional Water Quality Control Board

The Central Coast Regional Water Quality Control Board (CCRWQCB) is the principal regulatory agency responsible for overseeing the discharge of any water that could impact California water resources in this region. This authority comes from the Porter-Cologne Water Quality Control Act (Porter-Cologne) that established the California State Water Resources Control Board (CWRCB) and nine Regional Water Quality Control Boards. The CCRWQCB is one of these nine regional boards.

The CCRWQCB, in its role of implementing the State Policy for Water Quality Control, has adopted a Basin Plan that identifies the beneficial uses of the various existing water resources in the region, including surface and ground water. Any discharge from this project would most likely occur within the Salinas Hydrologic Unit. This hydrologic unit is subdivided into various sub-units and each sub-unit has its own set of beneficial uses.

All beneficial uses are protected by the development of water quality objectives that, in turn, are used to establish local waste discharge requirements (WDRs). The WDRs must also comply with the existing State Implementation Policy related to the National Toxics Rule (NTR) and the specific California Toxics Rule (CTR).

Authorization from the CCRWQCB is required for any discharge that may have an impact on the region's water resources. Two types of authorization are issued. The first is the National Pollutant Discharge Elimination System (NPDES) permit, a national program delegated to the State and Regional Boards for implementation. This permit affects any discharge to a water of the U.S. (primarily surface waters). The second is a set of WDRs which are a California authorization intended to protect state waters not covered by the NPDES permit program. In practice, it is common for the CCRWQCB to issue one permit that covers both program requirements.

The permit requirements under various water discharge (delivery) and water use scenarios are described below:

Water Quality Regulations Related to Delivery of Treated Produced Water through the Salinas River

In this scenario, produced water for irrigation would be treated and then discharged directly to the Salinas River. The treated water would need to meet the requirements found in the following regulations and/or policy documents:

- 40 CFR 435.30 *et seq*,

- 40 CFR 435.50 *et seq*,
- NTR)the CWRCB Policy for Implementation of Toxics (Resolution 2000-015 as amended by Resolution 2000-30),
- The Anti-degradation Policy (Resolution 68-16), and
- The narrative and specific numeric water quality objectives contained in the Central Coast Basin Plan for the Salinas River and any groundwater that might be impacted by the discharge.

40 CFR 435.30 *et seq.*

This is a federal regulation promulgated by the Environmental Protection Agency (EPA) in which effluent guidelines for the oil and gas extraction industry were developed. Specifically, 435.30 *et seq.* addresses discharges from the "onshore" subcategory of the oil and gas extraction industry that are located landward of the inner boundary of the territorial seas. In section 435.32, the effluent guideline states, "there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment" to the west of the 98th meridian. Unless wastewater discharge to the Salinas River is subject to other provisions contained in 40 CFR 435 (see below), the Water Board will not allow any discharge of wastewater to the Salinas River.

40 CFR 435.50 *et seq.*

This section of the federal regulations addresses onshore facilities "located in the continental United States and west of the 98th meridian for which the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters". Onshore facilities in the San Ardo Field are located in the continental United States and they are located west of the 98th meridian. The wastewater would be treated before discharge to meet quality standards for use in agricultural applications. In 435.51, the term "use in agricultural or wildlife propagation" is defined to include produced water of sufficient quality to be used for agricultural uses. Discharge would be subject to certain limitations specified in 40 CFR 435.52, namely, that the produced water (after treatment) does not exceed a daily maximum limitation for oil and grease of 35 mg/l and other limitations as discussed below.

NTR and CTR, Water Board Implementation Policy

These two regulations and the State Board policy are intended to limit the discharge of "toxics" into navigable waters. CTR, promulgated in 2000, specifies water quality criteria for 128 priority pollutants based on their toxicity to aquatic species. These limits, presented in EPA Federal Register (USEPA, 2000), are generally lower than NPDES discharge limits based on Basin Plan criteria. Compliance with some of these limits would require significant, additional treatment processes and increased treatment cost.

Anti-degradation Policy

The CWRCB adopted this policy in the late 1960s to maintain the quality of existing water resources. Under this policy, the discharge must not cause a degradation of the existing quality of the receiving water unless it has been demonstrated that the change will be consistent with

maximum benefit to the people of California, that it will not unreasonably affect the present and anticipated beneficial use of such water, and that it will not result in water quality less than that prescribed in the policies.

Central Coast Basin Plan

The CCRWQCB is responsible for adopting and implementing the Basin Plan that defines beneficial uses of surface and groundwater in the project area and sets narrative and numerical water quality objectives for the designated use. Accordingly, the beneficial use designations for the Salinas River include Municipal and Domestic Water Supply (MUN) as well as Agricultural Water Supply (AG) and Industrial Water Supply (IND) uses among other uses. In addition, the Basin Plan defines narrative and numeric criteria for groundwater recharge and agricultural use when the water is not delivered through the river. The Water Board may require that the produced water be treated to meet the appropriate criteria of the narrative and specific numerical water quality objectives as identified in the Basin Plan prior to discharge.

Water Quality Requirements Related to Delivery of Treated Water for Agricultural Irrigation by Hard Piping

In this scenario, the end user would get deliveries of treated water for agricultural irrigation by a hard pipe. The CCRWQCB would require a WDR for this use. The treated water must meet the following water quality criteria:

- Crop water quality requirements
- Water quality requirements of the Central Coast Basin Plan

Compared with delivery through the Salinas River, there would be fewer monitoring requirements. For example, a shorter list of parameters may be issued to routinely treat and report. These differences may or may not alter the treatment process train for the produced water.

Water Quality Requirements Related to Discharge of Groundwater into the Salinas River through Water Trade Agreement with Farm Owners

Under this scenario, treated water delivered for agricultural use would be traded for groundwater. The “freed–up” groundwater would then be pumped into the Salinas River for conveyance to downstream users. The groundwater pumped into the river must meet all the requirements specified in an earlier section for the discharge into the Salinas River.

Regulations Related to Water Rights

California Water Resources Control Board – Division of Water Rights

The CWRCB Division of Water Rights (DWR) is responsible for ensuring that water is shared equitably among all downstream users, based on historical or legally determined water rights. As such, the DWR establishes removal quotas or pumping limits based on the adjudicated volumes of water provided by the various sources. The addition of new sources of water, such as treated produced water, would likely need to be allocated to downstream users. The process

requires identification of the volume of water and the potential downstream user. The permit to appropriate the released water by the identified user would be based on the amount of water delivered and potential losses during conveyance. The proposed use of the appropriated water must also be specified. The permit application must indicate the details of the diversion works (direct diversion by pump, storage dam, etc.). The permit application would have to be filed well in advance of the construction of diversion work.

The proposed project may be subject to the California Environmental Quality Act (CEQA) which requires agencies to consider environmental effects. This process may involve obtaining a certification of exemption, a negative declaration or a preparation of a full Environmental Impact Report (EIR). More details regarding the appropriation process is provided in the three pamphlets issued by the DWR (CWRCB 2000, 2000a, 2001).

Regulations Related to Storage

Due to potential differences in supply and demand for the treated produced water storage facilities may be required to store the water produced during non-peak demand period. For example, the peak water demand for agricultural use is between June and August. Depending on the location, size and funding source various agencies would be involved in the permit process for construction of storage facilities. Permit requirements from these agencies are briefly discussed below:

California Department of Water Resources – Division of Safety of Dams

The Division of Safety of Dams (DSD) would be involved with any project that creates a structure to impound water in a "navigable" water as defined by EPA if the structure is greater than 25 feet high or the impoundment contains more than 50 acre-feet of water. In this role, the DSD would ensure that the structural integrity of any jurisdictional dam (storage structure) is adequate for its intended purpose. Furthermore, the DSD would usually be the State representative for the US Army Corps of Engineers.

Water storage structures that are built solely for agricultural use and not located across a stream channel, watercourse, or natural drainage area are not considered to be a dam and not subject to the jurisdiction of the DSD. (California Water Code (CWC), Division 3, Part 1, Chapter 1, §6004(b)). The jurisdiction of the DSD normally applies to any structure that is 25 feet or more in height or has or will impound a capacity of 50 acre-feet or more. (CWC, §6002). However, the CCRWQCB would be involved because any water discharge into the storage area could have the potential to impact waters of the state, i.e. groundwater.

US Army Corps of Engineers

The Corps of Engineers is not normally involved in such projects unless there is direct U.S. Government funding for the construction of a dam. As such, the Corps of Engineers would rely upon the DSD to oversee any construction that does not involve federal funding (i.e., the COE will be directly involved only if the project receives federal funding).

Monterey County Planning and Building Inspection Department

The feasibility of local water storage in surface impoundments (ponds) on individual farmlands was explored. In order to install a pond, a farmer would be required to obtain grading permits from the Monterey County Planning and Building Inspection Department. As part of the permit process, the farmer must submit five sets of plans for each area where ponds are planned.

Central Coast Regional Water Quality Control Board

Chapter 3 of California Code of Regulations (Title 27, Division 2, Subdivision 1) classifies wastes to determine where the wastes can be discharged (stored). This chapter presents geologic and siting criteria for waste management units to store various waste streams. The CCRWQCB is responsible for defining the storage siting criteria if seasonal storage is required for treated produced water. However, an exemption from this requirement might be available if the waste (treated produced water) meets the criteria for inert waste as defined by section Ch15:§2524. An "inert waste" is a subset of waste that does not contain hazardous substances or soluble pollutants at concentrations in excess of applicable water quality objectives and does not contain significant quantities of decomposable waste.

Regulations Related to Wildlife Protection

California Department of Fish and Game

Any structure constructed for discharge of treated water into a waterway would require a stream alteration permit from the California Department of Fish and Game (CDFG). In addition, CDFG is responsible for ensuring sufficient water flow downstream of any water diversion point at all times in order to protect fish and wildlife resources. (Section 5937, Article 2, Chapter 3, Part 1, Division 6 of the California Fish and Game Code). Approval from the CDFG may be required to obtain water appropriation by an end user.

Summary

In summary, an evaluation of regulations indicates that, for delivery of treated water to agricultural land by hard pipe, the treated water quality must meet crop water quality and basin plan water quality requirements. WDRs must be obtained from the CCRWQCB. For delivering water via the river the following would be required:

- The released water must facilitate agricultural or wildlife restoration requirements.
- The water quality must be in compliance with NPDES, NTR, CTR and anti-degradation requirements.
- A permit from the CWRCB must be obtained for water appropriation.
- Approval from the CDFG may be required for the appropriation of water to verify that the loss of water will not have an adverse effect on fish and wildlife resources.

Finally, storage of water during periods of low demand may involve regulations from the DSD, Monterey County Environmental Health & Planning Department, and the CCRWQCB depending on storage location and water quality.

References

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3) California State Water Resources Control Board Division of Water Rights. *How to file an application to appropriate water in California*. Sacramento, CA: State Water Resources Control Board, 2000.

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CONTROLLED RECOVERY INC.

CLOSED LOOP SOLIDS HANDLING SYSTEMS

Controlled Recovery Inc. is an oilfield disposal company that has been in business since 1991. During this time we have seen a marked trend for oil producers to be more in tuned to the environment and have worked tirelessly to improve their impact on surface lands and ground water. The most obvious and lasting impact during drilling operations are, of course, the reserve pits. The utilization of closed loop drilling systems will eliminate this problem.

Reserve pits, while convenient, present several risk and cost factors. The risk factors include leakage through liners, overflow, personal injury, wildlife impact, and area exposure. The costs associated with pits include excavation, lining, increased location size, fencing, dewatering post TD, encapsulating solid waste, and either burying or removal of solid waste. The most potential for cost is the long term liability a producer will incur with the use of these pits. Utilization of a closed loop drilling system will eliminate or reduce this potential liability.

We at Controlled Recovery (CRI) have developed a system that efficiently manages drilling waste in a clean, controlled manner. Originally closed loop programs incorporated a type of steel pit that required a backhoe to scoop drill cuttings from the steel pit and deposit them into a dump truck. This technique caused some what of a mess by the cuttings overflowing from the backhoe bucket while transferring the cuttings. Once the cuttings were loaded into the dump truck there was often leakage from the truck during the transfer to a disposal site. This has lead to shutdowns of drilling operations when the Oil Conservation Division has received complaints of this contamination. Problems and operations such as this spurred CRI into action.

We use a track and sealed bin set-up to collect and transport these cutting with no spillage or further contamination. The tracks come in three pieces of 30 foot sections that are connected by use of pins. When connected this track system is 90 foot in length. We assemble these sections behind the steel mud pits using either a fork lift or a boom truck. They are spotted with consideration of where the shell shaker is situated and where the centrifuge and de-watering system are to be located. This track system is very low profile to allow for the bins to be located as low as possible. When the rail system is situated we align and unload two bins for collection of cuttings. The track system allows for two bins to be on the rails at the same time. This allows for unloading into one bin and when it is full we pull it forward while moving the empty in its place to allow for continuous filling with cuttings in a smooth transition. These bins are loaded and unloaded with roll-off trucks. Our track system is designed for loading and unloading from either end depending on the particular rig and location. The bins we use have a capacity of twenty cubic yards and are sealed to allow for fluid containment if needed. This means that during pickup operations there is no leakage of cutting or free fluids. When we pickup a loaded bin we also install an empty bin so that there are two bins on the rails at all times.

The tops of the bins open by sliding doors. This allows maximum opening to facilitate the dumping of solids into the bins from the shale shaker slides, the centrifuge, and other de-watering units that may be used during the closed loop process. While we do not provide or operate solids control equipment we have worked closely with all the service companies to minimize any problems with these combined operations. We also recommend the use of a diaphragm pump to keep as much free liquid pumped off of the bins as possible. This fluid is re-circulated back into the mixing tanks for further use. We have these pumps or the drilling rigs will provide them if needed. We also incorporate the use of a "bin mover" to pull full bins forward if a roll-off truck is not on location. This device is a winch setup on a dolly system powered by batteries attached to the dolly.

There is a general misconception that a closed loop drilling program is vastly more expensive than a conventional pit program. Given the correct circumstances a closed loop system could be <u>much less expensive</u>. Several factors that determine the cost of a closed loop system are, depth of well, size of hole, length of drilling time, and of course the proximity to a disposal facility. The following are some actual cost incurred by various producers:

Well A} 32 miles from our facility; well drilled in 18 days; 324 cubic yards of cuttings; 9622 foot TD; Total cost of CRI **$19321.26**
Well B} 56 miles from our facility; well drilled in 27 days; 546 cubic yards of cuttings; 12,923 foot TD; Total cost of CRI **$24588.38**
Well C} 188 miles from our facility; well drilled in 20 days 144 cubic yards of cutting; 4964 foot TD(we ran closed loop system on long string with oil-based mud only); Total cost of CRI **$18244.15**
Well D) 18 miles from our facility, well drilled in 14 days, 402 cubic yards of cuttings; 8796 foot TD; Total cost of CRI **$15112.84**

Typically, solids control equipment costs approximately the same as our total charges. This includes the centrifuge, de-watering system, and personnel. Consequently, when a typical pit is dug, lined, de-watered, and closed out, it is not much if any more costly to incorporate the closed loop system. The elimination of possibly long term liabilities associated with pits is, to coin a phrase, **Priceless**.

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FURTHER ADVANCES IN PRODUCED WATER DE-OILING UTILIZING A TECHNOLOGY THAT REMOVES AND RECOVERS DISPERSED OIL IN PRODUCED WATER 2 MICRONS AND LARGER

M.J. Plebon, Marc Saad, Serge Fraser
EARTH (Canada) Corporation
Montreal, Quebec Canada

ABSTRACT

In upstream oil and gas operations, saline water is co-produced with the crude oil. On a global spectrum, it is estimated that 3 barrels of water is produced for every barrel of crude oil [1]. As the asset matures, the ratio of water produced vs. crude oil begins to increase. In North America, the ratio is approaching 10:1. Treatment and disposal of produced water is becoming a leading economic factor in the viability assessment of the asset. This is especially so with offshore platforms where produced water must meet and exceed environmental regulations.

EARTH (Canada) Corporation have developed and validated a technology, Total Oil Remediation and Recovery (TORR™) [2], [3], [4], [5] to remove and recover dispersed oil in water 2 microns and larger. The technology is a combination of filtration, coalescence and gravity separation. Solutions for several challenging aspects of produced water properties have been developed and tested, through both field trials (onshore and offshore) and laboratory experimental simulations. Results obtained have been measured with an advanced video imaging particle size-distribution apparatus that measures samples on line and in real time. The results show that the technology has been successful in polishing produced water to oil-in-water concentrations of less than 10 mg/L without the need for chemicals or additional heat. The theory behind the technology will be explained and laboratory and offshore field results will be presented to support the technology's claims.

KEYWORDS – Produced Water Polishing, dispersed oil recovery, oil/water separators, oil recovery, de-oiling.

TECHNOLOGY OVERVIEW

The technology is a multi-stage adsorption and separation system having the capacity of multi-phase separation of large and small oil droplets (free-floating and emulsified) present in produced water. This is done by means of an adsorbent media, the Reusable Petroleum Adsorbent (RPA®, the media) [6], [7], and [8]. This material is a polyurethane-based, oleophilic, hydrophobic, non-toxic, media coalescing agent. The technology is also available in axial flow version.

The technology's separation process consists of routing the oily water to its inlet. The oily water passes through multiple vessels containing media cartridges and a recovery chamber. The media continuously adsorbs the oil emulsions, coalesces and desorbs them into larger oil droplets. In the recovery chamber, oil droplets desorbed by the media float to the top of the chamber in accordance with Stoke's Law. Inside the top of the vessel, the final separation occurs between the oil, gas and the water. The oil and gas are retrieved for re-use. The effluent water from the technology is treated to the customer's requirements. The third vessel is a standby for redundancy. (See Fig. 1)

Technology Operation Parameters

Although upstream oil and gas production and produced water characteristics can vary from one operation to the other, the technology has reached a stage in produced water treatment where it is developed and tested to operate within the following parameters: (See Fig. 2)

- Oil Densities: API° 15 and above.
- Fluid Temperature: up to 100 ºC
- Solids management capability
- Oil concentrations up to 2000 mg/L
- Oil droplet and oil emulsion diameters down to 2 µm
- Flow rates up to 60,000 BWPD

Additionally, depending on the characteristics of the produced water to be treated, the efficiency of the system can be enhanced by providing optimized solutions on a case-by-case basis. This implies optimizing the two basic principles behind the technology: oil coalescence and gravity separation.

Measurement Methods

The major measurement method used to evaluate the performance of the process is the Visual Process Analyzer (ViPA) [9]. This combines a high-resolution video microscope with an image analysis system. It captures images of the particles in a process flow and allows the monitoring and analysis of those particles in real time (See Fig. 3 & 4). Information on the shape, size, optical density and fourteen other parameters are recorded for each particle in the image before the data is saved and the next image is captured. Up to eight particle types – or sub-populations – can be stored. Approximately fifteen images are analyzed each second.

Oil in water emulsions - as all liquid in liquid emulsions - is characterized by their almost perfectly spherical shape. In sharp contrast, sand particles are crystalline and therefore very different in shape to the oil droplets. The analyzer can differentiate such geometries and organize them in a database.

This measuring device can plot recorded parameters as an overall distribution for each or all sub-populations. The graphs are reported on screen and on the optional 4-20 mA output. The analyzer is also equipped with a comprehensive suite of trend analysis software. It determines the trends and trigger alarms. This provides vital time, especially on the field, before a process goes out of specifications, to take corrective action and prevent process upsets.

This measurement tool allowed recording findings both in the laboratory and in the field. It monitored oil and sand size distribution and concentration between the stages, based on particles sizes within the volume of produced water.

Basic Separation Theory

The removal of oil and grease from produced waters can be accomplished by the use of several well-known and widely accepted techniques. However, the performance of any given separation technique will depend entirely on the condition of the oil-water mixture. Present techniques for the separation of oil from water are based on their difference of density. Stoke's Law states that rising velocity (V_r) is a function of the square of the oil droplets' diameter.

Equation (1) $V_r = g\, d^2 (\rho_w - \rho_o) / 18\, \eta$

Where V_r = rise velocity of oil droplet
g = acceleration due to gravity
ρ_w = density of water
ρ_o = density of oil
d = oil particle diameter
η = viscosity of water

From Stoke's Law, it can be seen that droplet size has the largest impact on the rising velocity rate. Consequently, the bigger the droplet size, the less time it takes for the droplet to rise to a collection surface and thus the easier it is to treat the water. The oil in the produced water can be present as free-oil, and/or emulsified, and/or dissolved states in different proportions. This oil droplet size distribution is one of the most important factors affecting the design of oil-water separators.

Free-oil is defined as an oil droplet of 150 microns, which will float immediately to the surface due to its large size and high rise velocity. An emulsion is defined as oil which is dispersed in the water in a stable fashion due to its small diameter and thus to its low rise velocity.

Emulsions can be classified into two categories: mechanical and chemical emulsions. Mechanical emulsions are created through the process of pumping, large pressure drops through chokes and control valves. Chemical emulsions are sometimes intentionally formed using chemicals to stabilize the emulsions for an industrial process need or other use. Gravity separation is the mechanism most commonly used for the removal of oil from wastewaters. This process primarily affects free oil. Tight oil emulsions and dissolved oil will not be removed by gravity separation alone. The objective in treatment of wastewater containing emulsified oils is to destabilize the emulsion so that the oil will separate by gravity or flotation. Essentially what is done is to promote inter-droplet contact with the purpose of developing larger droplets that will be easier to remove. Once the emulsion is broken, the same removal techniques applicable to free oil can be utilized. Small oil droplets are always difficult to separate. The smaller the droplets, the lower their rising velocity will be. A prerequisite for efficient separation is, therefore, that oil droplets coalesce (become larger and rise more rapidly).

A large number of simple gravity oil separation devices are available, varying from API (American Petroleum Institute) separators to Parallel Plate Interceptor (PPI) and Corrugated Plate Interceptor (CPI). The API gravity separator removes oil globules of 150 microns or greater where PPI and CPI separators can remove oil droplets down to 30 microns.

The second common method of oil and grease removal is through induced (IGF) or dissolved (DGF) gas flotation. Gas is introduced (either at atmospheric pressure or dissolved under pressure) to produce bubbles, which tend to attach to the oil droplet, decrease its specific gravity and float it quickly to the surface. Rapid oil removal is achieved when compared to gravity separation alone. Finally, it is often necessary to use chemical coagulants with flotation units. Chemicals such demulsifiers, alum, ferric chloride and cationic polyelectrolytes are used to improve the efficiency of oil and grease removal.

Another factor that affects the rise velocity of an oil droplet is the acceleration force (see Stoke's Law). Hydrocyclones are mainly governed by the centrifugal (g-force) applied to a spherical droplet in a centrifugal separation field. A liquid-liquid hydrocyclone separates free and dispersed oil from wastewaters with an applied centrifugal force many orders of magnitude greater than gravity (usually between 2000 to 3000 g). Centrifugal force causes the heavier water phase to migrate to the vessel wall while the lighter oil phase forms a central, low-pressure core from where it is recovered. Treatment chemicals may enhance hydrocyclone performance by facilitating emulsion breaking and droplet coalescence. Field applications showed that emulsions larger than 15 to 20 microns are removed efficiently by hydrocyclones.

The centrifuge is another enhanced gravity separation process, which combines high acceleration forces (5000 to 10,000 g-force) and a large settling area to simultaneously separate dispersed oil down to 3 to 7 microns droplets from oily-waters.

Filtration, another category of the oil separation process, is used but in limited applications due to its high maintenance cost requirements. In filtration, oily water is passed through a porous medium with or without the addition of treatment chemicals.

Applied pressure is used to overcome the flow resistance of the filter medium. Oil is usually retained and removed in the medium. The end of the filtration run is indicated when the filter medium becomes excessively contaminated with oil, at which point the medium must be cleaned or replaced. A single or multi-bed media material can be used as filtration medium. The most commonly used are sand, anthracite, crushed walnut and pecan shells, which can be used as a single-media or a combination of those. All of these materials must be backwashed or replaced when saturated which will create subsequent treatment and disposal problems (frequency of backwashing depends on service but 24 hour cycles are not uncommon). Performances vary widely depending on the type of filter, the operating conditions and the oily water's unique characteristics.

The Challenge of Removing Small Oil Droplets

Even under favourable conditions, oil droplets smaller than about 30 μm in water are known to be quite difficult to separate. Oily water with small droplets < 30 μm may then represent such a high proportion of the oil content that it is impossible to achieve discharge specifications with conventional equipment. It is important to fully understand the characteristics of the produced water. The size distribution curve for the dispersed oil in water must be measured in order to effectively address the issues and meet and exceed the set discharge targets.

Fine Emulsion Coalescence and Recovery

The uniqueness of the technology is in its ability to remove and recover dispersed oil droplets 2 microns and larger thus covering the broadest spectrum of the hydrocarbon size distribution curve. Laboratory measurements were conducted and analysis of the performance of the two-stage radial technology design system was monitored. Special emphasis was placed on observing the technology's ability to address the handling and recovery of small oil emulsions (in the ranges 2 – 5 μm and 2 – 10 μm). (See Table 1 & 2) The visual process analyzer was utilized to measure the performance results. (See Fig. 5)

The oil injected in this process had an API density of 20. The technology was treating the water at a rate of approximately 600 BWPD (equivalent to 3.8 m^3/hr, the design flow rate for the unit) and a water temperature of 23 ºC. The above measurements were taken when the unit had treated 641m^3 (4031 bbls) with continuous inlet oil concentration of 800 – 1000 ppm. Total inlet concentration into the technology was approximately 800-1000 ppm. Oil emulsions having diameters in the range 2 – 5 μm constituted 7.5 ppm of the overall concentration, while oil emulsions in the range 2 – 10 μm constituted 30ppm of that same overall value. Treatment of these emulsions in the two-stage technology shows that it is capable of removing up to 90% of oil emulsion having diameters in the range of 2 – 10 μm and up to 70% of oil emulsions in the range of 2 – 5 μm.

The nature of the tests (heavy-oil, low temperature, high inlet oil concentration…) contributes to lowering the efficiency of the unit in small oil emulsion handling. It is expected that this performance be enhanced in favourable field conditions (higher operating temperatures, lower concentrations…).

OFFSHORE FIELD TRIAL RESULTS - NORTH SEA

Trial A

Context of Field Trial

A field trial for the testing of the performance of the technology in treating the produced water (PW) on a FPSO (Floating Production, Supply and Offloading) vessel was recently conducted in the North Sea. Seven days were allocated for the offshore trial that was divided upon three test locations. These locations were slipstreams off the PW line downstream of two separate hydrocyclones (HC-1 and HC-2), and downstream of a degasser unit. The trial allowed for the demonstration of the performance of the technology's process in terms of oil recovery and lowering the PW oil concentrations to levels meeting the OSPAR 2006 legislation requirements and a target of 6mg/Liter.

Field Trial Unit

The field trial unit consisted of a two-stage 10.7bar rated system. The unit had a nominal flow rate capacity of 300 BWPD and maximum operating pressure and temperature of 10bar and 100ºC respectively. A twin-set of bag filters (5 micron filters) was installed upstream of the technology's process to capture any solid particles in the fluid. Four sample points on the unit allowed for sampling at the inlet of the bag filters, inlet of the first process stage, inlet of the second process stage and outlet of the whole technology's process unit. (See Fig. 18, Table #3)

Analysis Method

Oil-in-water (Total) analysis was performed on water samples from the inlet and outlet of the technology's field unit using a DTI approved infrared (IR) method in the chemical lab on board the FPSO. Oil concentration results are presented in parts-per-million for total (soluble, free-floating and emulsified) oil.

Field Trial Results

Oil concentration measurements at the inlet (after the bag filters) and at the outlet of the technology's field trial unit are reported for the three test locations. Sampling was done after approximately 2m³ intervals of PW treated. A new set of bag filters upstream of the field trial unit was used at the beginning of individual tests at the three locations. The bag filters had minimal pressure drop throughout the duration of each trial and did not require replacement. The fluid temperature was around 60 - 70ºC.

Test Location # 1 - Downstream of Hydro-Cyclone 1

The technology's field trial unit was first tested downstream of Hydro-Cyclone 1 (HC-1). The produced water from this stream had a temperature of 65ºC and a crude oil APIº density of 42.2. Chemicals injected upstream in the process included a demulsifier, a scale inhibitor, a corrosion inhibitor and low amounts of a defoamer. The average flow rate through the technology process was 1.36 m³/hr. Samples analyzed yielded the results displayed in Figure 6. Average oil concentrations downstream of the HC-1and at the inlet of the technology's process had a value of 98.2 ppm, while the effluent from the technology had an average oil concentration of 2.9 ppm.

Test Location # 2 - Downstream of Hydro-Cyclone 2

The technology's field trial unit was then tested downstream of Hydro-Cyclone 2 (HC-2) without replacing the media cartridges from the previous trial. The produced water from this stream also had a temperature of 65ºC and a crude oil APIº density of 31.8. Chemicals injected upstream in this process line included a demulsifier, a scale inhibitor, a corrosion inhibitor, a defoamer, and polymers. The average flow rate into the technology's process unit was 1.21 m^3/hr with large amounts of gas separated and recovered through the trial.

Average oil concentrations downstream of the HC-2 had a value of 313.4 ppm, while the effluent from the technology had an average oil concentration of 4.2 ppm. It was observed that the oil concentrations downstream of HC-2 fluctuated between 100 ppm and 850 ppm. The technology maintained a steady performance with an effluent oil concentration not exceeding 5.6 ppm. This showed that the performance of the technology is dependent on the specific particle size distribution of oil droplets in the tested produced water stream, rather than on the concentration (within ranges less than 5000 ppm). Figure 7 shows values of oil concentration at the inlet and outlet of the technology unit for the described test. Mentioned surges in oil concentration values can be observed along with the corresponding effluent concentrations.

Test Location # 3 - Downstream of Degasser Unit

The third location of the technology's trial was downstream of the Degasser unit joining the two produced water treatment streams described above. The fluid temperature was 60ºC and the injected chemicals' composition was the residual mix of the connecting two streams. Average flow rate through the technology's process unit was 1.54 m^3/hr. Results of analyzed produced water samples at the inlet and outlet of the technology are displayed in Figure 8. Inlet concentration values fed to the technology from downstream of the degasser unit were steady at around 44 ppm, while outlet concentration values had an average of 2.6 ppm.

Trial B

Context of Field Trial

A field trial for the testing of the performance of the technology in treating the produced water (PW) on the semi submersible platform was conducted at the request of the facility owner and operator. The offshore trial was to be conducted at two different locations. These locations were slipstreams off the PW line downstream Hydrocyclone fed pumps (directly upstream of the overboard (O/B) discharge point) and downstream of the separator.

The trial allowed for the demonstration of the performance of the technology in terms of oil recovery and lowering the PW oil concentrations to levels meeting the trial target of 15 mg/Litre OIW or below. Department of Trade and Industry (DTI) approved methods of oil-in-water analysis were conducted as a primary method for measuring the inlet and outlet oil concentrations from the technology. Results showed that the oil concentration removal efficiency across the technology was maintained at levels around 93%.

The offshore platform produces an approximate 6500 BBL of oil (API° Gravity 37.6) and 65,000 BBL of water per day. Production fluids come from several wells through the production platform. Through the first part of the trial, the technology was to treat the PW downstream of the hydrocyclone feed pumps (directly upstream of the overboard (O/B) discharge point). The OIW concentration at that location is expected to be around an average of 30 mg/L. The second part of the trial was to be performed downstream of the separator (and upstream of the hydrocyclones), where the PW effluent that is discharged overboard has an average OIW of 80 mg/L.

The production chemicals existent in the fluid stream entering the technology included:

- Corrosion inhibitors injected at approximately 12 ppm.
- Scale inhibitors injected at approximately 60 ppm.
- Demulsifiers injected at approximately 10 ppm.

Field Trial Unit

See Fig. 18 & Table #3

Analysis Method

Oil-in-water (Total) analysis was performed on water samples from the inlet and outlet of the technology using a DTI approved infrared (IR) method and the operations procedures in the chemical lab on board the platform. Oil concentration results are presented in mg/L for total (soluble, free-floating and emulsified) oil. Samples were consistently taken at the inlet and outlet of the technology. Volume of samples was 500 ml each. Inlet samples were taken at the corresponding sample points upstream of the technology. Outlet samples were taken from the discharge hose of the technology.

Oil concentration measurements are presented below separately for the two parts of the trial. OIW removal efficiency is determined across the two stages of the technology. That is; measured inlet and outlet oil concentration values are used to calculate the efficiency. The technology was preceded by a set of 25µm bag filters. These filters were replaced at the start of each trial. The pressure drop across the bag filters never reached the 15 psig value required for replacement.

Test Location # 1 – Oil Removal Results

The technology treated around 30 m^3 of produced water at an average flow rate of 1.83 m^3/hr (275 BWPD). New bag filters were installed at the beginning of the trial. At the start of the trial, upset conditions were observed (due to bringing online of the test separator) where inlet OIW values of 300 mg/L and 125 mg/L were observed. (See Fig. 9) The Inlet OIW then levelled at average OIW concentrations of around 26 mg/L while the overall average outlet OIW concentration was 2.7 mg/L from the technology throughout the whole trial. OIW Removal Efficiency calculated values give an average efficiency of 93% with the specific produced water characteristics from the O/B discharge location. These values are directly related to the mean oil droplet size in the influent (data on mean droplet size not available).

Pressure readings were logged throughout the trial. These provided values for pressure drop across each individual stage of the technology as well as across the bag filter elements. Pressure drop across the media cartridges is a function of inlet OIW concentration. Maximum operating pressure drop measured across both individual stages was 6 psi.

Test Location # 2 – Oil Removal Results

Second part of the trial was performed downstream of the separator and upstream of the PW hydrocyclones. Steady-state inlet OIW concentrations into the technology had an average of 76 mg/L with a maximum measured value of 235 mg/L. Effluent from the technology had an average OIW concentration of 7.2 mg/L, with a minimum measured value of 5mg/L and a maximum of 11 mg/L. All measured results are presented in Figure 10 below. The calculated OIW removal efficiency had values ranging up to 96% with an average of 92%. It is to be noted that the separator has no demulsifier or oil separation enhancing chemicals injected in it. This further shows the adaptability of the technology to treating the mentioned produced water with high levels of OIW removal efficiencies. Similar pressure readings to those in the first part of the trial were observed, where the pressure drop across every stage of the technology did not exceed 6 psig.

Trial C

Context of Field Trial

A field trial for the testing of the performance of the technology in treating the produced water (PW) on a platform was conducted at the request of the owner. The offshore trial was to be conducted at two different locations. These locations were slipstreams off the PW line downstream of the first stage B separator and downstream of the B-WEMCO unit.

The trial allowed for the demonstration of the performance of the technology in terms of oil recovery and lowering the PW oil concentrations to levels meeting the trial target of 15 mg/Liter OIW or below. Department of Trade and Industry (DTI) approved methods of oil-in-water analysis were conducted as a primary method for measuring the inlet and outlet oil concentrations from the technology. Results showed that the oil concentration removal efficiency across the technology was maintained at levels around 95%.

The platform produces an approximate 4000 BBL of oil (API° Gravity 39) and 100,000 BBL of water per day. Production fluids come from the platform pass through the production platform prior to the oil/water being routed to the onshore gathering facilities. Through the first part of the trial, the technology was to treat the PW downstream of the first stage separator (separator B) and upstream of the WEMCO separators. The OIW concentration downstream of the separator is expected to be around an average of 250 mg/L. The second part of the trial was to be performed downstream of the WEMCO separators, where the PW effluent that is discharged overboard has an average OIW varying between 40 to 50 mg/L.

The production chemicals existent in the fluid stream entering the technology included:

- Corrosion Inhibitor injected in the Bravo produced fluids at approximately 39 ppm.
- Scale Inhibitor injected in the Bravo produced water at approximately 15 ppm.
- Demulsifier injected in the Bravo produced fluids at approximately 15 ppm.
- Demulsifier injected in the Alpha produced water at approximately 4 ppm.
- Deoiler injected in the Alpha produced water prior to O/B discharge at approximately 4 ppm.

Field Trial Unit

See Fig. 18 & Table #3

Analysis Method

Oil-in-water (Total) analysis was performed on water samples from the inlet and outlet of the technology using a DTI approved infrared (IR) method and operator standard protocols and procedures in the chemical lab on board the platform. Oil concentration results are presented in mg/L for total (soluble, free-floating and emulsified) oil. Samples were consistently taken at the inlet and outlet of the technology. Volume of samples was 500 ml each. Inlet samples were taken downstream of the 25 µm bag filter elements located upstream of the technology (to capture any solid particles having a nominal size of 25 µm and above). Occasional samples were taken after the first stage of the technology.

Test Location # 1 – Oil Removal Results

The technology treated around 300 m^3 of produced water at an average flow rate of 1.8 m^3/hr (271 BWPD). Bag filters were changed four times during this part of the trial. Average inlet OIW concentrations were around 283 mg/L while the overall average outlet OIW concentration was 16.8 mg/L from the technology. Maximum inlet and outlet OIW concentrations measured were 610 mg/L and 38 mg/L respectively. Minimum outlet OIW concentration measured was 4.5 mg/L. The mean oil droplet size at inlet was 7µm (measurements provided by operator). (See Fig. 12 for Inlet/Outlet Visual Samples)

It is shown from the results in Figure 11 that as the inlet OIW concentration feeding the technology increases, the outlet OIW concentration increases. However, this increase in outlet OIW concentration takes place with a lower slope than that of the inlet OIW. This is due to the corresponding increase in droplet count of oil droplets having a mean diameter less than 10 µm in size. As the number of these droplets increases in the feed, their rate coalescence increases proportionally and thus resulting in a lower increasing slope of outlet OIW concentration.

The Oil Removal Efficiency of the two-stage technology for this part of the trial is presented in Figure 13. Lower efficiency values correspond to events when new bag filter elements were being installed and thus capturing a major part of the feed oil, resulting in a significant drop in inlet OIW values into the technology. These values were used in calculating the overall efficiency. OIW Removal Efficiency calculated values give an average efficiency of 93.5% with the specific produced water characteristics from the first stage separator. These values are directly related to the mean oil droplet size of 7µm in the influent.

Pressure readings were logged throughout the trial. These provided values for pressure drop across each individual stage of the technology as well as across the bag filter elements. Pressure drop across the media cartridges is a function of inlet OIW concentration. Maximum operating pressure drop measured across both individual stages was 6 psi. Results are presented in Figure 14 below.

Test Location # 2 – Oil Removal Results

The second part of the trial was performed downstream of the B WEMCO separator, just before the overboard discharge point. Inlet OIW concentrations into the technology ranged had an average 57 mg/L with a maximum measured value of 77 mg/L. Effluent from the technology system had an average OIW concentration 0f 10.9 mg/L, with a minimum measured value of 7 mg/L and a maximum of 14 mg/L. All measured results are presented in Figure 15. It is to be noted that a centrifugal pump was used to feed the unit. This might have further sheared the oil droplets in the feed water to the technology.

The calculated OIW Removal Efficiency is presented in Figure 16. As the larger oil droplets and emulsions have already been separated in the WEMCO, the oil droplet size distribution (made even smaller with the pump action) comprising the measured inlet OIW concentrations between 24 mg/L and 77 mg/L were recovered with an efficiency lower than that of the previous part of the trial. However, the calculated OIW removal efficiency had values ranging up to 90%. As for the pressure drop readings (Figure 17) for the second part of the trial, these cannot be interpreted with conclusive certainty. This was due to the fact that the pump was running at a lower capacity (than nominal for the technology in use).

CONCLUSIONS

The technology merits serious consideration for the applications of de-oiling produced water. Overall one can conclude the following:

- The technology can adsorb, coalesce, desorb and recover dispersed oil in water 2 microns and larger.
- The technology is effective in lowering the hydrocarbon concentrations of produced water especially for offshore facilities where strict discharge regulations must be adhered to.
- The technology has the capability of good performance even during upset inlet conditions.
- Chemicals are not needed to enhance the oil removal efficiency.
- Additional heat is not required to obtain favourable results.

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[9] R. GASKIN. The ViPA, Jorin Limited, http://www.jorin.co.uk/vipa.htm.

Table #1 – 2-5 Microns

2 – 5 µm range	Concentration (ppm)
Average at Inlet	7.48
Average at Outlet	2.38
% Removal (ppm)	68.22

Table #2 – 2-10 Microns

2 – 10 µm range	Concentration (ppm)
Average at Inlet	29.84
Average at Outlet	2.88
% Removal (ppm)	90.36

Table #3 – Field Demonstration Equipment Specifications

Design Parameters	Vessel Enclosure	Stainless Steel SS 316
	Design Pressure	ASME 150 psig (10.2 Barg)
	Design Temperature	110° C
	Class	Zone 1/ Division 2
Operating Parameters	Nominal Capacity	300 BWPD
	RPA® Stages	2 Radial
	Operating Pressure	Max 150 psig
	Operating Temperature	Max 95°C
	Inlet Oil Concentration	Max 2,000 PPM
	Inlet Suspended Solids	Max 50 mg/L
	Chemical Additives	N/A
	Bag Filters	1-25 µm
	Sample Points	1 per stage
Instrumentation	Flow Rate	Turbine Meter + Indicator
	Pressure	4 x Pressure Gauges
	Interface Indicators	N/A
	Control Valves	N/A
Safety	PSV	Set @ 135 psig
Dimensions	Overall Footprint	L 160 cm X W 85 cm X H 105 cm
	Estimated Dry Weight	530 kgs
	Estimated Wet Weight	600 kgs
Procedures	Turnover/Inspection	Inspection/Precommissioning Manual
	Pre-Commissioning	Inspection/Precommissioning Manual
	Start-up/Operation	Operating/Instructions Manual
	Emergency	Operating/Instructions Manual

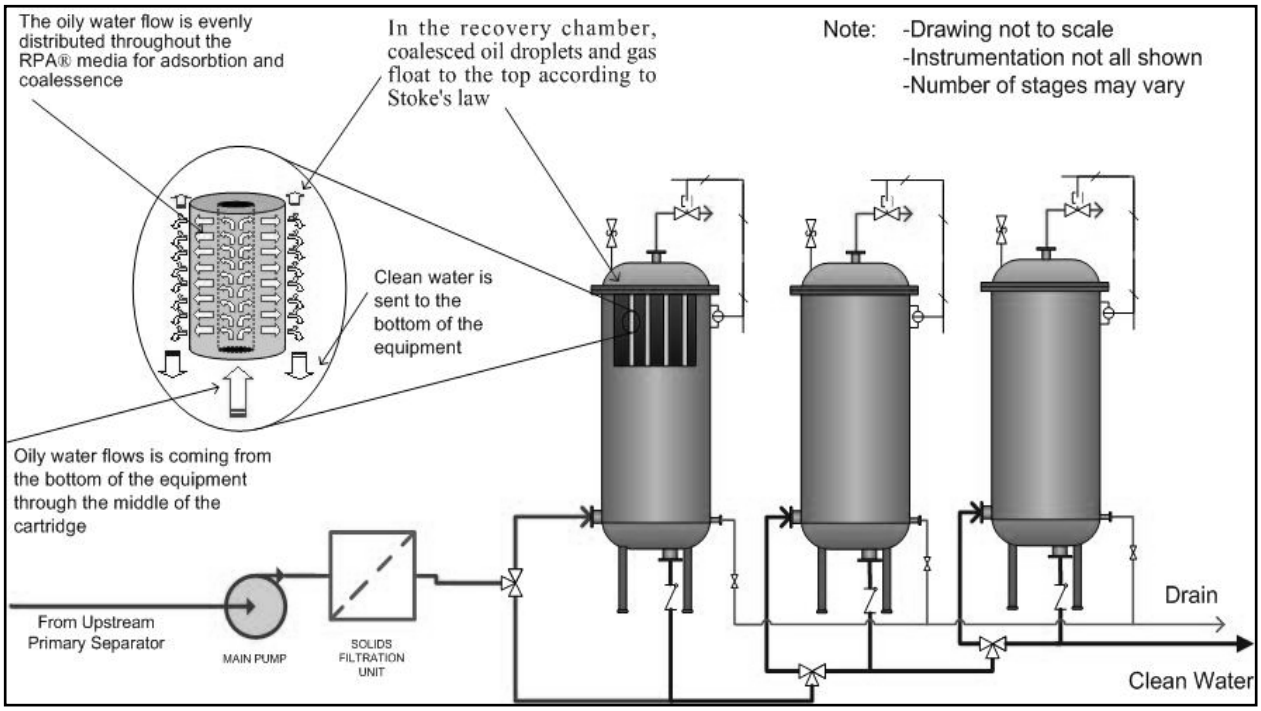

Figure 1. - Process Flow Diagram of the Technology

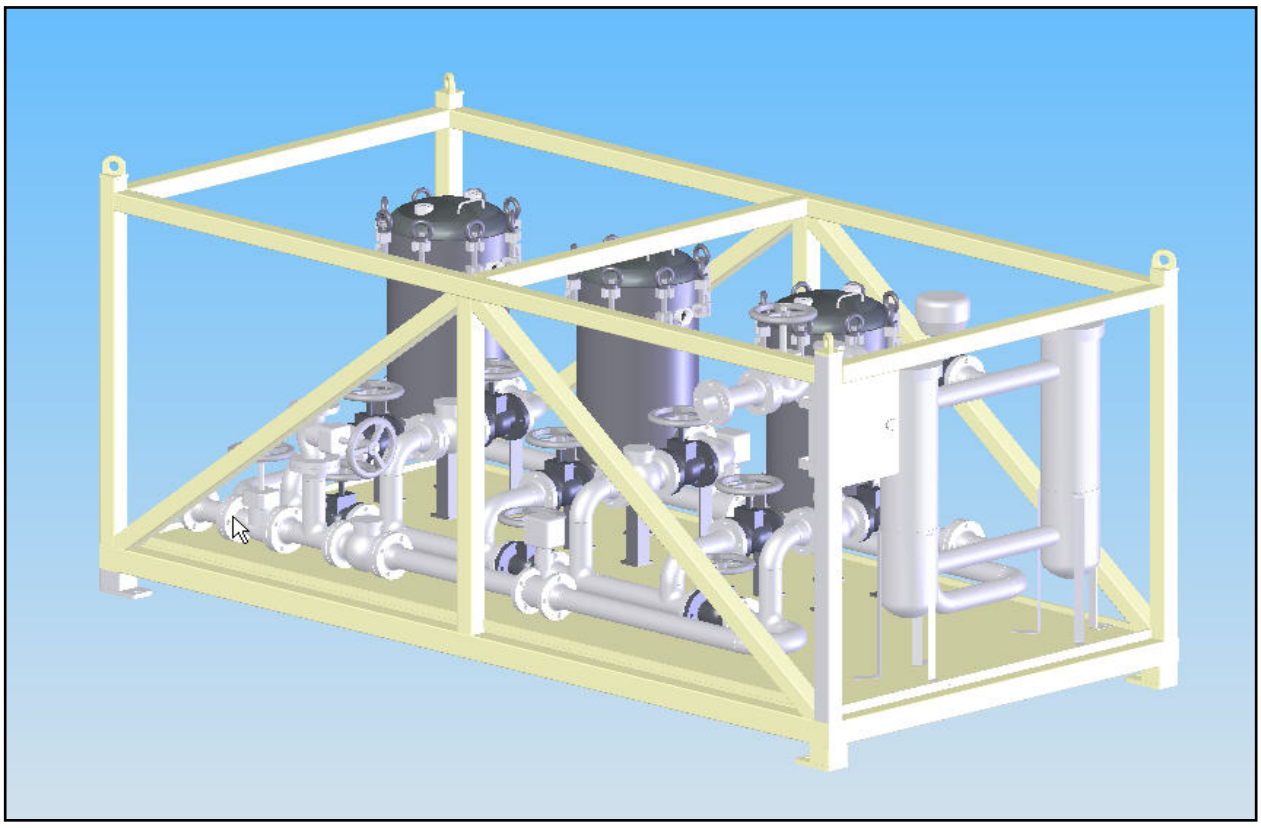

Figure 2. - Typical 3D Design of Technology

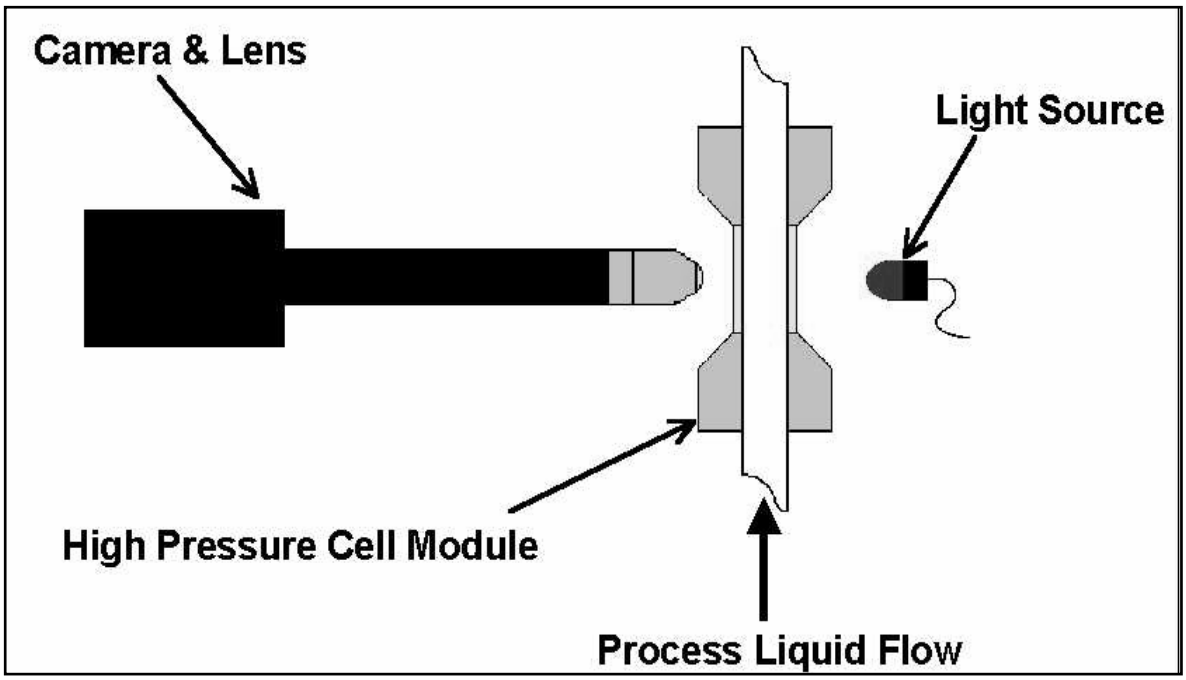

Figure 3. – Video Imaging Process Analyzer Operating Principle

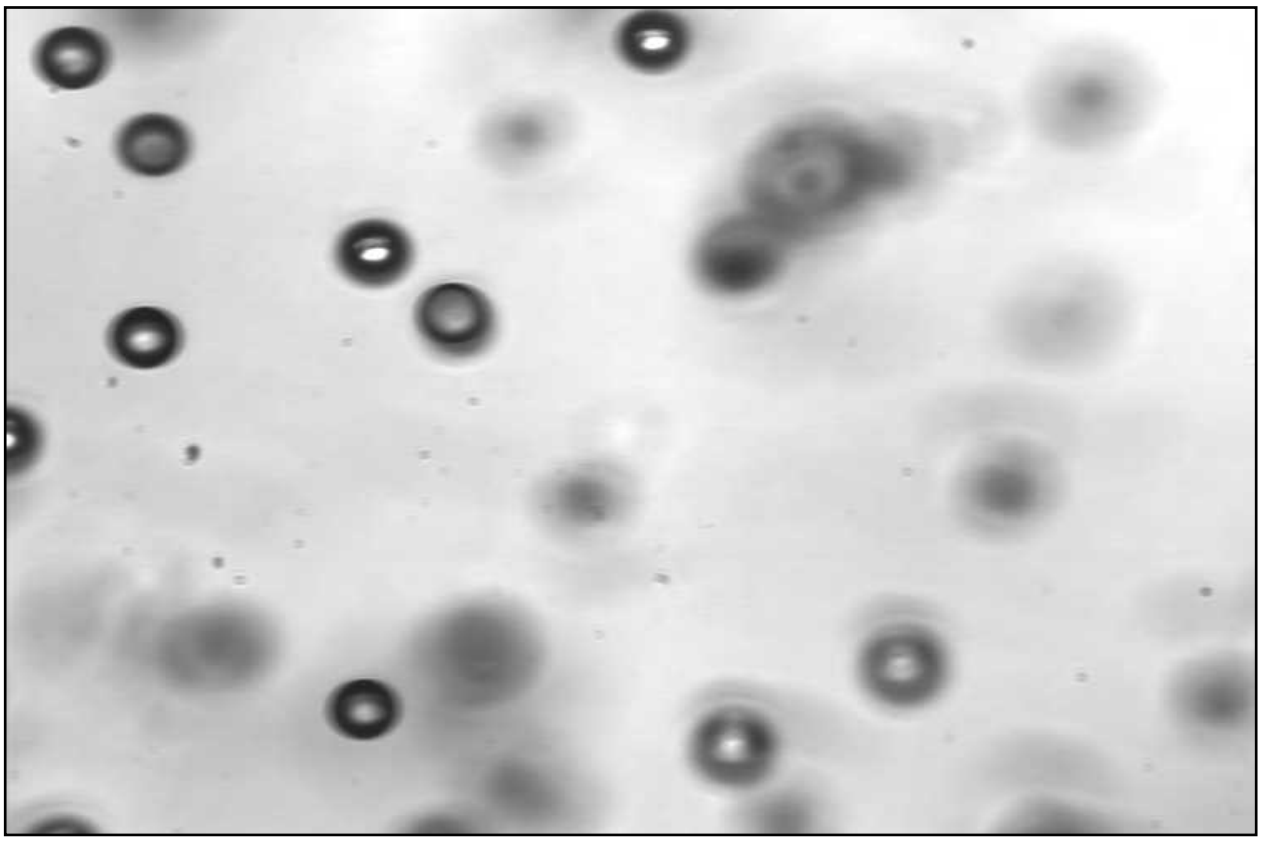

Figure 4. – Image of Droplets as Seen by Analyzer

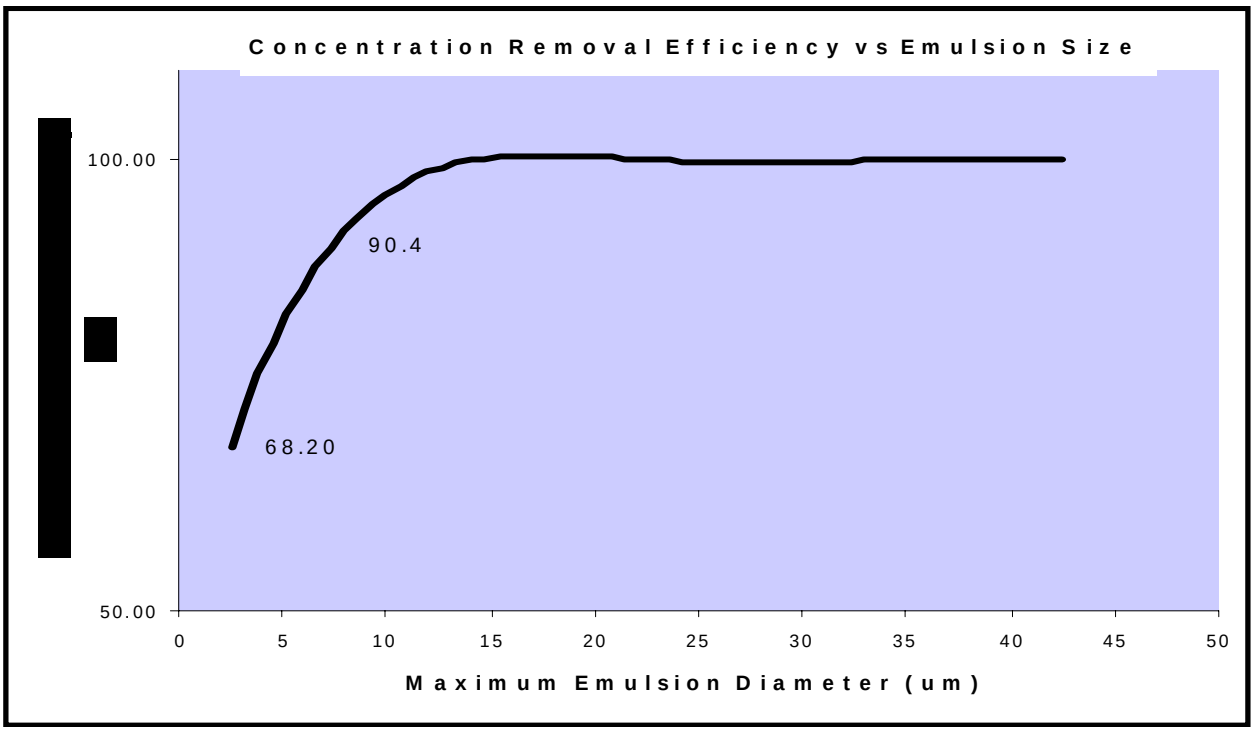

Figure 5. – Concentration Removal Efficiency vs. Emulsion Size

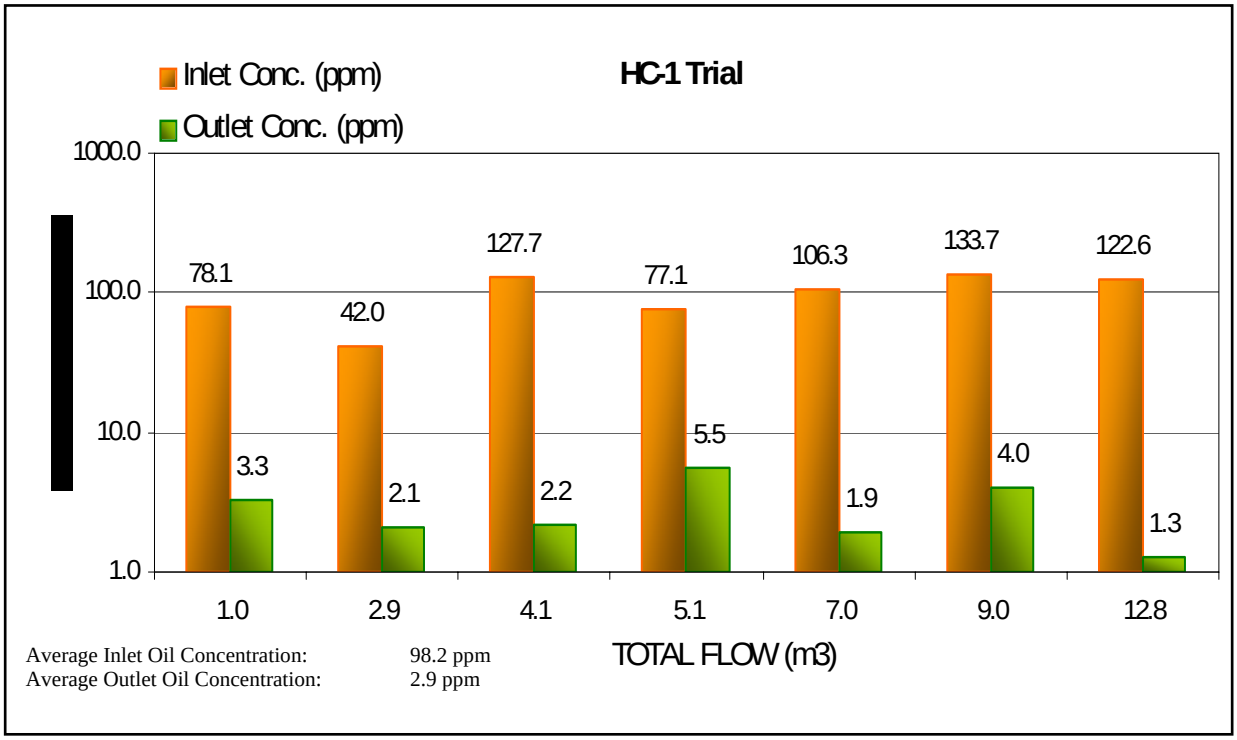

Figure 6. - Oil Concentration Values as Determined by Lab IR Method at Inlet and Outlet of the Technology's Field Trial Unit at Trial A, Location 1

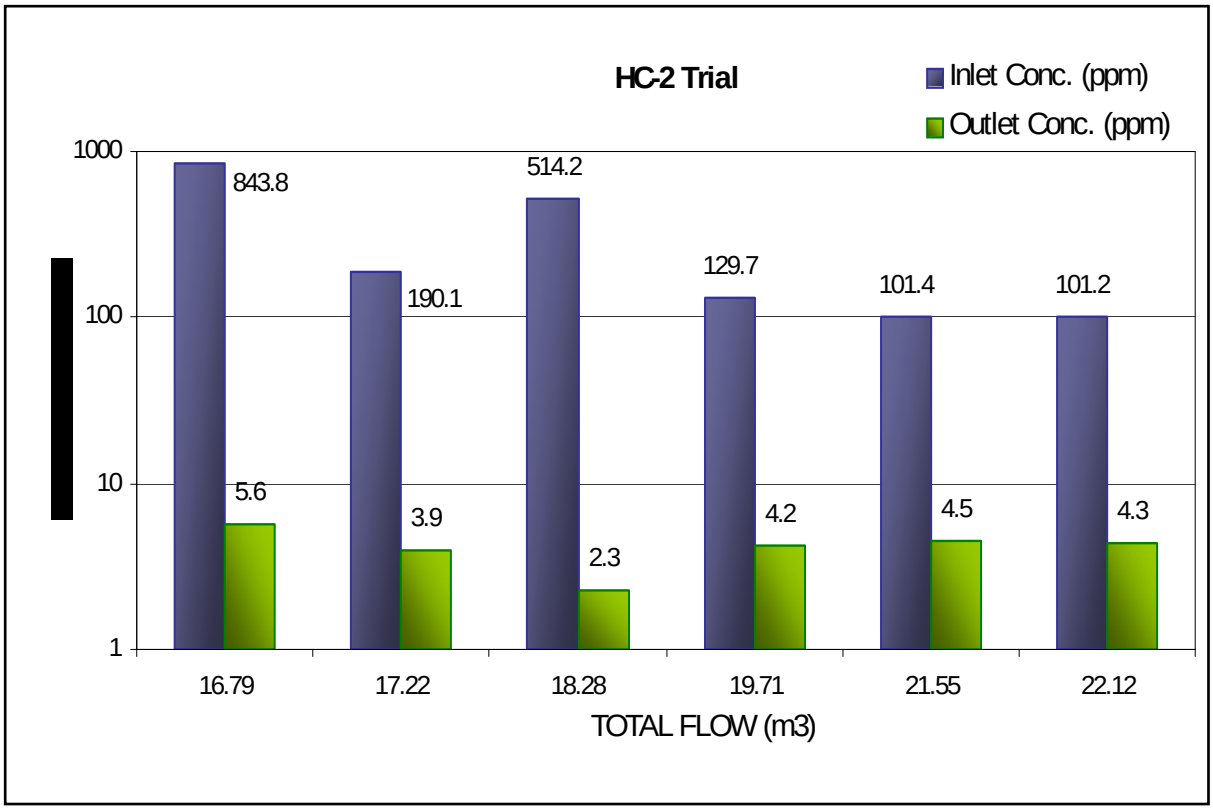

Figure 7. - Oil Concentration Values as Determined by Lab IR Method at Inlet and Outlet of the Technology's Field Trial Unit at Trial A, Location 2.

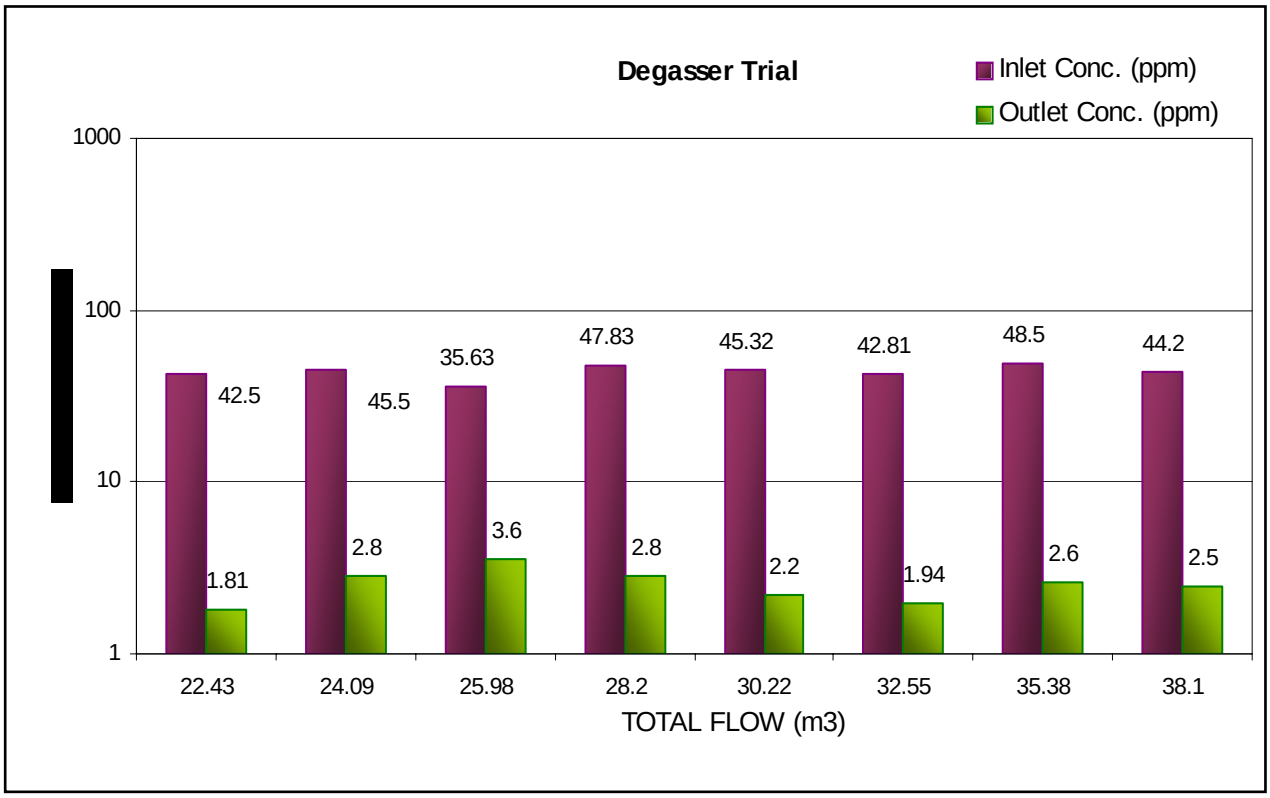

Figure 8. - Oil Concentration Values as Determined by Lab IR Method at Inlet and Outlet of the Technology's Field Trial Unit at Trial A, Location 3.

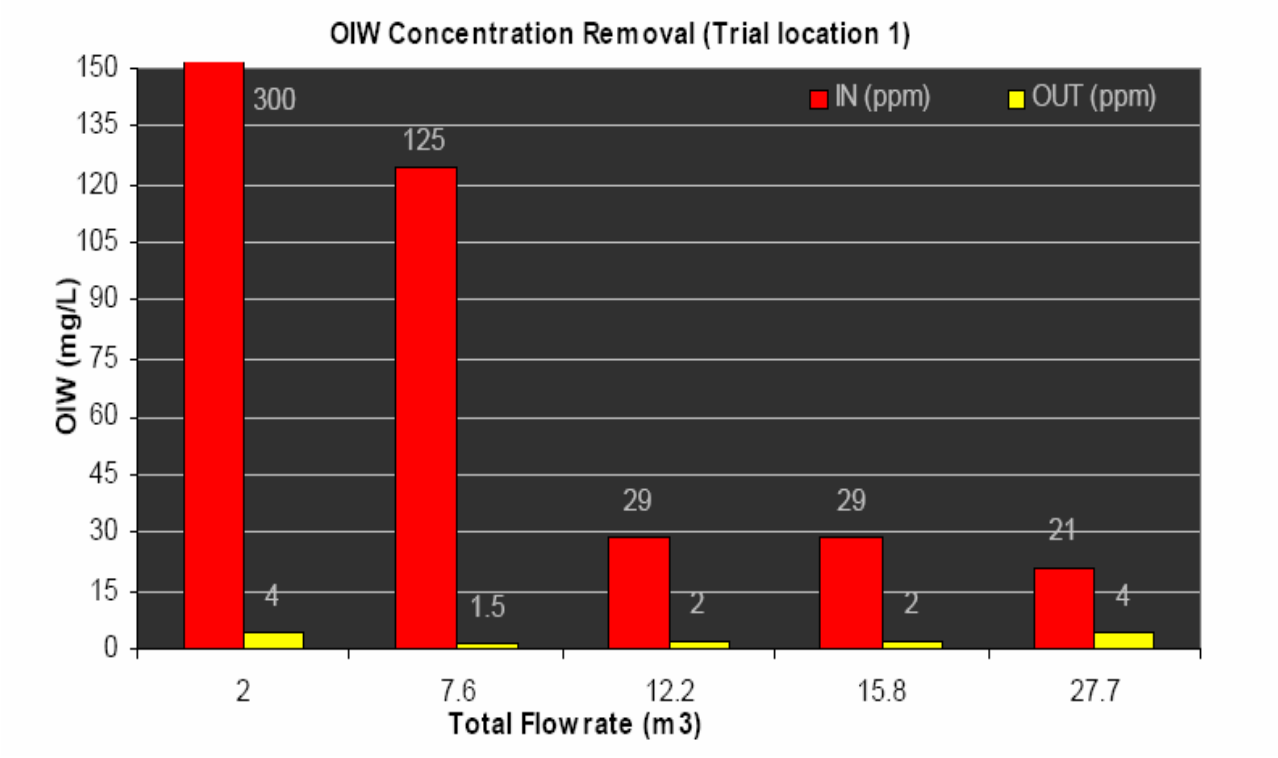

Figure 9. – Trial B, Location #1

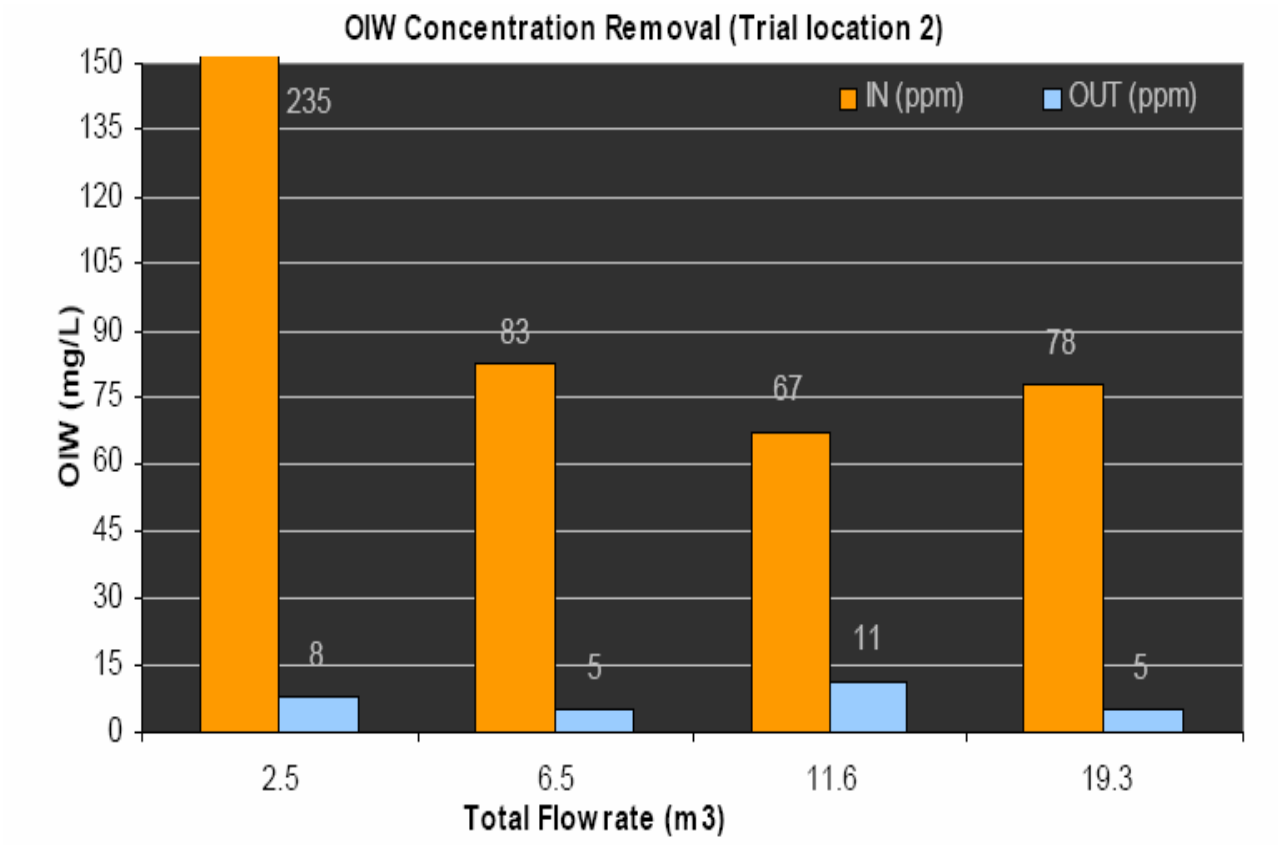

Figure 10. – Trial B, Location #2

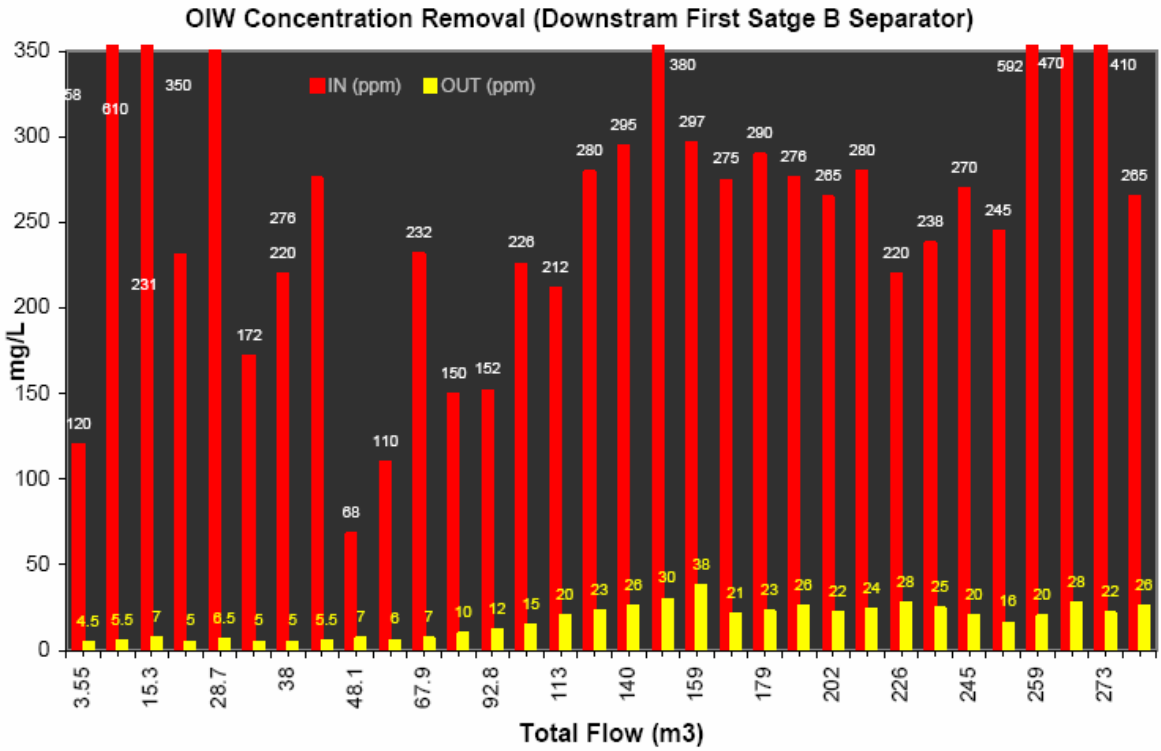

Figure 11. – Trail C, Location #1

Figure 12. – Trial C, Location #1 – Visual Samples of Outlet and Inlet from the Technology

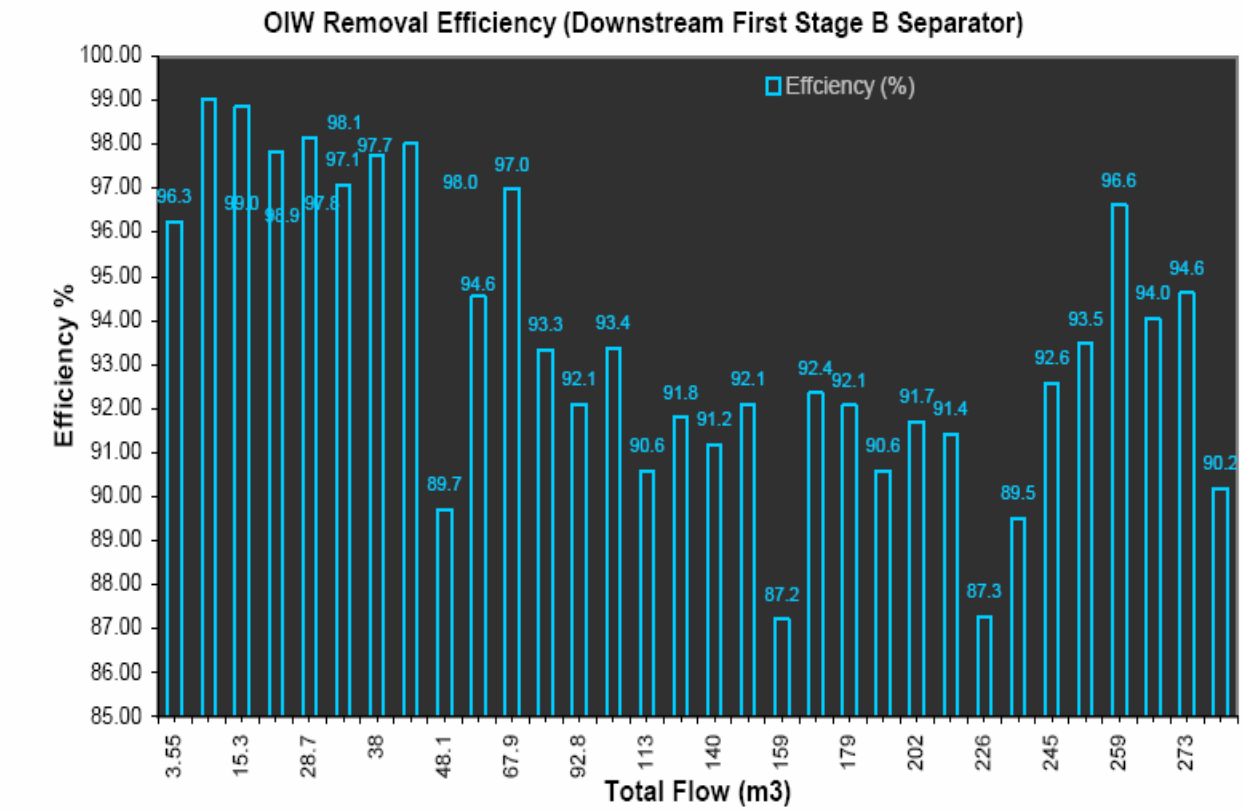

Figure 13. – Trail C, Location #1 – OIW Removal Efficiency

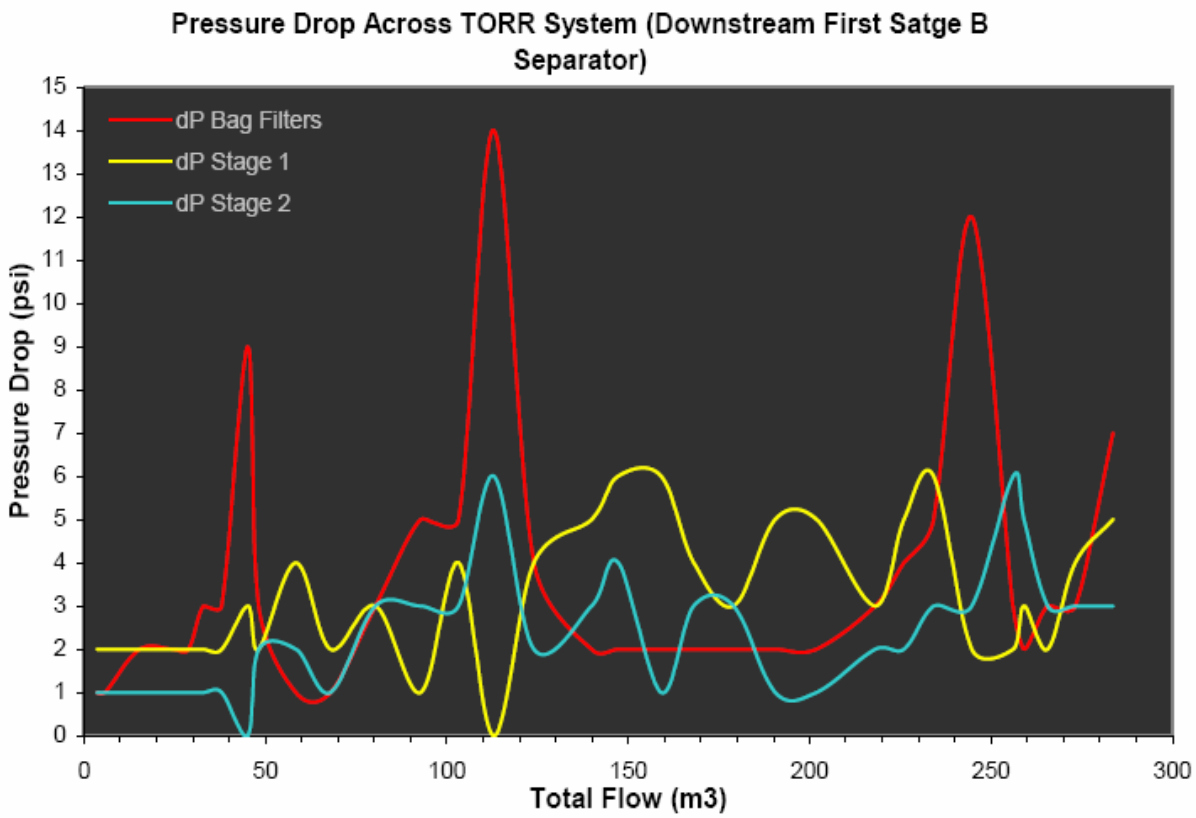

Figure 14. – Trial C, Location #1 – Pressure Drop Observations

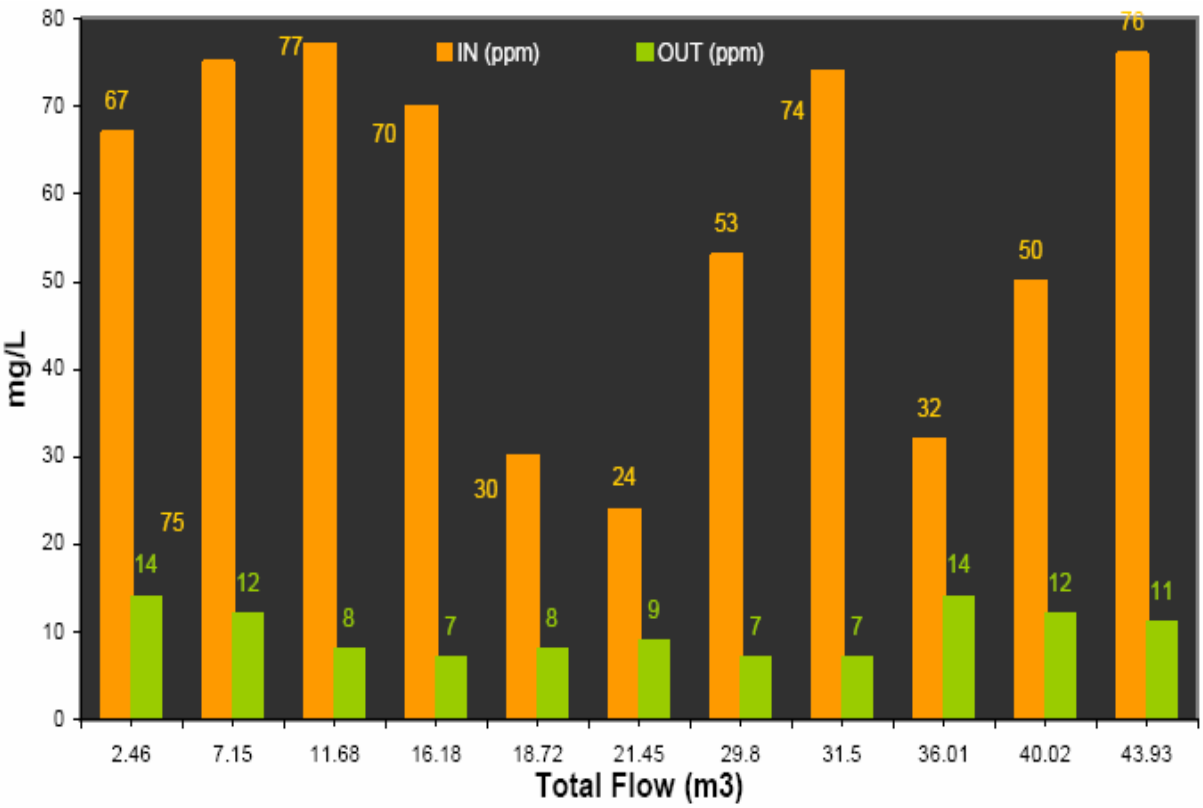

Figure 15. – Trial C, Location #2 OIW Inlet & Outlet Measurements

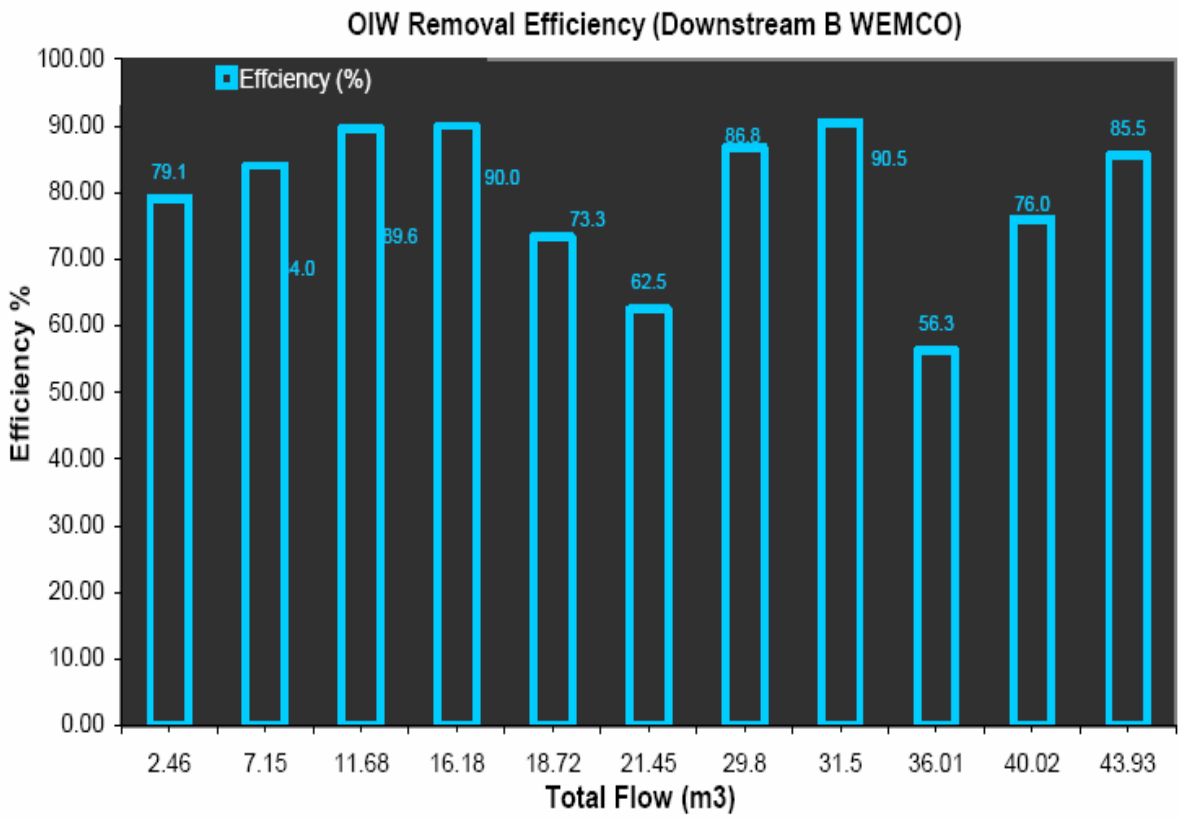

Figure 16. – Trial C, Location #2, OIW Removal Efficiency

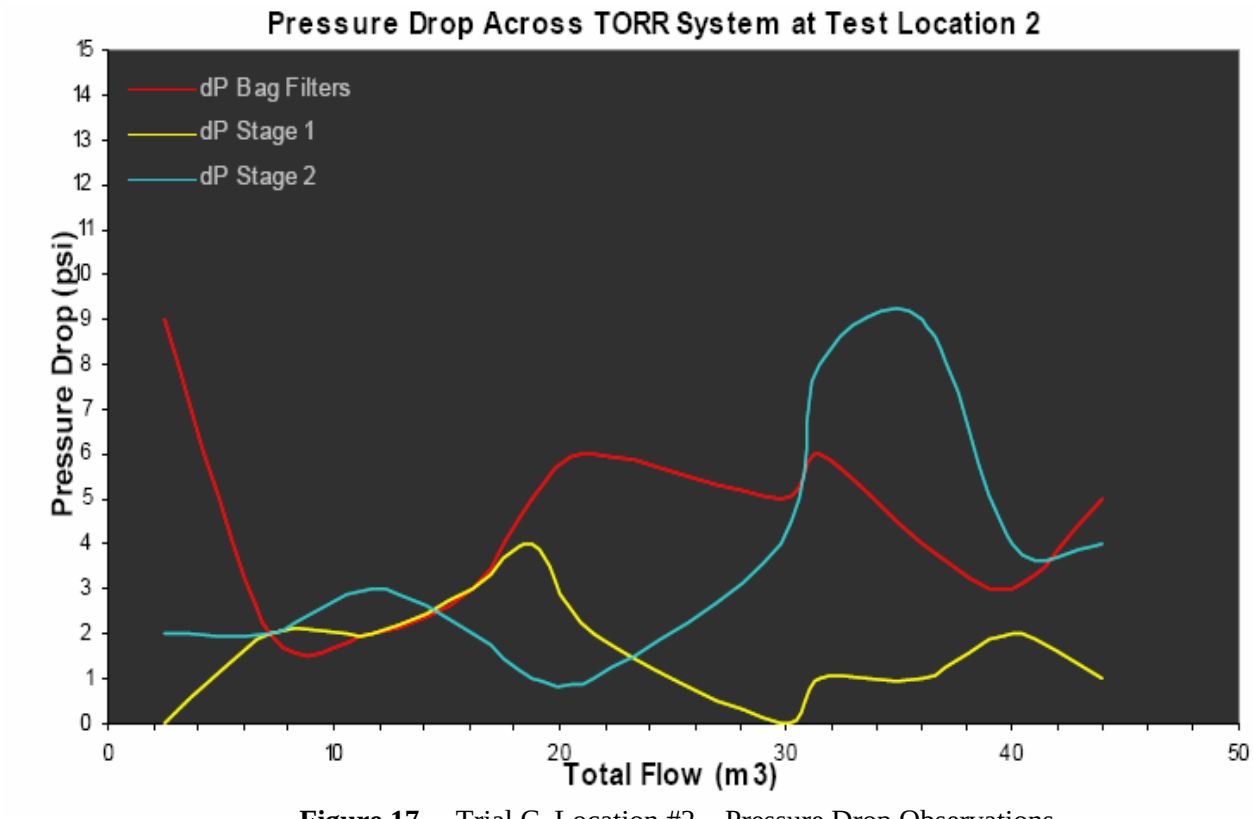

Figure 17. – Trial C, Location #2 – Pressure Drop Observations

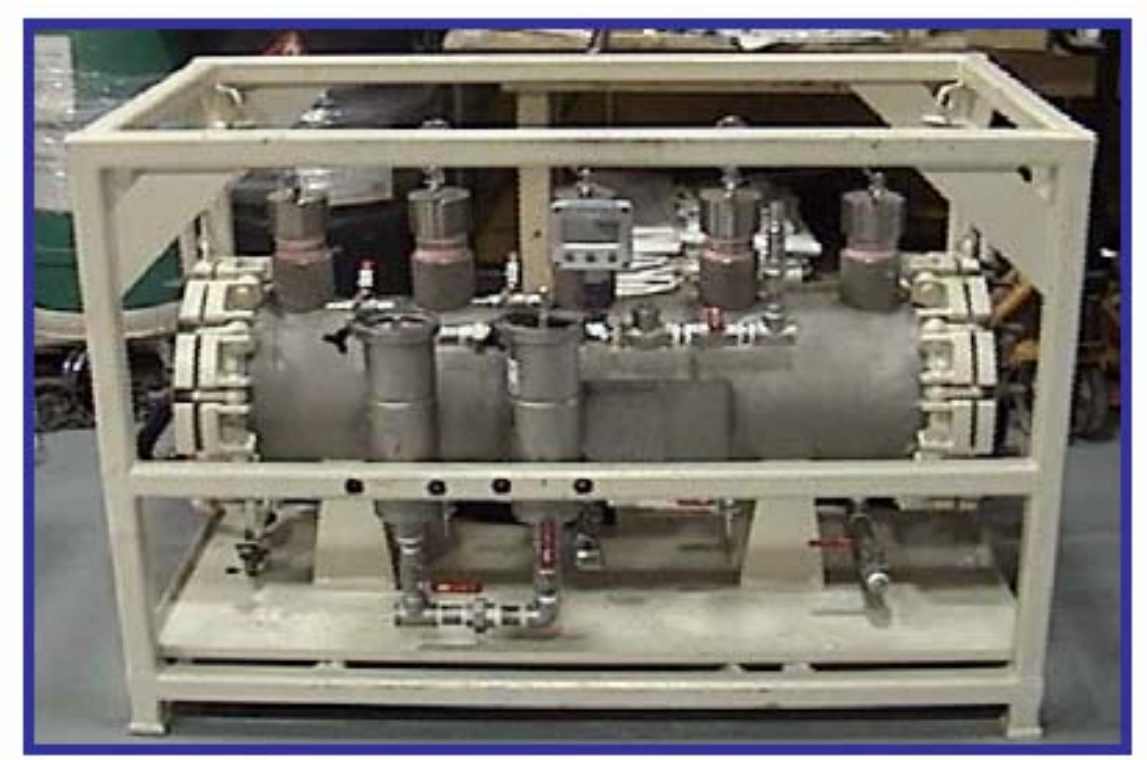

Figure 18. – Technology Demonstration Unit for Offshore Trials

The Application of a Salt-Free High Performance Water Base Mud for Minimizing Environmental Impact in The Oriente Ecuadorian Basin

Mario A Ramirez, Pablo Benalcazar and Diego Paz

Baker Hughes Drilling Fluids

ABSTRACT

The application of inhibited fluids containing salts has been an extended practice in the Ecuadorian Basin. However, the environmental regulations have changed in the last few years in Ecuador and there is a particular concern about the disposal of cuttings with high concentrations of salts. A typical approach to this problem has been the use of containing no chlorides, such as potassium nitrate and potassium Sulphate. However, an addition to the extra cost, there are additional concerns with the nitrate and sulfate ions that remain in the cuttings. A new drilling fluid has been proposed and applied with success and introduced as a novel technology that doesn't compromise wellbore stability while it addresses environment concerns.

The novel approach focuses on the environment in two ways. On one hand, the well bore stability achieved along the wells minimizes the volume of cuttings generated thus decreasing the dilution requirements. On the other, both the liquid and solid waste does not require additional treatment for proper disposal.

The inhibited part of the system consists of polymers of aluminum-silicates which resembles the structure of the natural clays . The product used for controlling both the swelling and non-swelling clays becomes part of the clay structure and can be disposed while complying with the environmental regulations.

Although the system design considers the wellbore stability as a basis of design for minimizing waste generation, this paper focuses on its environmental benefits. The operational benefits resulting from wellbore integrity has been the subject of another paper.

The paper presents waste volumes and waste disposal cost data that compares the application of potassium salts with the application of aluminum complex.

INTRODUCTION

A multitude of new drilling fluid products, systems and treatment processes have been developed in the recent years in response to increasingly stringent environmental regulations. New water-based mud systems are approaching the performance levels typical of conventional oil-base muds, levels largely achieved by the new syntethic-base fluids. However, drilling fluids performance is not the only aspect to be consider. For instance, potassium/polymer muds would play a most important role in reducing shale stability problems in many areas around the world. Unfortunately the LC-50 limitation essentially eliminated potassium from use in the Gulf of Mexico in the quantities thought necessary to achieve the desired performance. High salt (sodium chloride) polymer muds are now being used in the Gulf of Mexico instead of more effective potassium systems. Potassium muds are being used in the North Sea and other areas where regulations are not biased against the addition of potassium to seawater.

Regulations in land operations also had different requirements and the use of salts is generally prohibited due to cuttings contamination. In addition to this, the waste waters are usually returned after proper treatment to the rivers making the requirements even more stringent. This phenomenon is particularly critical in the jungle of the Amazonian basin, a natural reserve that has the largest variety of fauna and flora in the world. The Amazonian basin covers a large portion of south America east of the Andean mountains covering of the countries of Colombia, Ecuador, Peru and Brazil. Of particular importance in the Ecuadorian basin is the presence of multiple native communities still untouched by the modern world, which live around the exploration and production areas of the country. .. ..

Waste discharge of salt inhibited muds in marine waters is accepted in many exploration areas around world on the basis that there is minimum impact of discharging small amounts of waste into a large reception body.. In the case of land operations in the tropical rainforest, the environmental impact of salt waters in the rivers is significant. Several studies and extended field experience have demonstrated the adverse effects of using potassium-based systems in the area. In such cases both the mud toxicity and the excess of waste contributed to a substantial increase in the negative environmental effects of salt inhibited drilling fluids.

The drilling fluids industry has been taking steps to reduce the environmental impact of discharging fluids and cuttings by replacing the more toxic fluid components with less toxic ones, by reducing the total waste volume through improved drilling and waste disposal practices, and by promoting the processing and reuse of drilling fluids. When trying to reduce the environmental impact, drilling fluids companies usually face a trade off between addressing the qualitative vs. the quantitative aspects of the fluid. That is, by using less inhibitive muds with low toxicity levels there is less risk of pollution from the type of products used but the dramatic increase in the volume of waste has highly detrimental effects on the environment. On the other hand, a highly inhibitive mud reduces the volume of fluid and cutting waste but increases its negative effects by means of a more hazardous composition.

The novel approach taken in the Ecuadorian basin was to decrease fluid toxicity without compromising the objectives of waste disposal minimization and optimum drilling performance. The Aluminum complex system that forms the core of the fluid design is able to maintain wellbore stability while drilling troublesome shale sections. This excellent stability minimizes the need for continuous reaming and backreaming operations that are required when drilling with fluids traditionally employed in the area. Consequently, a proper fluid design controls and reduces the excessive volumes of waste that have characterized these wells in the past..

ALUMINUM CHEMISTRY

The versatility of aluminum chemistry can be discussed in the context of general characteristics of this element. Various aspects of aluminum chemistry[11-12] featured in drilling applications include:

- Aluminum can exist as compounds that may be soluble or insoluble in water (**Table 1**) depending on the counter ion and solution pH.
- Aluminum ions, formed by the dissolution of soluble aluminum salts, exist as hexahydrate ions in an octahedral configuration (**Fig. 2**). The high charge of aluminum ions results in the loss of hydration shell protons that produces a series of hydrolysis products (**Fig. 3**). Aluminum induced hydrolysis produces acidic solutions for virtually all water-soluble salts.
- Aluminum exhibits a complex, pH-dependent chemistry in aqueous systems and the ability to produce important effects from either acidic or alkaline aluminum sources. Solutions of aluminum salts contain only $Al(H_2O)_6^{3+}$ at pH values below 3. When pH values are between three and five, aluminum species are distributed between a mixture of hydroxo species including $Al(OH)^{2+}$, $Al(OH)_2^{+}$, and various polynuclear (containing two or more aluminum atoms) cations. At pH values between 5 and 6, $Al(OH)_3$ appears. As the pH becomes more alkaline, $Al(OH)_4^{-}$ becomes dominant.

- Under appropriate conditions, aluminum forms an amphoteric hydroxide which at higher pH forms soluble tetrahydroxyaluminate anion (**Fig. 4**).
- Aluminum hydroxides exist in several crystalline or amorphous forms (**Fig. 5**).
- Wellbore stability is enhanced by precipitation of aluminum hydroxides within shale pore throats and micro-fractures.

ALUMINUM MECHAMISM FOR STABILITY AND WASTE MINIMIZATION

The environmental impact of drilling fluids is determined by two main variables: the volume of of solid and liquid waste and the toxicity of the same. The quantity of waste depends on the volume of drill solids generated while drilling the well. When drilling troublesome shales like those encountered in the Ecuadorian basin, wellbore stability plays an important role in both drilling efficiency and waste disposal. The amount of solids waste is significantly increased while attempting to control wellbore instability problems by conducting continuous reaming operations that increase the hole diameter and therefore the load of solids incorporated to the mud. The dilution rates required to handle the additional load of solids also increase the volume of liquid waste. Under these circumstances, a preventative approach that carefully designs the drilling fluid is preferred over a remedial one. Contrary to other areas around the world, the use of potassium based systems in the area has demostrated to be the cause of wellbore stability problems and the subsequent increase of environmental impact.

The aluminum chemistry approach to shale stability is based on changing the physico-chemical behavior of the shale. Contrary to the widely investigated ionic exchange between fluid and shale, this approach is based on aluminum chemistry designed to precipitate as aluminum hydroxide which may eventually become incorporated into the mineral matrix of the formation. This aluminum precipitate greatly enhances the stability and physical strength of a sensitive shale section and forms a physical barrier to further filtrate invasion of the shale.

The aluminum hydroxide complex (AHC) dissolves in the aqueous drilling fluid and generates tetrahydroxyaluminate ions, $Al(OH)_4^-$. Chemical literature implies that the tetrahydroxyaluminate anion is the dominant soluble species for the drilling fluid environment.[14] As AHC is added the drilling fluid, aluminate immediately enters solution. AHC treatments will generate a mud pH of 10 to 12, depending on the quantity added. The mud pH will determine the distribution of tetrahydroxyaluminate and aluminum hydroxide.

If sufficient AHC is maintained in the mud, excess tetrahydroxyaluminate will be present in the filtrate. When exposed to a lower shale pH, aluminum hydroxide [$Al(OH)_3$] will precipitate from the filtrate. Precipitation is accelerated when the alkaline mud filtrate is exposed to connate water, possessing pHs as low as 4 to 5, in the shale microfractures. Aluminum hydroxide may exist as an amorphous precipitate or in a variety of crystalline forms such as: gibbsite, bayerite, nordstrandite, boehmite or diaspore. The type of aluminum hydroxide that forms is dependent on many factors including temperature as well as other ingredients in the fluid such as electrolytes and organic acids.[15-20] Under certain conditions, the aluminum hydroxide may initially precipitate in one form but later change to another form or allotrope.

Because hydroxides and aluminate are the most common aluminum species at typical drilling fluid pH levels, the generation of aluminum hydroxides from aluminate is the critical process in AHC mud systems. This prevents hydration and enhances borehole stability. This same hypothesis explains the stabilizing effects of mud filtrate on shale cores. The filtrate is exposed to a lower pH environment when it penetrates into the shale wall and microfractures, causing the excess AHC in the mud filtrate to precipitate as hydroxides along the filtrate front (**Fig. 6**). The precipitated hydroxides may eventually change to crystalline forms. Subsequently, the aluminum hydroxides may become part of the shale crystal structure, helping stabilize the shale. This chemical process would greatly reduce the induced pore pressure transmission inside the shale microfractures.

ALUMINUM CHEMISTRY AND THE ENVIRONMENT

Only leaching by strong acids results in the transport of ecologically significant concentrations of aluminum to surface waters. The speciation of Al in surface waters is a function of many factors, including the supply of ligands and Al, pH, concentration of complexing ligands. One of the most significant reactions involving Al is complexing with organic ligands. The Al mobilized to surface waters is neutralized and immobilized by basic cations and retention of strong acid anions (e.g., SO4, NO3), and biological processes in saturated soil/sediments. Natural organic substances (fulvic and humic acids), dissolved in surface waters has been found to complex a significant proportion of dissolved Al content of such waters.. The organic substances of various types also play important role in the complexation of Al in soils and sediments. They are of great importance in modifying the reaction of Al on clays and acid soils. The adsorption of polynuclear and monomolecular Al onto soil constituents is reported to be affected by the surface properties of the constituents as well as the presence of associated systems that compete for Al. The adsorbed Al has been reported to affect both the chemical and physical properties of clays and soils. Most noted chemical changes are CEC reduction and improved catalytic and adsorbant properties. Most noted physical changes are increased aggregate stability and enhanced colloidal interaction. The Kaolinite fixes more Al more rapidly and with greater reduction in CEC than any other clay when compared on a unit CEC basis. The reason for these unexpected strong reactions of Kaolinite with Al most lie in the nature of bonding sites.

The presence of Al in surface waters as a consequence of natural soil acid lixiviation is much more important than Al originated by waste waters containing Al complex included in drilling formulations. Despite of being a source of Al, the presence of fulvic and humic acids in natural waters are buffers and immobilize the Al. In addition to this the Al complex used in drilling fluids contains humic acid in the formulation to sequester excess of Al in waste waters.

ENVIRONMENTAL COMPLIANCE

The Aluminun complex has been tested for environmental compliance in both the Gulf of Mexico and the Uk sector of the North Sea.

Chrome-free ligonosulfonate containing 6.0 ppb of Aluminum Complex was tested for 96-hour LC-50 using an EPA protocol for toxicity testing of drilling fluids. The results from this test indicated a LC-50 greater than 100%(>1,000,000 ppm SPP) using the Moving Average Method calculations. Copper was used as a reference toxicant which indicates a 48 hr LC-50 0f 263 ug/l with an 89% confidence level. An HTHP drilling fluid containing 3.0 ppb of Aluminum Complex indicated an LC-50 greater than 100% (1,000,000 ppm SPP) as well.

A study was made to investigate the acute toxicity of Aluminum Complex to *turbot* (scopthalmus maximus) by using the 96 hour medium lethal concentration, which is defined as the concentration which kills 50%, of exposed fish after 96 hour exposure period at 15º C. The results indicate that at a concentration of 1,800 mg/l, the Aluminum Complex is non-toxic to turbot. Therefore the LC-50 at 24 to 96 hours was estimated as > 1,800mg/l. A mortality of 0% was observed in the control tank at the end of the test period. The test was conducted as per OECD guidelines for testing chemicals fish acute Toxicity test.

A sample of Aluminum Complex was tested for a 10-day Static Sediment Toxicity by using *Corophiun volutator* as required by CHARM 2.1 (chemical Hazard Assessment and Risk Management of Offshore Exploration & Production Chemicals). CHARM 2.1is accepted as the U.K. protocol for toxicity testing of drilling fluid chemicals. The results from this test indicate a 10-day LC-50 of >60,000 mg/l using the Moving Average Method calculation. Cadmium chloride was used as a reference toxicant which indicates LC-50 of 10.4 mg/l.

A sample of Aluminun Complex was tested to observe the effects on Skeletonema Costatum in a Marine algae growth inhibition test. The testing was conducted in accordance with Good Laboratory

Practices and ISO Protocol ISO/TC 147/SC 5 Marine Algal Growth Inhibition Test. After 72 hours, the E_TC_{50} was determined to be 319,018 mg/l using the Linear Interpolation Method of calculation. Potassium dichromate resulted in a E_TC_{50} of 2,2892 mg/l under the same test conditions.

The toxicological and Ecological data of Aluminum Complex is indicated in **Table 3,** as well mud formulation for EPA test **(Table 4**).

FIELD EXPERIENCE

The wells located in the eastern part of Ecuador presented significant challenges while drilling the Napo shale formation. The use of potassium based systems lead to two sidetracks in the first well drilled in the Yuralpa field. The wellbore problems increased the drilling cost and, in particular, the waste disposal cost caused by the excess of drill solids that required massive mud dilutions.

The Aluminun-Based fluids were introduced in 2000 by the operator to replace salt inhibited drilling fluids that had caused severe wellbore instability problems. Since then, more than thirty (30) wells that include multiple directional and horizontal sections have been drilled very successfully. **Figure 11** shows the learning curve for the application of the new system as compared with the conventional inhibited potassium system. Optimized drilling fluid design has been minimized reaming and back reaming operations due to enhanced wellbore stability. The excess of waste generated during those operations in another areas of Ecuadorian basin significantly increase the environmental impact. The waste volume generated in the field is very consistent and averages 0.9 bbl of waste per foot of well drilled. **(Fig.12).** A typical mud formulation used in the Ecuadorian basin appears in **Table 2.**

THE NEW FRONTIER OF ALUMINUM CHEMISTRY TO IMPROVE ENVIROMENTAL QUALITY- HIGH PERFORMANCE WATER BASED MUD (HPWBM)

The high performance term suggests that a HPWBM will deliver a level of performance beyond what is currently attainable using conventional water base mud. Researchers and engineers often focus on delivering a single, specific performance attribute when designing water-based alternatives to emulsion–based fluids. The addition of an ROP enhancer to a water-based mud may deliver drilling rates equivalent to those of an OBM or SBM; however, it is unlikely that it alone will match the overall drilling performance of emulsion muds.

In departure from conventional approaches, the HPWBM design team focused on delivering a high performance system rather than a novel product. The first step of the development process centered on identifying the drilling attributes of emulsion systems that make them so attractive for challenging wells operations. The key attributes of emulsion systems were identified as: 1) shale stability. 2) clay stability. 3) cuttings stability. 4) rates of penetration. 5) bit balling and accretion. 6) torque and drag.

The next stage was to research and identify the mechanisms by which the emulsions delivered these attributes, and then to duplicate them in a HPWBM. It was immediately recognized that simply combining existing products would not work and that a step-change in design approach was required to achieve the desired results. The design team recognized and accepted that some required technology may not be available in current oilfield chemical use and would be accessed from non-oilfield industries. This lead to a very time-consuming process of research, product screening, system compatibility and environmental compliance testing specifically for the new system.

The outcome of this work is a new HPWBM based on a system design approach whereby state-of-the art technology is combined in a system designed to emulate the key drilling attributes of emulsion base muds. The system is based on a novel "total inhibition" concept, whereby shale, clay and cuttings stability are systematically provided along with benefits in key areas such as ROP, accretion control and torque and drag reduction. The uniqueness of the system is such that it has been awarded a US patent. The new system delivers performance approaching that of emulsion muds systems, while offering complete environmental compliance in all key exploration areas around the world.

The novel HPWBM is a new step in the development of Aluminum based drilling fluids that emulate the drilling performance of oil-based muds without the concerns of environmental liability. The mud system is also a major step towards a better environmental performance based on a superior wellbore stability and cuttings inhibition that reduce mud dilution rates and volumes of waste for disposal. Additionally, the system has passed all the necessary toxicity tests established in the environmental regulations of the Gulf of Mexico and the UK sector of the North Sea. In particular, the application of this system in land operations requires the use of a salt-free HPWBM combined with the superior technology of aluminum.

CONCLUSIONS

1. The use of conventional salt-inhibited water-based muds to drill the challenging wells of the Ecuadorian sector of the Amazonian basin based is not an option. The potassium-based mud systems usually considered the best for fluid inhibition, have produced severe wellbore instability problems that have increased the overall drilling costs. In addition, the environmental impact is significantly amplified due to the excessive volume of waste fluid and drill cuttings.toxicity Attempts to replace chloride salts with nitrates and sulphates have also failed.
2. The reason for that unexpected behavior is the incompatibility between potassium and Kaolinitic shales that lead to wellbore instability, long reaming operations and expensive sidetracks.
3 A novel approach was introduced in the first well of the project and consisted of an aluminum complex, sealing agents, extreme pressure lubricants and an ROP enhancer.
4 The application of Aluminum chemistry for stability has been decreased the waste volume from 2.5 bbl per foot drilled while using potassium inhibited fluid to an average of 0.9 bbl of waste per hole drilled
5. The mud system is environmentally friendly in two ways: 1) no chloride salts are used for inhibition, and 2) reduced cuttings generation from wellbore stability that occurs since the aluminum hydroxide precipitates are compatible with formation geology, and then the precipitates are incorporated into the shale crystal structure formed by alumino-silicates.
6. Although further improvements to this new water-based system are anticipated, this system is a first step toward changing the paradigm of oil-based mud as the only solution for wellbore problems.
7. Operators must strike a balance between the environmental benefits and the availability of more reliable formation evaluation with the increased operational risks associated with the use of a water-based mud.
8. A new generation of HPWBM based in the same chemistry has been developed to emulate the performance of oil emulsion systems. Due to this enhanced performance the system will provide environmental quality improvements in two dimensions: 1) The possibility of substituting oil-based muds in challenging wells 2) the improvement in drilling efficiency with better wellbore stability that optimizes waste disposal volumes.

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SI Metric Conversion Factors

bbl × 1.589873	E–01	= m^3
gal × 3.785412	E–03	= m^3
cp × 1.0	E–03	= Pas
inch × 2.54	E+00	= cm
lbm × 4.535924	E–01	= kg
ft × 3.04	E–01	= m
psi × 6.894757	E+00	= kpa
psi × 6.894759	E–02	= bar
ppg × 2.853	E+00	= kg/m^3
lbm/gal × 1.198264	E+02	= kg/m^3
lb/100 ft^2 × 4.788026	E–01	= Pa
(°F-32) ÷1.8	E+00	= °C

TABLE 1 - Examples of Aluminum Compounds

Name	Formula	Water Solubility	Aqueous Solution pH
Aluminum Chloride	$AlCl_3$	S	<7
Aluminum Sulfate	$Al_2(SO_4)_3 \cdot 16\ H_2O$	S	<7
Potassium Alum	$KAl(SO_4)_2 \cdot 12\ H_2O$	S	<7
Aluminum Lactate	$Al(C_3H_5O_3)_3$	S	<7
Aluminum Stearate	$Al[O_2C(CH_2)_{16}CH_3]_3$	I	—
Sodium Aluminate	$NaAlO_2$ or $Na_2O \cdot Al_2O_3$	S	>7

S=Soluble I=Insoluble

TABLE 2 – Typical Mud Formulation for Ecuadorian Well	
Component	**Concentration**
Bentonite	9.0 lb/bbl
PHPA	1.5 lb/bbl
Aluminum Complex	3.5 lb/bbl
Amine	5.0 lb/bbl
Low Vis PAC	1.0 lb/bbl
Regular PAC	0.7 lb/bbl
Blown Asphalt	4.0 lb/bbl

TABLE 3- Ecological and Toxicological Data for AHC	
Test Method	**Result**
US EPA *M. bahia* LC_{50} for 6 ppb in Chrome-Free Lignosulsonate System (See Table 9)	>1,000,000 ppm suspended particulate phase
72hr EC_{50} *Skeletonema costatum*	1250 mg/L
Acartia tonsa 48 hour LC_{50}	>1000 mg/L
96hr LC_{50} *Scophthalamus maximus* (mg/l)	>1800
5 day EC_{50} *Abra alba* (ppm total medium)	289
28 day Aerobic Biodegradation (OECD 306), %	21 (Organic component)
Bioaccumulation Potential (Octanol/water partition co-efficient – log P_{ow})	2.4
HQ Band	Gold (No Substitution Warning)

TABLE 4 - Seawater Mud Formulation for US EPA *Mysidopsis bahia* bioassay	
Component	**Concentration**
AHC	6 lb/bbl
Bentonite	20 lb/bbl
Carboxymethyl Cellulose	0.5 lb/bbl
Lignite	3.0 lb/bbl
Sulfonated Styrene Copolymer	0.5 lb/bbl
Xanthan Gum	5.0 lb/bbl
Chrome-free Lignosulfonate	1.0 lb/bbl
Sodium Hydroxide	1.0 lb/bbl
Soda Ash	1.0 lb/bbl
Barite	137 lb/bbl

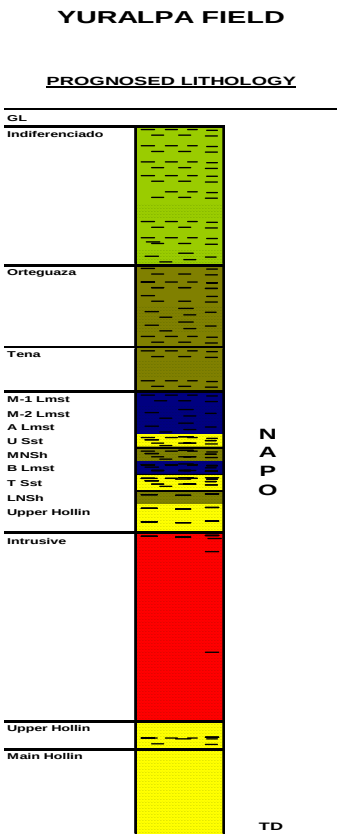


Figure 1 – Yuralpa Field Location in the Jungle of Ecuador

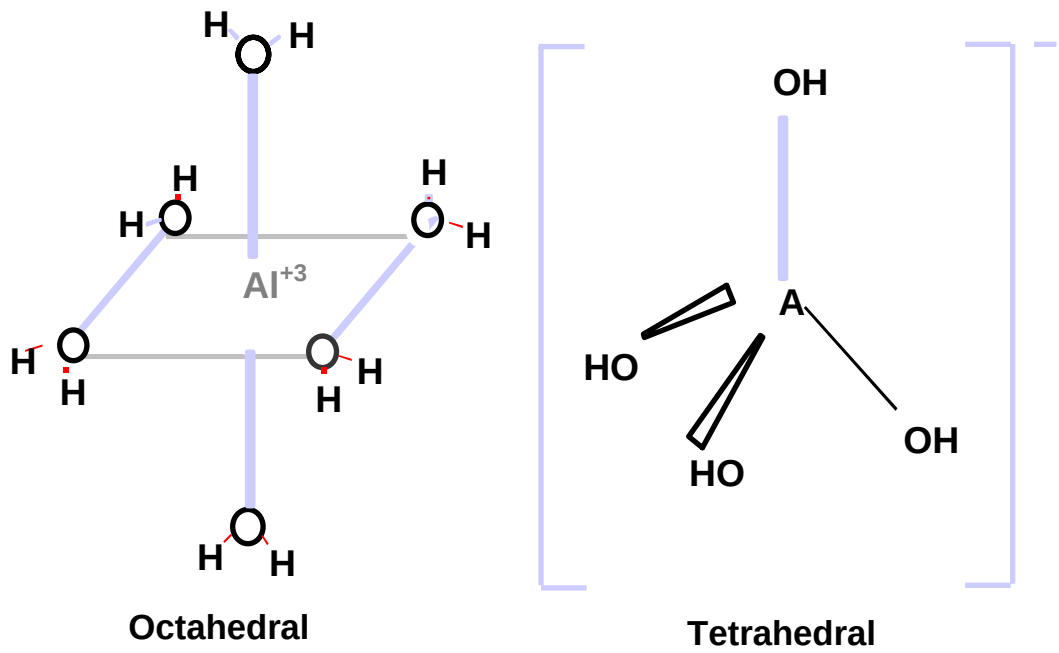


Figure 2 – Configuration of soluble aluminum salts

$$Al^{+3} + H_2O \longrightarrow Al(OH)^{+2} + H^+$$

$$Al^{+3} + 2H_2O \longrightarrow Al(OH)_2^{+} + 2H^+$$

$$Al^{+3} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$$

$$Al^{+3} + 4H_2O \longrightarrow Al(OH)_4^{-} + 4H^+$$

Figure 3 – Hydrolysis of aluminum cations

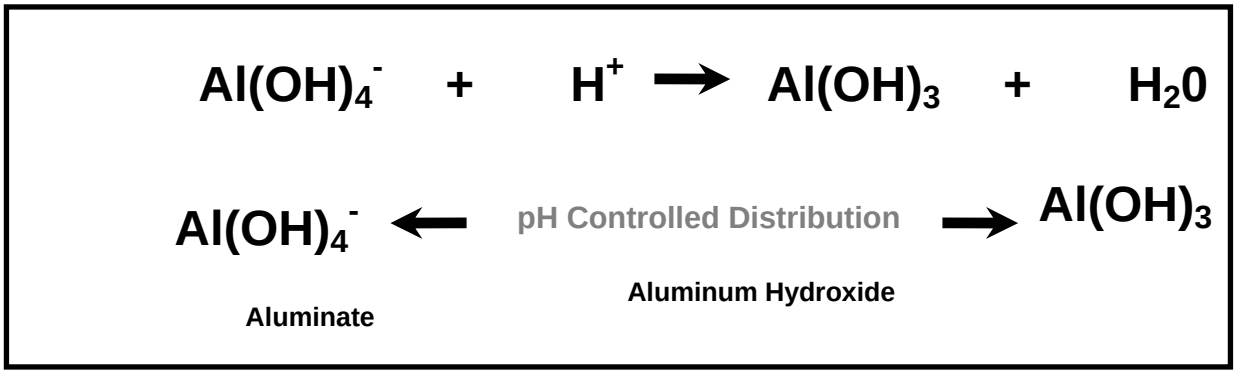


Figure 4– Hydrolysis of aluminum cations and precipitate formation

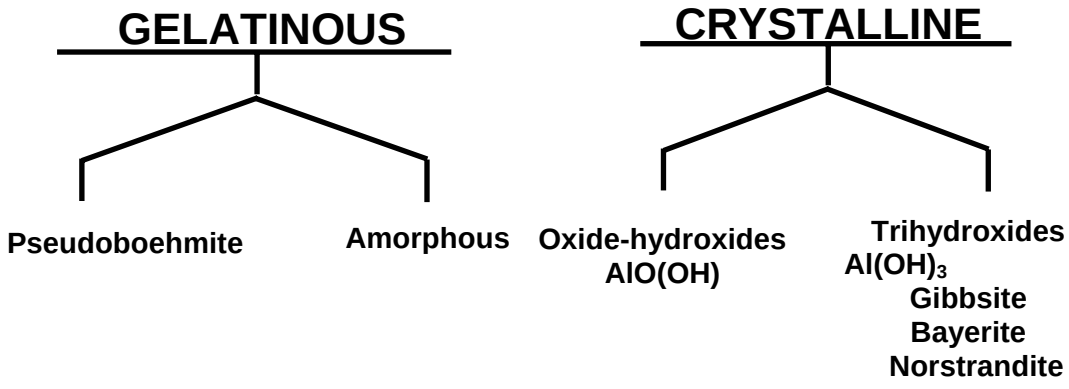


Figure 5 – Crystalline and non-crystalline or gelatinous forms of aluminum hydroxide

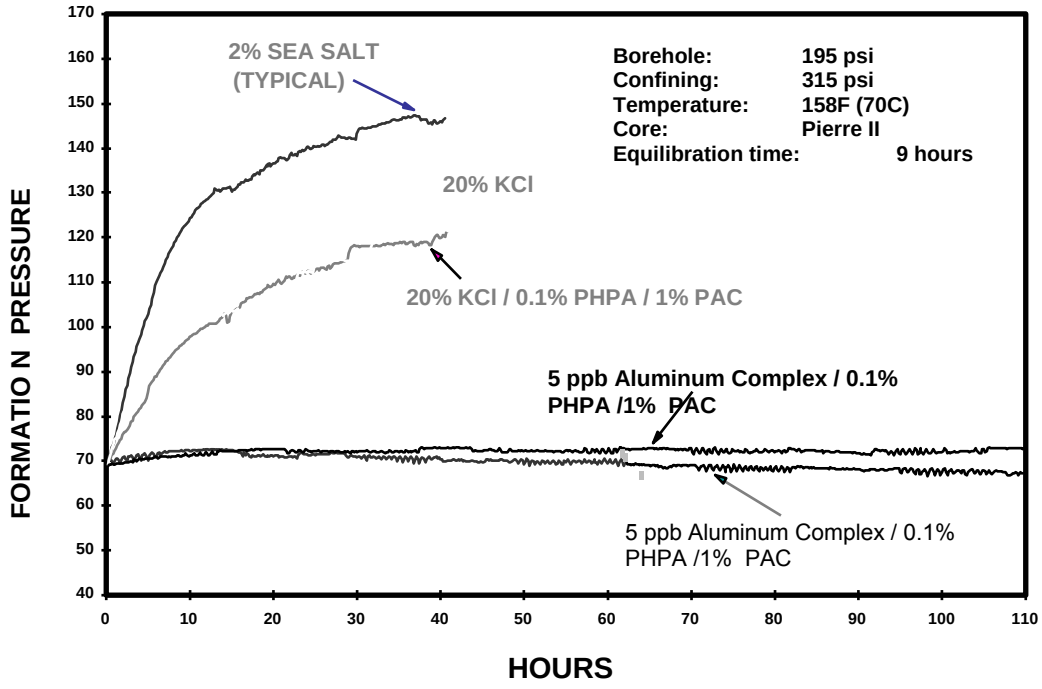


Figure 6 – Pore Pressure Transmission of aluminum based drilling fluid

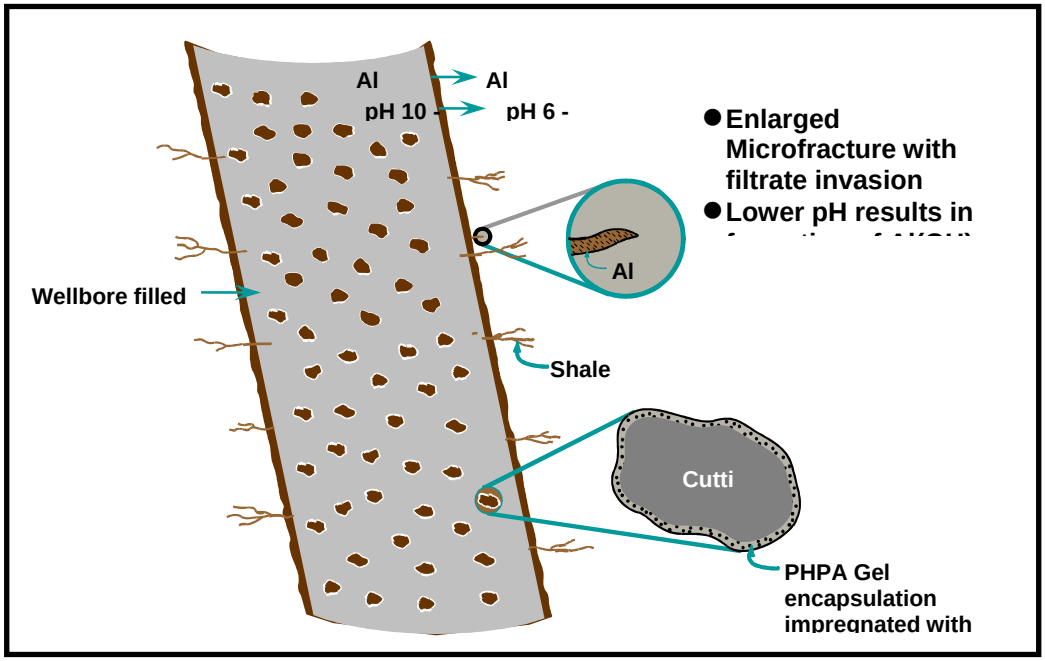


Figure 7 - Wellbore stability is enhanced by precipitation of aluminum hydroxides within shale pore throats and microfractures. Drill solids integrity is maintained by a combination of partially hydrolyzed polyacrylamide and aluminum complex.

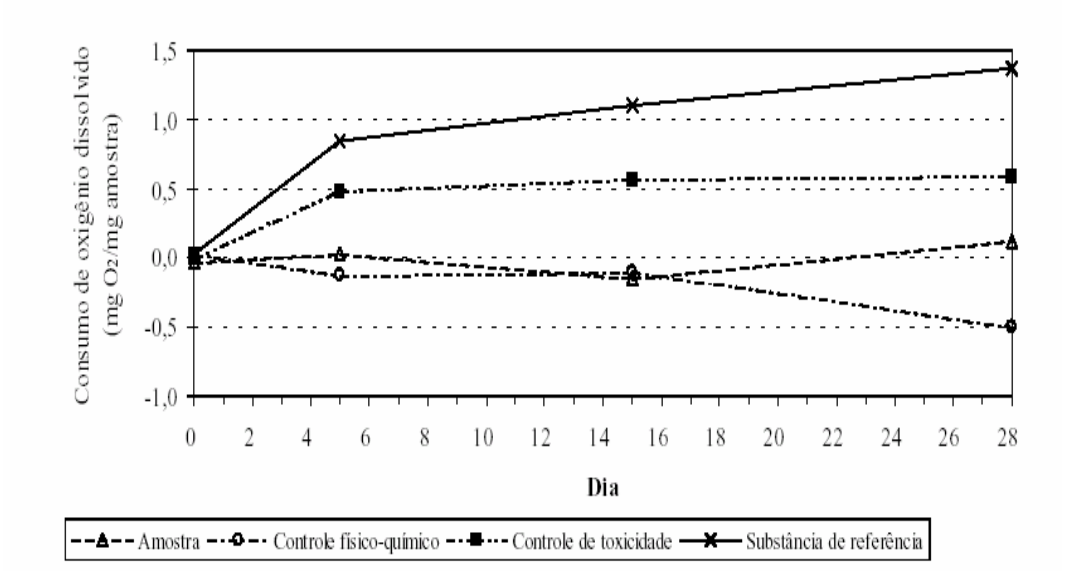


Figure 8 – Oxygen Demand Biodegradation Test-Aluminun Complex/Amine

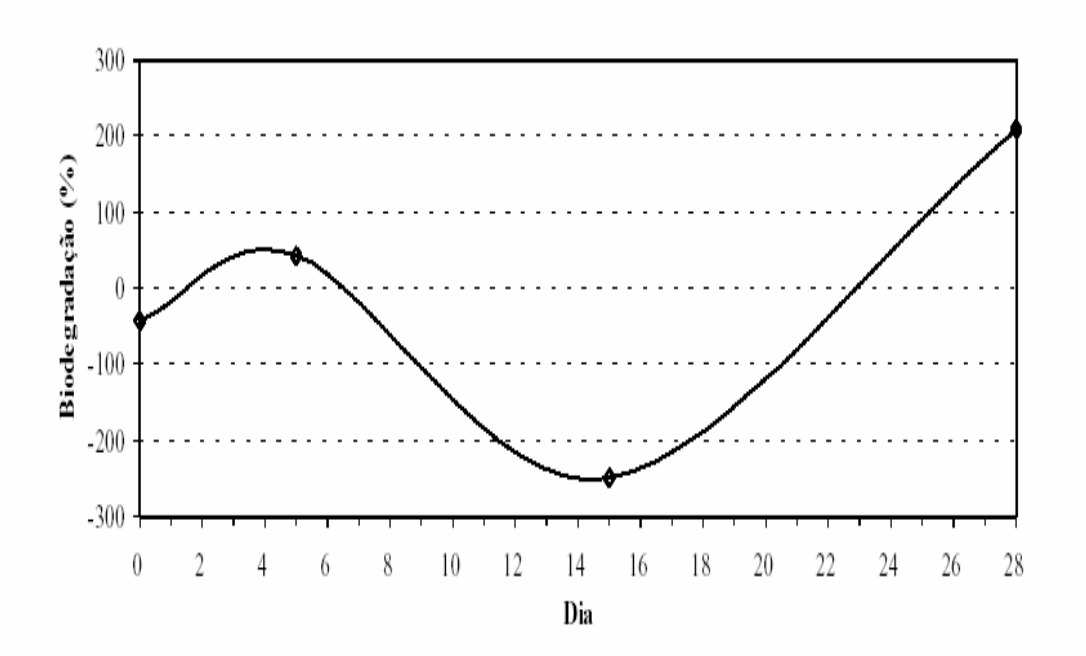


Figure 9 – Biodegradation Curve-Fluid: Aluminum Complex/Amine

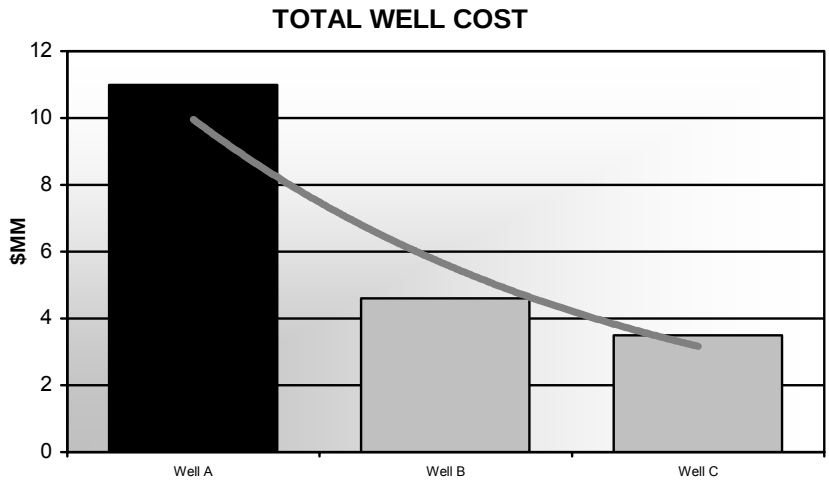


Figure 10 – Field application of aluminum-based drilling fluid to replace potassium Inhibited fluid system in the Yuralpa field-Ecuador

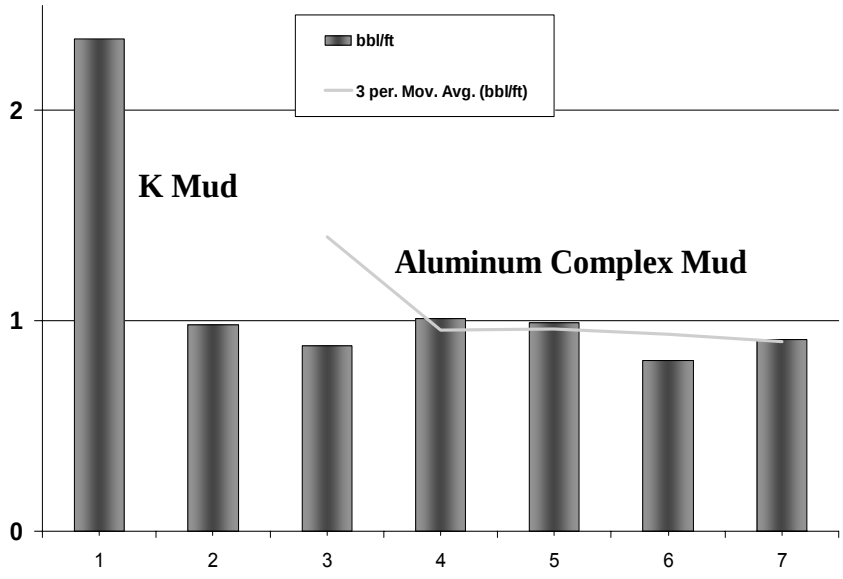


Figure 11– Performance review of Aluminum Complex Mud vs K Mud regarding waste volumes reported as bbl waste per foot hole drilled.

Safety considerations for flow and level instrumentation on oil storage tanks.

Wayne Shannon
Magnetrol
Downers Grove, Illinois

Randy Webb
Myers Aubrey Company
Tulsa, Oklahoma

ABSTRACT

The paper "FIELD DEMONSTRATION AND TECH-TRANSFER FOR THE COUNTINUOUS MEASUREMENT OF CRUDE OIL STOCK TANK EMISSIONS" by R. E. Babcock of the University of Arkansas used instrumentation for continuous measurement of the exhaust flow rate and the level from oil storage tanks.

A thermal dispersion mass flow meter was used to continuously measure the emission rate in SCFM from the vessel and a guided wave radar was used for continuous level measurement. The two sets of data were set to a data logger to provide a record of these variables.

Safety issues need to be considered when installing electronic instrumentation in a tank containing flammable or explosive materials. Both the TA2 mass flow meter and the Eclipse Guided Wave Radar required electrical power to operate and produced a 4-20 mA output signal that was sent to the data recorder. These devices put energy into a potentially explosive environment. The instruments can be safely installed following appropriate standards. They are approved for use in hazardous areas by third party agencies.

The selection and installation of the instruments must consider the appropriate agency approvals. Consideration must be given to:

1) Area classification. Hazardous areas are specified by the type of material (Class), the frequency of a hazardous condition occurring (Division) and the type of media present (Group). Both the area inside the tank and piping as well as the area surrounding the tank must be reviewed.

2) Protection Method. The primary protection methods used in instrumentation are explosion proof, non-incentive, and intrinsic safety.

Each protection method has special requirements for selecting and installing the instrument. Examples will be discussed for installing the instruments for different protection methods and in different area classifications.

INTRODUCTION

Level and Flow electronic instrumentation used by Dr.Babcock provides a continuous measurement of these process variables. The products used in the demonstration involved two relatively new technologies for level and flow measurement.

Continuous level measurement is obtained using Magnetrol's Eclipse guided wave radar. This technology has just been introduced during the past 7 years and is gaining wide acceptance. One key advantage of this technology is obtaining a level measurement without consideration to the properties of the fluid. This technology has also been proven to provide accurate level measurements in demanding applications of varying media, vapors, turbulence, or foam over a broad range of pressures and temperatures.

The measurement of emission rates from the tank was made using Magnetrol's TA2 thermal dispersion mass flow meter. This instrument offers benefits of directly obtaining a mass flow measurement of the emission flow rate in SCFM over a very wide range of operating conditions. This technology has excellent low flow sensitivity enabling it to measure very low flow rates and provide high turndown capabilities. The instrument provides a measurement of the flow rate plus the totalized flow and elapsed time indication to give total emission rates over a specific time interval. This instrument is very easy to install in the tank exhaust piping.

Both of these instruments require electrical power and provide a 4-20 mA output signal which can be sent to data logger or other device for maintaining a record of these variables.

An illustration showing the installation of these instruments is shown in figure 1.

Safety Concerns

There are safety concerns when installing an electrically powered device in a tank with flammable or explosive fluids and vapors. Standards are developed by the National Electric Code (NEC) for use of equipment in hazardous areas. Third party agencies such as Factory Mutual provide testing to insure that these standards are obtained and that the equipment is safe to use in hazardous areas.

When dealing with the use of instrumentation in hazardous areas consideration must be given to:

- Definition of the area classification and
- Protection Method used to meet these standards.

Area Classification

Area classification is defined by:
- Class – Category of the type of material
- Division - Frequency of a hazardous condition occurring
- Group – Type of flammable material based on its ignition energy

Class: Type of material

Class I – Flammable gases, vapor, or liquids are present in the air in quantities sufficient to produce an explosive atmosphere.

Class II – Combustible dust and power suspended in the air in quantities sufficient to produce an explosive atmosphere.

Class III – Flammable fibers suspended in the air in quantities to produce an explosive atmosphere.

Applications in the petroleum industry deal almost exclusively with hazardous liquids, vapor and gases which are Class I service. Approximately 85% of the all hazardous locations in North America are defined as Class I.

Division

Division: Indication of the frequency of a hazardous condition occurring. The National Electric Code as defines these:

Division 1 – Hazardous locations are where an explosive atmosphere exists continuously or intermittently under normal operating condition and under fault conditions.

Division 2 – Hazardous locations that are adjacent to a Division 1 location or where an explosive atmosphere infrequently exists when there is a fault or breakdown of equipment.

When dealing with oil storage tanks, concern must be given to both the conditions inside the tank and in the surrounding area (Figure 2). For instance, the area inside the tank is a Division 1 area where a hazardous condition continuously exists while the area outside the tank can be Division 1 or Division 2 hazardous area. This boundary between a Division 1 area and a Division 2 area outside of the tank is up to the discretion of the individual responsible for certifying an area.

Group

Group: The group classification specifies the type of the flammable material with regard to the type of vapor. The groups are based upon the ignition energy of the material. For Class I service dealing with flammable liquids and vapors, the Groups are divided into:

Group A – Atmospheres containing acetylene

Group B – Atmospheres containing Hydrogen plus a few other hydrocarbons

Group C – Atmospheres containing ethylene and similar vapors

Group D – Atmospheres containing methane, ethane, propane and other similar gases.

Groups C and D are the most common and are of concern to applications for vapors from oil storage.

Temperature Code

The last consideration is the amount of heat generated by the instrument. An instrument is classified for a specific maximum surface temperature which the device can reach during normal and fault conditions. To properly apply an instrument in a hazardous area the maximum surface temperature of the device must be less than the auto ignition temperature of any potential gases or vapor that may come in contact with the device.

The National Electric Code has established various temperature codes, which identify the maximum surface temperature that the instrument can reach. This code is part of the approval listing of the instrument.

The next step in safely applying instrumentation in hazardous areas concerns the selection of the protection method to meet the area classification.

Protection Method

There are three main protection methods used:

- Explosion Proof
- Non-Incendive
- Intrinsically Safe

Explosion proof and intrinsically safe are suitable for use in both Division 1 and Division 2 areas while non-incendive is useable only in Division 2 areas.

Explosion proof

Items that are explosion proof are designed so that the enclosure will contain an explosion and prevent flame propagation to the external atmosphere. An explosion is allowed to occur but it is confined within an enclosure built to resist the pressures created during the explosion.

This requires that the enclosure walls be thick enough to contain an explosive force. The internal pressure created during an explosion depends upon the gas or vapor that was ignited. As a result, explosion proof designs require the heavy-duty enclosure that is frequently seen in petroleum processing.

Explosion proof enclosures have historically been the primary method of protection in the petroleum industry for over fifty years.

Intrinsically safe

Intrinsically safety is a technique that insures that the amount of energy available in the instrument is too low to ignite the explosive mixture of vapor and air. The energy to the instrument is limited with the use of an intrinsically safe barrier that is located in a non-hazardous area. This limits the voltage and current going to the instrument. The power to intrinsically safe instruments is 24 VDC and the amount of current required will vary between 4 and 20 mA. See Figure 3.

Intrinsically safe designs do not depend upon the enclosure design however many instruments will use the same enclosure for both explosion proof and intrinsically safe designs. This is often a question of economics for the instrument manufacturer.

Non-incendive

The non-incendive method of protection is suitable only in Division 2 areas where hazardous conditions exist only under upset conditions. To obtain non-incendive approval, the electrical circuit is not capable of igniting an explosive atmosphere – there are no arcing or sparking components. It is important to note that this approval is based on hazardous conditions occurring only during fault conditions and not during normal operation.

The primary advantage of this method of protection is that it is less expensive to install than if the device is installed using explosion proof requirements.

Choosing a Protection Method

The decision on which protection method to use depends upon several factors – the main ones are the instrument design, installation costs, and the user's preferences.

Instrument Design.

The Eclipse Guided Wave Radar is available in either an intrinsically safe design or explosion proof design. The enclosure and external appearance is the same for both designs. The only difference is internal circuit between the intrinsically safe and explosion proof design.

To understand this difference it is necessary to look at the probe design. Because the probe has internal o-ring seals it cannot withstand an explosion. Thus the probe itself is not rated explosion proof. Therefore, to meet the safety requirements for a Division 1 area, the amount of energy going into the hazardous area of the tank must be limited. If installed as an intrinsically safe device the external safety barrier limits the energy to the instrument. However, if installed as an explosion proof design there is nothing external to the instrument to limit the energy. In order to install the probe in a hazardous area the explosion proof design incorporates internal barriers that limit the energy into the tank. Technically, this is referred to as an explosion proof design with intrinsically safe probe circuit.

Some instruments are only available as in explosion proof design such as the TA2 thermal dispersion mass flow meter. To operate this instrument requires more energy than can

be supplied over a traditional intrinsically safe circuit. Four wires are required to operate this instrument – two wires for input power and two wires for the output 4-20 mA signal. The input power can be either 120/240 VAC or 24 VDC depending upon user preference. Being able to power this instrument with AC power is a preference for some customers depending upon power availability at the job site.

The probe used on the TA2 is all welded and thus meets explosion proof requirements; therefore, there is no need to limit the energy to the probe. The principle of operation requires that power, in the form of heat, is required to make the flow measurement. There is potential concern about the amount of heat that can enter the process through the probe. Testing is performed by a third party (Factory Mutual) during the approval testing of the instrument. The National Electric Code has established "T Ratings" which determine the maximum surface temperature that the instrument can obtain during a fault. With the TA2, the normal temperature difference is typically 8° C or less. For safety considerations, testing is also done under worse case conditions, which could exist if the normal protection circuit in the instrument fails. The instrument is given a T code depending on this testing. For the TA2, the T code is a T6. This is the lowest surface temperature classification. Per the NEC, a T6 code indicates that the maximum surface temperature of the probe will be no greater than 85° C. This means that the TA2 can safely be used in any application if the auto ignition temperature of the liquid or vapor is greater than 85° C.

The NFPA (National Fire Protection Association) has established Auto Ignition Temperatures for many liquids, gases, and vapors. All hydrocarbons have Auto Ignition Temperatures well in excess of 200° C. Thus the TA2 is safe to use in any application where hydrocarbon gas or vapor exists.

Installation Costs.

As indicated above, the Eclipse Guided Wave Radar is available in either an explosion proof or an intrinsically safe design. Because the explosion proof design incorporates the intrinsically safe probe circuit, this design is more expensive than the intrinsically safe design. However, the intrinsically safe design requires the use of an external barrier in the control room,. The cost of this separate safety device is greater than the price adder for the internal intrinsically safe probe circuit included in the explosion proof design of the Eclipse.

There are however, other costs saving issues by using an intrinsically safe implementation. By using the intrinsically safe installation, the wiring from the control room to the instrument can be simpler and less expensive. Heavy duty explosion proof conduit is not needed with IS designs. An all intrinsically safe installation permits the wiring to and from the instrument to be placed in cable trays. Simple cable glands can be used to seal the wiring at the instrument.

Due to savings in wiring cost, an all intrinsically safe installation may be less expensive than an explosion proof installation. However, sometimes this is not the case due to the typical preference of using conduit even in those installations when not required.

If an explosion proof installation is selected, the installation costs of the instruments can be reduced if the instrument is installed as a Division 2 non incendive device. While Division 1 is defined as inside the tank and immediately adjacent to the tank, this boundary between

Division 1 and Division 2 is subject to interpretation by the individual user. If installed in accordance with Division 1 practice, rigid explosion conduit and conduit seals between the instrument and the conduit must be installed. Installing the instrument in accordance with Division 2 practice permits the use of flexible conduit and eliminates the need for conduit seals, see figure 4. As a result Division 2 installation is less expensive than Division 1 installation. Due to cost savings, there is a growing trend to use Division 2 installation methods.

User Preference

The major determination in selecting the protection method is user preference. Typically, installations in North America use explosion proof designs while installations in Europe are generally intrinsically safe.

This is especially true in the Petroleum Processing Industry in North America, which has an overwhelming preference to explosion proof designs. It is estimated that over 90% of the installations in petroleum processing are explosion proof.

Other industries such as chemical processing and pharmaceutical may use some intrinsically safe installations, but the preference still is towards explosion proof in North America.

Conclusion.

Electronic flow and level instrumentation can safely be installed in potentially explosive environments, which exist inside oil storage tanks. Consideration must be given to the area classification and the protection method. Some instruments can be installed as either explosion proof or as intrinsically safe while others are only available as an explosion proof design. The decision on which type of installation to use is subjective generally depending upon the preferences of the individual user.

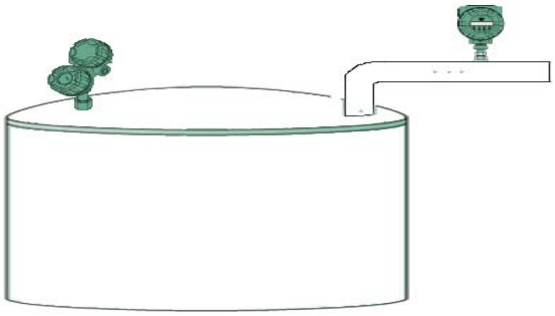


Figure 1
Eclipse and TA2 installed in oil storage tank

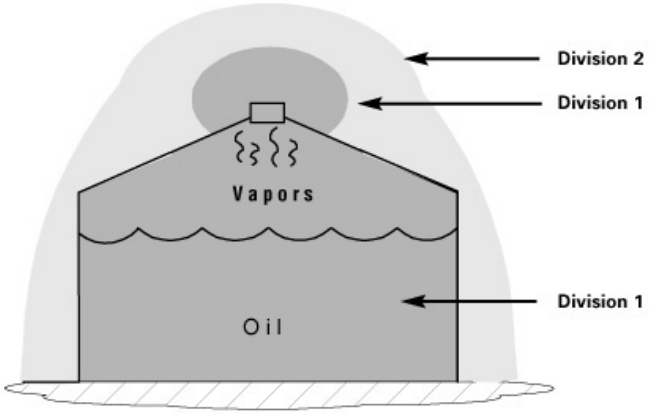


Figure 2
Area classification around a tank

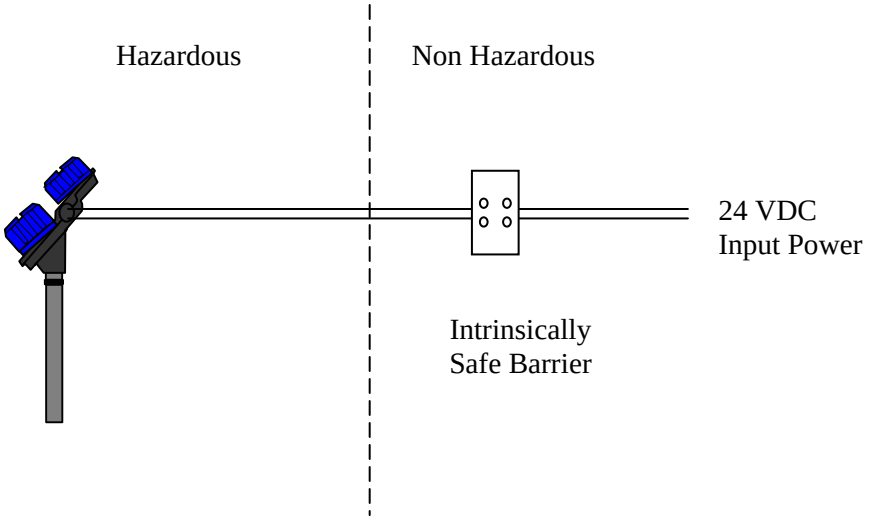


Figure 3
Intrinsically safe
installation

Figure 4
Non-incendive installation of TA2 Thermal
mass flow meter for natural gas

Global Warming Prevention Scheme "CO_2 - EOR"

Masaki Iijima (Mitsubishi Heavy Industries, Ltd. CO_2 Business Development Group)
Yoshihiro Tsukita (Kyushu Institute of Technology Center for Cooperative Research)

Introduction

Humankind has begun to use petroleum fuel in the Industrial Revolution. In these years, consumption of petroleum fuel has sharply increased, and it is apprehended that a short supply will be occurred in around 2010, or within 2～3 years at the earliest chance.

On the other hand, as the result of using petroleum fuel as the principal energy, the global warming has been actualized, and its countermeasure has become urgent issue.

As one of the countermeasures, Mitsubishi Heavy Industries, Ltd. (MHI hereafter) and Kyushu Institute of Technology (KIT hereafter) have researched and developed "CO_2 - EOR" system to use EOR (Enhanced Oil Recovery) by recovering CO_2 from flue gas.

"CO_2 - EOR" is the system that recovers CO_2 with amine as solvent from flue gas from thermal power stations and refineries and gas process plants where consume a lot of oil or gas as fuel, and inject the recovered CO_2 into oil well after pressurizing and dehydrating so as to increase oil extraction.

"CO_2 - EOR" confines CO_2 which should be emitted into atmosphere into oil field. Consequently it also works as a global warming prevention measures.

Therefore, "CO_2 - EOR" is also a system enabling the issues with energy and environment to solve simultaneously.

Explanations shall be given herewith for the following paragraph.

- What the motive to plan the "CO_2 - EOR" was.
- What the "CO_2 - EOR" is.
- How feasibility of the "CO_2 - EOR" was verified.
- What phase the "CO_2 - EOR" is now.

It is requested from us to confirm our consensus for the following matters before explaining about "CO_2 - EOR".

The important circumstance for humankind is how fast we put a life style to economize energy in practice in order to solve issues with energy and environment which are urgent measures for us.

It is considerable that our system enables such activities to supplement.

1. System of CO_2 - EOR

The concept of CO_2 - EOR shall be introduced. CO_2 will be recovered from flue gas coming out of thermal power stations locating near oil fields in oil production countries by means of the recovering plant, and the recovered CO_2 will be injected into an oil well, recovery of oil will be increase with miscible effect of CO_2. Meanwhile, injecting the CO_2 results in reduction of exhausted CO_2.

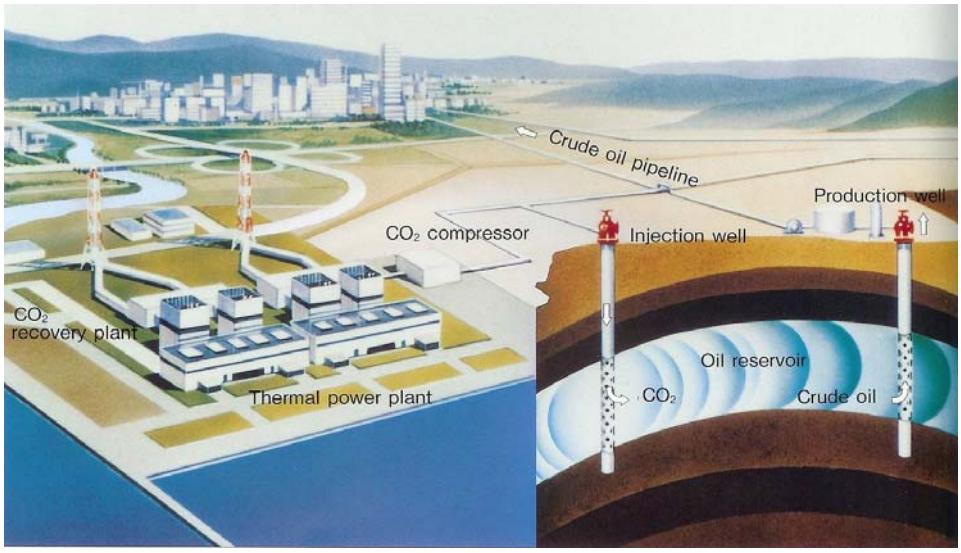


Fig. 1 System of CO_2-EOR (Enhanced Oil Recovery)

2. History

In winter 1996, a local news announced that, in Abu Dhabi, since natural gas was tight due to increase of demand for people's livelihood, natural gas for increasing recovery of crude oil (EOR) will be imported from Qatar.

CO_2 having EOR effect higher than natural gas drew attention. Worldwide status for CO_2 recovery technology from flue gas was investigated. It was confirmed that the MHI's CO_2 recovery technology is the highest in the world.

Quantity and cost of recoverable CO_2 exhausted from the plants in Abu Dhabi were investigated by performing the site survey under co-operation of the Abu Dhabi National Oil Company (ADNOC). The survey results indicated yearly production of usable low cost CO_2 for EOR was 16 million ton.

In winter, 1997, establishment of JI and CDM in Kyoto Mechanism was planed so as to qualify CO_2 - EOR as an effective CO_2 reduction measure. We submitted the proposal document to the representatives of Japan and intelligent member in the Kyoto Conference so as to advise to establish JI and CDM and Kyoto mechanism could have JI and CDM.

MHI carried out marketing activities of this system to oil production countries. ADNOC examined for on-shore Bab oil field. MHI carried out the F/S. ADNOC confirm feasibility through 3rd party's evaluation. Now ADNOC are studying pilot test.

To continue PR by announcing in international conventions and research to improve the CO_2 recovery technology.

Co-operation promotion general agreement was concluded between MHI and KIT in 2004.

MHI commenced the joint research with ARAMCO in Saudi Arabia.

3. EOR in Oil Recovery System

In order to enhance oil recovery, countermeasures will be applied primary recovery, secondary recovery and tertiary recovery in order.

For the main production increase methods, there are artificial lift to pump up oil, pressure maintenance to supplement oil reservoir lowered due to oil and gas production, thermal to heat up oil reservoir with steam so as to ease oil flow, and so force.

CO_2 - EOR is the tertiary recovery, the point for miscible effect is such that CO_2 forced into reservoir rock at 1000～3000m deep under ground becomes supercritical state and is freely mixed with oil to form a single phase so as to reduce the oil viscosity. Natural gas is also used for gas to be forced in, however unless otherwise the oil reservoir is deep enough, it does not become a miscible state. CO_2 is used for oil field where CO_2 is easily obtained from neighboring. CO_2 has a feature to become miscible state under lower pressure, and is available wider application.

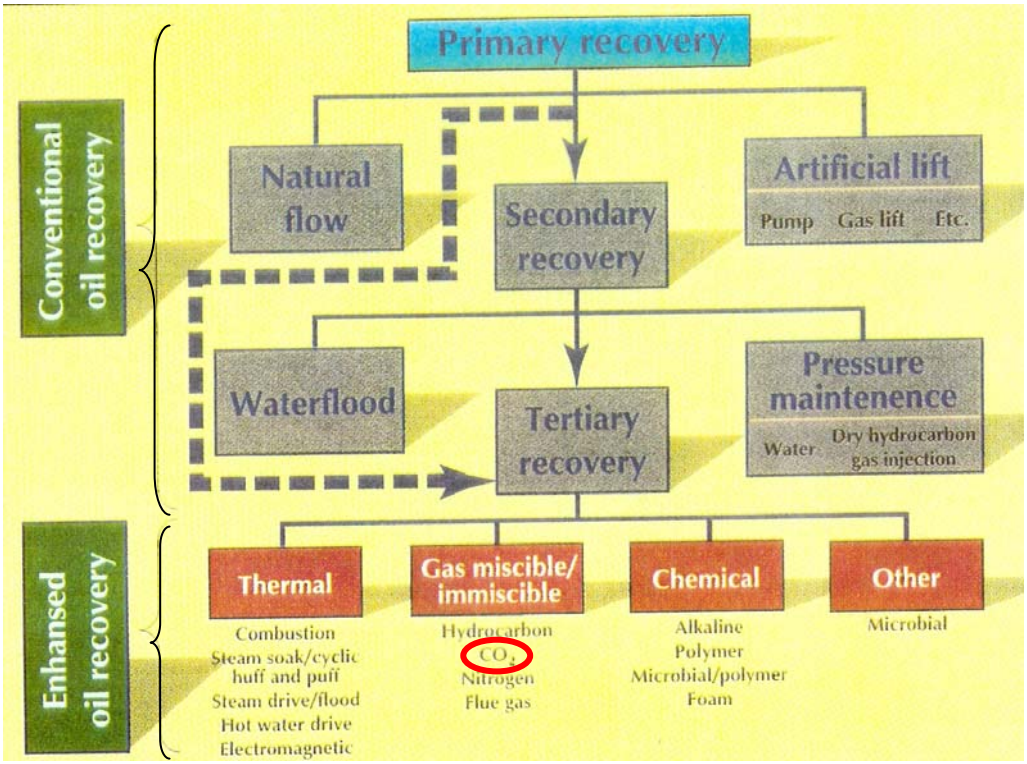


Fig. 2 EOR in Oil Recovery System

4. The Middle East Oil Field Area

The Middle East is a large oil field area. Surrounding Arabian Gulf, there are many major OPEC countries such as Saudi Arabia, Kuwait, Iraq, Iran and United Arab Emirates.

This area is called as "Middle-east Magazine" because it is an oil field area and the instability of a government succession. The countries where we are studying for the CO_2 - EOR are Saudi Arabia and United Arab Emirates

.

Fig. 3 Oil Field Zone (Middle East)

5. Map for Oil Fields and Potential CO_2 Sources

Abu Dhabi Emirate is the leading country in United Arab Emirates, and thermal power station for the people's livelihood, oil refinery, LNG plant and so forth are located in area near from the oil field.

Red circles in the map show the process plants for oil and gas, blue circles show thermal power stations, and red towers show oil fields. In the off-shore area there is the world seventh biggest Zakum Oil Field, for which Japan owns the concession as much as 12%. It was clarified as the result of simulation study that The Zakum oil field has high feasibility for enhanced oil recovery with CO_2 miscible. In the discussion with ADNOC, first an on-shore pilot plant will be constructed at Bab Oil Field located under Hubshan Gas Process Plant.

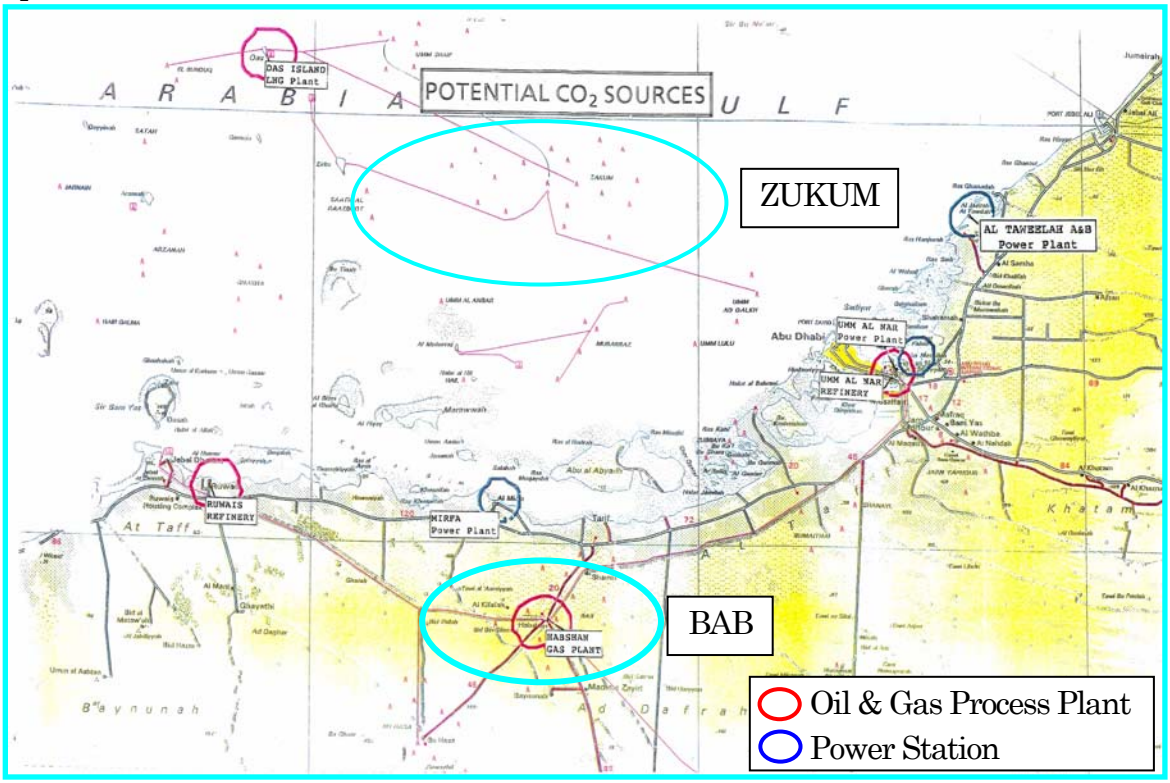


Fig. 4 Location of Oilfields & CO_2 Sources in Abu Dhabi

6. CO_2 Recovery Plant

The actual result of the CO_2 recovery plant shall be introduced. This plant is to recover CO_2 from steam reformer flue gas to be required for urea production, has operated since 1999
In Malaysia. Purity of the CO_2 recovered with absorbing solvent is 99.9vol%. 5 sets of MHI CO_2 recovery plants of which performance is the highest in the world are under construction.

160 T/D CO_2 Recovery Plant
Location: Keda, Malaysia Start up: October, 1999

Plant Specifications

Feed Gas	Steam Reformer Flue Gas
Application	Urea Production
Flue Gas Flow Rate	47,000 Nm^3/H
CO_2 Recovery Rate	160 Metric Ton/Day
CO_2 Purity	99.9 vol. % and Above(Dry Base)
Solvent	KS-1

7. Operational Flow of CO_2 Recovery Process

The process of the CO_2 recovery plant shall be explained. The flue gas entering from the left lower portion in the sketch will enter into the absorption tower after cooled down and goes up. The flue gas removing CO_2 by contacting with amine reversibly flowing will be discharged to the atmosphere from the top of the absorption tower. The amine absorbing the CO_2 will discharge the CO_2 by diffusing and heating, and will be regenerated to return into the absorption tower so as to be utilized to absorb the next CO_2. The discharged CO_2 will be recovered from the top of the regeneration tower. Because gas and supplied power to be used for the recovery plant are cheap enough in the oil production countries such as Abu Dhabi, the CO_2 recovery cost will become also cheap enough to use for EOR.

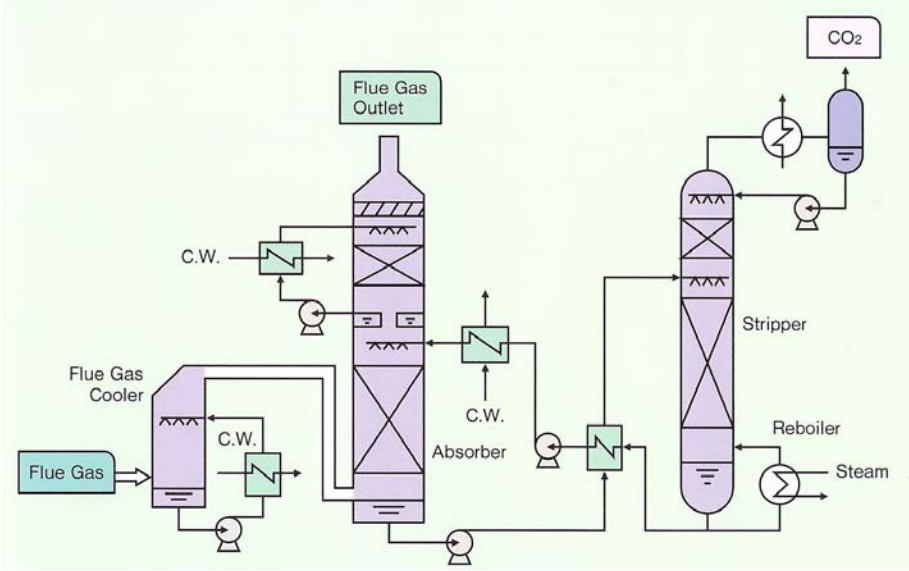


Fig. 6 Flow of CO_2 Recovery Process

8. Quantity and Recovery Cost of CO_2

The quantity and recovery cost of recoverable CO_2 were calculated from data acquired during surveying various thermal power stations by means of MHI CO_2 recovery system. Taking the X-axis for the recovery cost, and the Y-axis for the recoverable quantity, the generated quantities were piled up in order from the sources with cheaper recovery cost. The larger flue gas quantity the cheaper cost. It was clarified that recoverable CO_2 of which recovery cost is lower than the price of natural gas was Abu Dhabi, and the quantity reached up to 16 million ton per year (800MMSCFD).

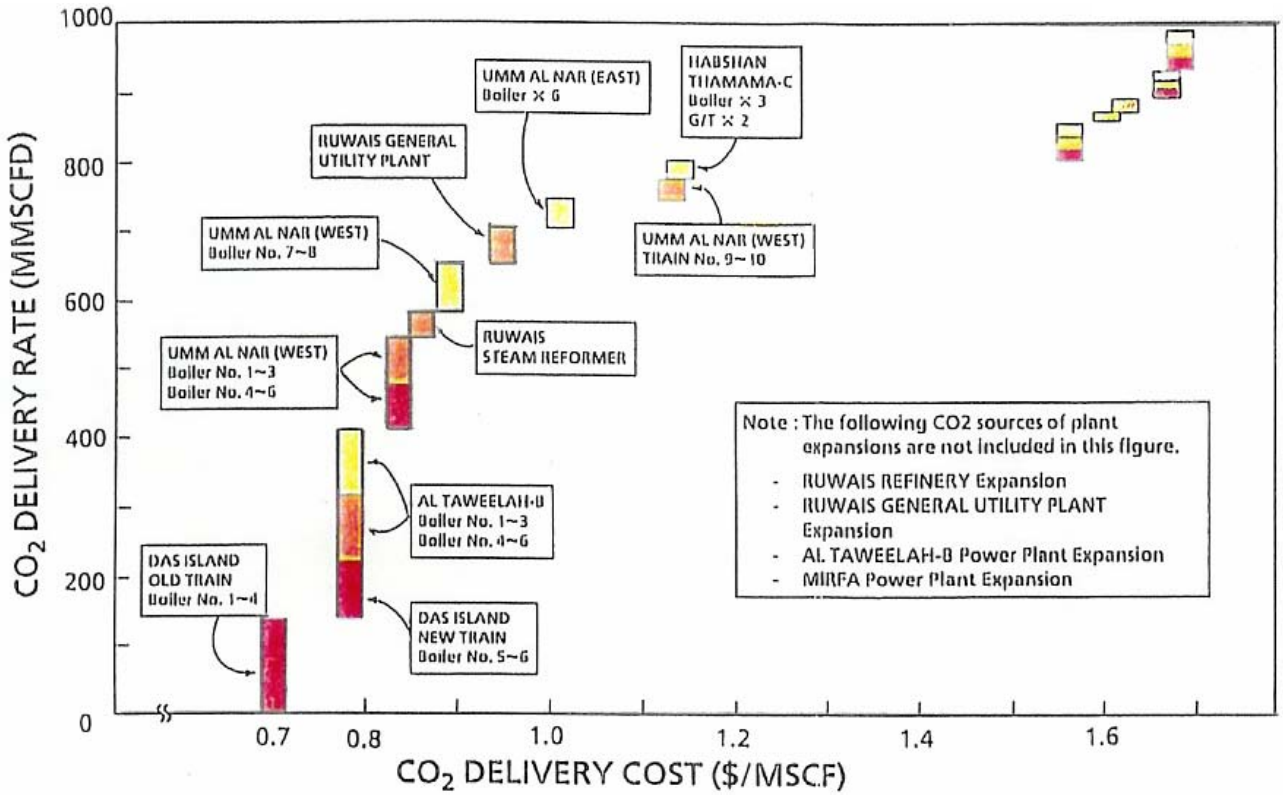


Fig .7 Recovery Volume & Recovery Cost of CO_2 in AbuDhabi

9. System of CO_2 - EOR

Outline of the CO_2 - EOR shall be explained. The CO_2 after pressured up and dehydrating will be injected into a oil reservoir rock under a cap rock from pressure inlet well at the upper left portion in the sketch and the CO_2 and crude oil become miscible state. The miscible-state CO_2 will be mixed with oil and lowers viscosity of the oil, thereby the oil will flow easily resulting in increase of the oil production. A part of the injected CO_2 will be recovered from the oil delivery well with oil, and the CO_2 will be injected into oil field again after separating from the oil.

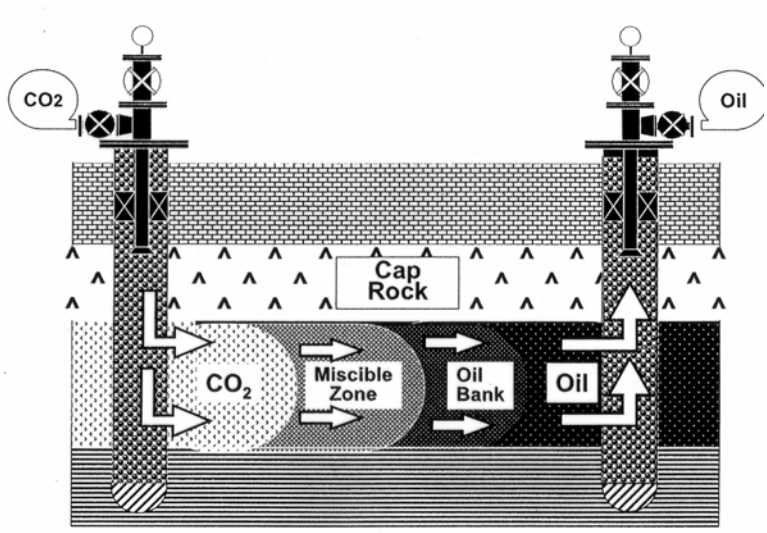


Fig. 8 System of CO_2 - EOR

10. EOR System and Crude Oil Recovery Ratio

When water injection of the secondary recovery has been accomplished, the oil recovery ratio reaches 25～35% level. When CO_2 is used, the miscible effect may be obtained in the lower part of hair hole in the reservoir rock because CO_2 is heavier than natural gas. Accordingly, further oil recovery may be practicable as mentioned here, increase of recovery ratio may be expected as much as around 15%.

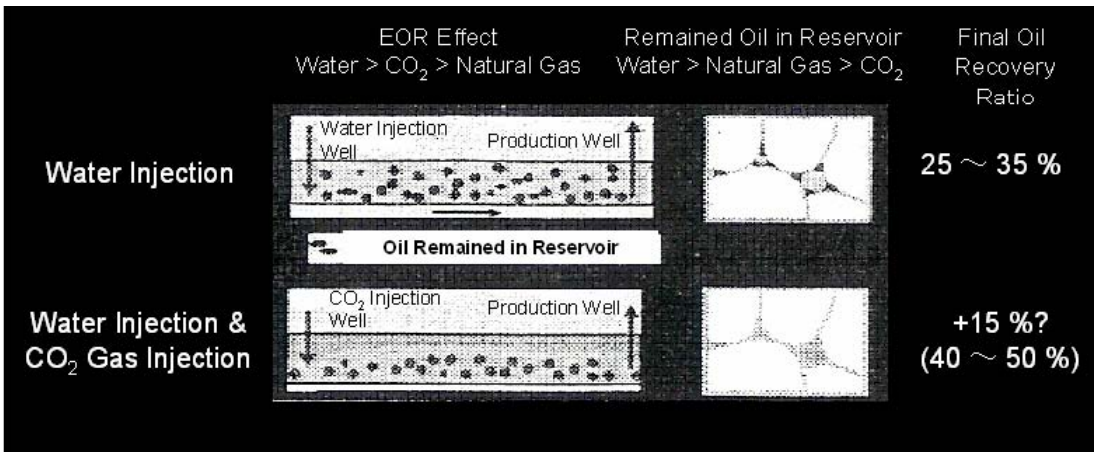


Fig. 9 Oil Recovery Ratio @ Each EOR System

11. Increase of Recovery Ratio by means of CO_2 - EOR

There is an actual effect for increased production by using natural CO_2 for EOR. As the result of injection of natural CO_2 supplied through pipelines from under ground natural CO_2 in States of Colorado and New Mexico USA into Permian Basin in Texas, the crude oil recovery ratio was increased around 15%.

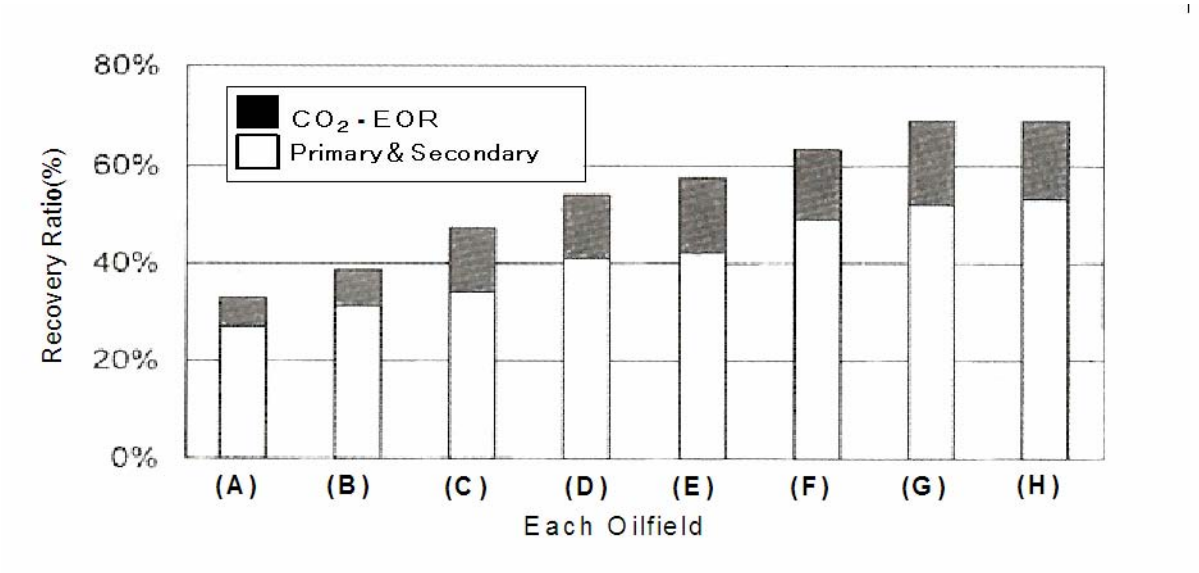


Fig. 10 Rise of Oil Recovery Ratio by CO_2 – EOR(Permian Basin in West Texas)

12. Prediction of Production obtained from creaming curve

Fig.11 shows the so called creaming curve of Shell. It plots discovery against exploration wildcats which are the wells that either do –or do not find a new oil field. The largest fields are usually found first for reasons, being too large to miss. Therefore first half of discovery-increasing curve is steep. In the latter half ,the curve flattens as new discovered oil fields are too small to be viable. Shell has found about 60 giga-barrel with 3600 exploration wells drilled over its entire history since 1895. If Shell drilled 3600 well again, it could expected to find only 16 giga-barrel. The oil discovery efficiency of the latter half will go down to 1/4 of the first half. Experimentally, oil production quantity begins to decline after oil field has produced half of reservoir. If decline quantity is larger than discovery quantity, oil supply begins to decrease.
(Ref. to Peak Oil by C.J.Campbell)

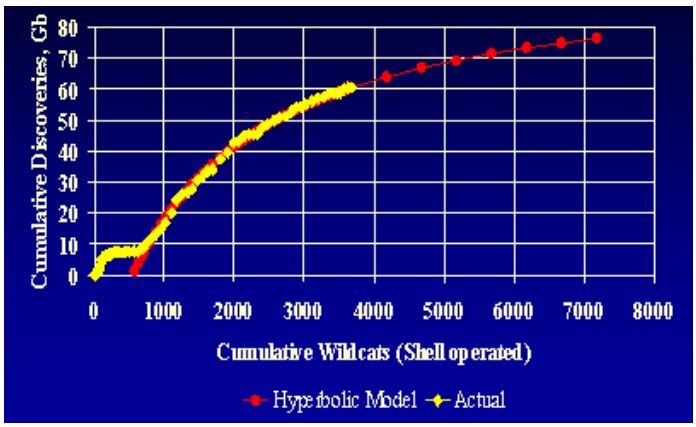


Fig. 11 Creaming Curve (Shell Experience)

13. Progress of Worldwide Oil and Natural Gas Productions

There are the history and prediction of the worldwide oil and natural gas production profile. The oil production consists of conventional oil, heavy oil, deepwater oil, polar oil and so forth, and the gas consists of natural gas, non-conventional gas (coal bed methane gas) and so forth, and the production profile is formed by summarizing them.

As the result of oil crisis accompanying with rising oil price up to up to $34/barrel in 1980, decreasing oil demand and stagnation of oil price were resulted in, and oil production countries encountered significant decrease in income. Now a day, crude oil supply faces tight situation, and the oil price is rising up to $70/barrel. Forecasting a tendency of worldwide depression, relieving scheme such as increasing oil production and energy saving shall be keenly required for oil crisis caused by short of oil supply expected in around 2010.

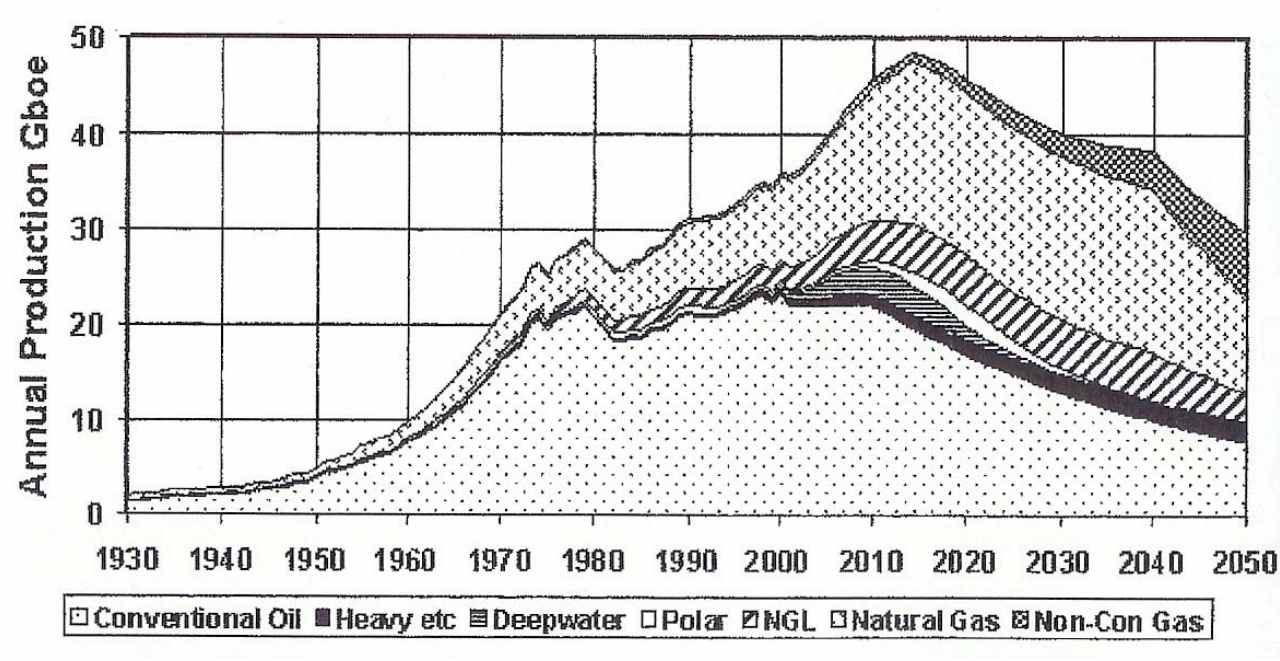


Fig. 12 Oil & Gas Production Profile (History & Future)

14. 12 Super Giant Oil Fields and Subjected Oil Fields

12 worldwide super-giant oil fields are listed here. In the 12 fields, oil production countries not located the Middle East area are only 4th largest Venezuela and 8th largest Mexico. These super giant oil fields such as Zakum oil field and other field s in the middle east are subjects of CO_2 – EOR development. .

Table 1 Studying Oilfields in Super Giant Oilfields

Rank	Oilfield	Country	Reserves (Billion bbl)	Discovery Year
1	Ghawar	Kingdom of Saudi Arabia	66 - 100	1948
2	Burgan	State of Kuwait	32 - 60	1938
3	Safaniya	Kingdom of Saudi Arabia	21 - 36	1951
4	Bolivar Coastal	Republic of Venezuela	14-36	1917
5	Berri	Kingdom of Saudi Arabia	10-25	1964
6	RumaliaN&S	Republic of Iraq	22	1953
7	Zakum	United Arab Emirates	17-21	1964
8	Akal	United Mexican States	11-20	1976
9	Manifa	Kingdom of Saudi Arabia	17	1957
10	Kirkuk	Republic of Iraq	16	1927
11	Gashsaran	Islamic Republic of Iran	12-15	1928
12	Abqaiq	Kingdom of Saudi Arabia	10-15	1941

(AAPG, OGJ, EIA)

15. Giant Oil Fields found recently and Example for Recovery increased with CO_2 - EOR

The following graph shows oil reserve in time series of oil field found recently to which the production increased with CO_2 - EOR of Zakum oil field is added. The increased production at Zakum oil field is positioned at midst between Kashagan (Kazakhstan : 10 billion barrel) and Azadegan (Iran : 5 billion barrel), it will be a much for the 2nd largest giant oil field (7.5 billion barrel). It is necessary that we should find out any oil field of which oil production has been reduced and there is a thermal power station near it. If the feasibility of CO_2 - EOR is confirmed, we shall start EOR project. CO_2 - EOR project will be also characterized that it has an advantage not to be necessary to take a risk for finding a new oil field because it subjects the existing oil fields.

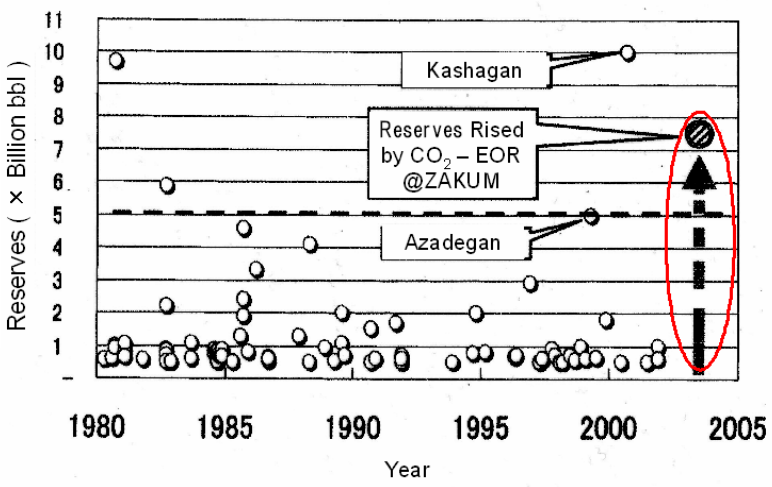


Fig. 13 Estimated Rise in Oil Recovery by CO_2 – EOR Compared with Recent Discovered Oilfields

16. Norma (norm) applied to Japan in reducing CO_2

The norm to reduce CO_2 assigned to Japan has been already risen to 168 million ton/year in 2002. The procedures and quantity of the reduction recommended by the government are 20 million ton/year with trading of greenhouse effect gasses emission quotes, 48 million ton/year with absorption of forests, 59 million ton/year with energy saving and 21 million ton/year with conversion to alternate fleon. 16 million ton/year by mean of CO_2 - EOR in Abu Dhabi is equivalent to 80% of trading of greenhouse effect gasses emission quotes. We must thoroughly reduce CO_2 discharge which has been increased by our wants for comfortable and convenient life.

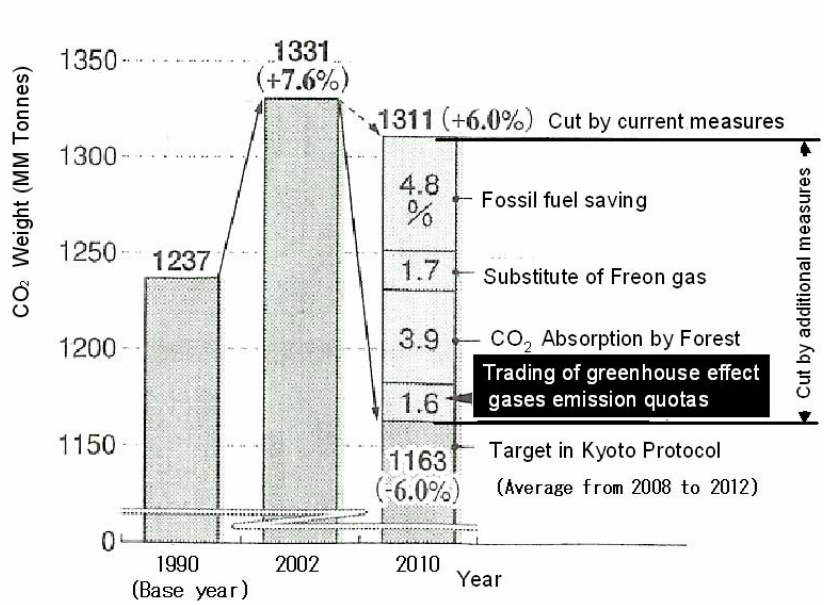


Fig. 14 Japanese CO_2 Cut Plan for target in Kyoto Protocol (Government)

17. Recent Tendency

ARAMCO of Saudi Arabia has started examining CO_2 - EOR corresponding to increase of oil demand, and requested MHI for cooperation. MHI accepted the request and has entered into the joint study. At this stage, ARAMCO, Ministry of Economy, Trade and Industry and MHI are discussing via TV conference.

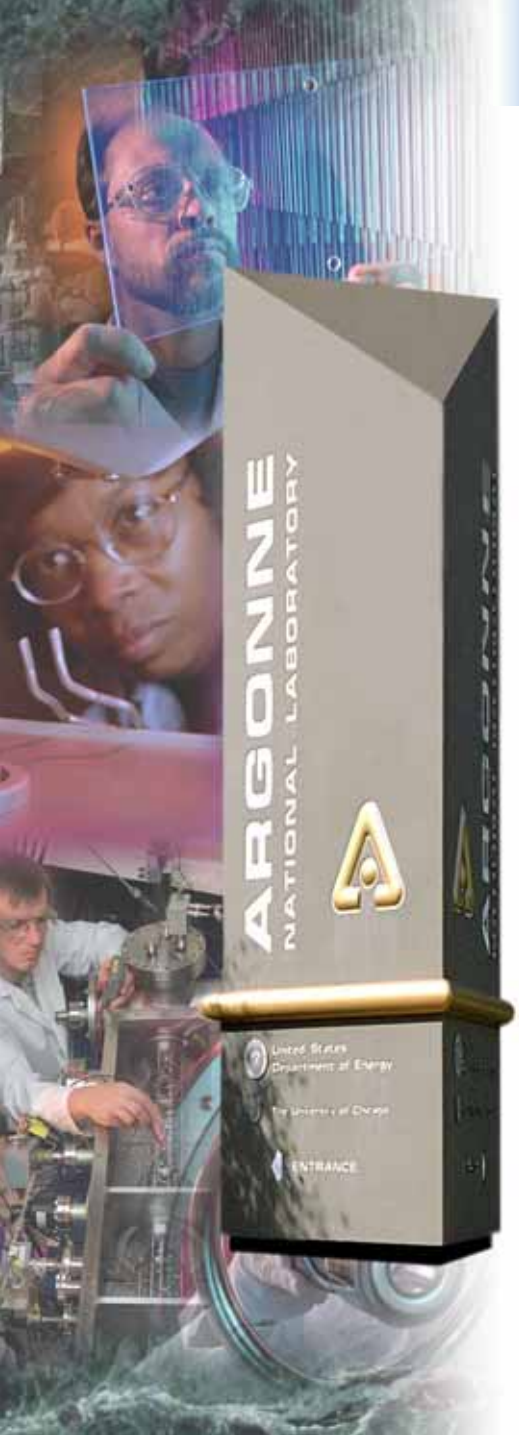
In the middle east we are discussing other CO_2 - EOR project with other oil company.

Another study of CO_2 - EOR for 2 oil fields with Indonesia which has become an oil importing country.

British and Norwegian governments are examining incentive measures with reduction of taxes for CO_2 - EOR projects.

18. Strategy in the Future

1) There is a fear that the oil demand and supply will be further tightened within several years. Driving the CO_2 recovery technology, we will extend EOR in the oil production countries. Japan shall contribute to increase oil production so as to secure own oil importing capacity.
2) In order to acquire that the CO_2 reduced with the EOR shall be authorized as a CDM by UN through diplomatic effort at IPCC and COP and shall succeed. Unachieved norm for the CO_2 reduction shall supplement with this CDM.
3) 2／3 of thermal power generation adopts coal burning facilities that are main source of CO_2 generation. Verifying countermeasure for foreign articles involved in flue gas, MHI shall establish the position to take the worldwide leadership in technology to recover CO_2 from coal flue gas.



Offsite Commercial Disposal of E&P Wastes

John A. Veil and Markus G. Puder

Argonne National Laboratory

Washington, DC

Presented at the 12th International Petroleum Environmental Conference

Houston, TX

November 7-11, 2005

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U.S. Department of Energy

National Energy Technology Laboratory

Topics for Discussion

- What are commercial disposal facilities?
- Review of earlier studies
- Description of current study
- Findings to date
- Next steps

What Are Commercial Disposal Facilities?

- Offsite businesses that accept E&P wastes for a fee
  - Typically are not part of the oil company
- Charge for:
  - Disposal/management of waste
  - Transportation
  - Cleaning of vehicles/tanks
  - Disposal of wash water
  - Some may charge for analytical fees
- Use various methods for disposal/waste management

Why Use Offsite Commercial Disposal Facilities?

- Comply with applicable regulatory requirements
  - States have lead role
  - Not all disposal methods allowed in all states
    - *Options and constraints driven by waste types, technologies, and locations involved*
- Save costs
  - Capital, operating and maintenance, transportation
  - Cost-effectiveness influenced by waste volumes
- Hedge against potential responsibility
  - Liability may not be avoided (Superfund)
  - Need to review business practices and compliance history

Background – 1985 and 1995 API Waste Surveys

Waste Stream	1985 API Survey (million bbl)	%Sent to Commercial Disposal	1995 API Survey (million bbl)	%Sent to Commercial Disposal
Drilling Waste	360	28	149	3*
Associated Waste	12	52	21	15*
Produced Water	21,000	2	17,911	0.5*

Source: American Petroleum Institute (API) – Studies/Surveys published in 1987 and 2000.

***** Percentage of <u>onshore</u> waste stream going to offsite commercial disposal facilities.

Previous Study and Current Project

- Argonne surveyed commercial disposal facilities used for E&P waste in 1997
  - Report can be downloaded at: **www.ead.anl.gov/pub/dsp_detail.cfm?PubID=98**
  - Report received significant interest and national attention

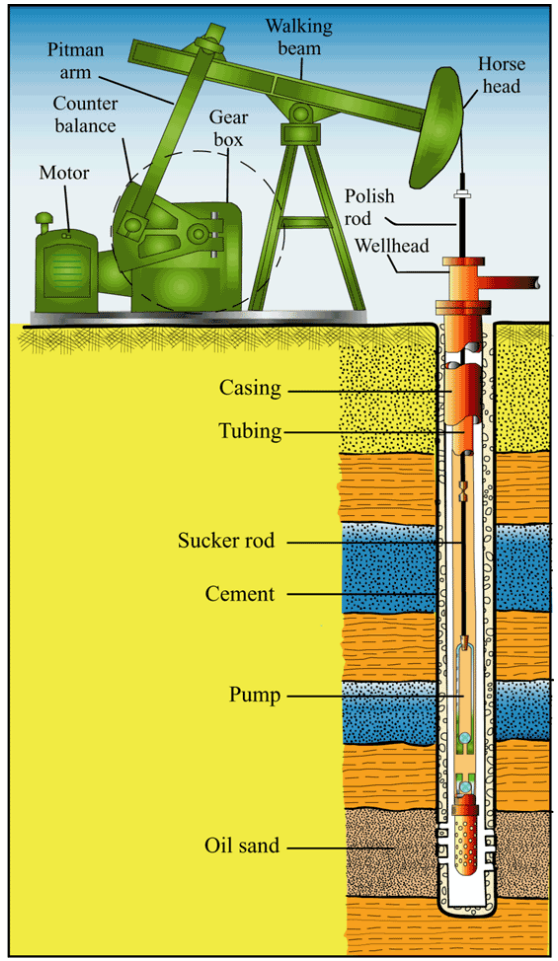
- New project to update 1997 report was launched in summer of 2005
  - Why use offsite commercial disposal facilities?
  - Where are offsite commercial disposal facilities located?
  - How do offsite commercial disposal facilities dispose of the wastes?
  - What are the costs charged by offsite commercial disposal facilities?

Commercial Management of Solid and Oily Wastes

- Landfarming
- Pits
- Slurry injection
- Landfilling
  - After evaporation, chemical stabilization, or biological treatment
- Thermal treatment/incineration followed by reuse or disposal of residues
- Evaporation in surface impoundments
- Salt caverns

Commercial Management of Produced Water

- Injection
  - Disposal and enhanced recovery
- Evaporation
  - In surface impoundments
- Treatment and discharge
  - Under NPDES permit
  - Through publicly owned treatment works



Source: California Department of Conservation

Commercial Management of Water-Based Drilling Wastes

- Landfarming
- Disposal pits
- Landfilling after evaporation
- Treatment and discharge
  - Under NPDES permit
  - Through local sanitary sewer to municipal water treatment plant
- Injection
- Treatment and reuse

E&P Waste Disposal Practices in the Gulf of Mexico from Three U.S. Majors (1997)

Waste	Company A	Company B	Company C
WB mud	all discharge	most discharge	all discharge
OB mud	recycle	all onshore	recycled
SB mud	recycle	recycle	recycle
WB cuttings	all discharge	most discharge	all discharge
OB cuttings	all onshore	all onshore	all onshore
SB cuttings	all onshore	most discharge	all discharge
Produced water	all discharge	all discharge	all discharge
Produced sand	all onshore	all onshore/inject	all onshore
TWC fluids	60%disch/ 40% onshore	disch/onshore	most disch
NORM	all onshore	all onshore (inject)	all onshore

Onshore means disposal at commercial disposal facility

WB = water based; OB = oil based; SB = synthetic based; TWC = treatment, workover, and completion fluids; NORM = naturally occurring radioactive material

Commercial Management of Offshore Drilling Wastes

- Historically, most offshore drilling waste hauled back to shore has gone to one major waste disposal company
  - Waste collected by barge at series of transfer stations and carried through the Intracoastal waterway to eastern Texas
  - Unloaded to trucks and trucked to site where it is screened and injected at low pressure

Other Commercial Management Competitors for Offshore Waste

- Salt cavern near Houston

- Land treatment sites in Louisiana

Commercial Disposal Costs ($/bbl) (1997)

Method	Solid & Oily Wastes	Prod. Water	Water-Based DW
Landspread	5.50 – 57.00		0.20 – 55.00
Landfill/pit	0.50 – 36.00		0.35 – 10.50
Treat/dispose	0.00 – 12.00	0.65 – 4.20	2.50 – 14.70
Salt cavern	1.95 – 6.50		1.95 – 6.00
Injection	8.50 – 11.00	0.06 – 9.50	7.50
Evaporation	2.50 – 2.75	0.01 – 2.50	
Incineration	10.50 – 38.00		

Note: includes just disposal fees

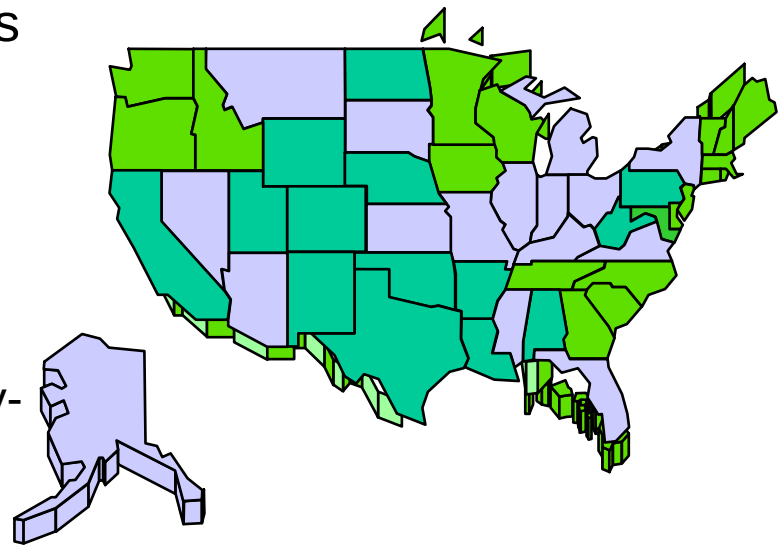
Onshore costs are a composite of all disposal facilities in 12 states.

First Project Phase: Identify Offsite Commercial Disposal Facilities

- First project phase – contact agencies
  - Contacted 31 oil and gas agencies and 6 environmental agencies in the 31 oil and gas producing states
  - Asked the regulators four questions to
    - *Identify offsite commercial disposal companies*
- Findings
  - 28 states responded, 3 in progress
  - Two trends

Oil and gas states without dedicated industry-specific commercial offsite waste disposal infrastructure

Oil and gas states with dedicated industry-specific commercial offsite waste disposal infrastructure



Where Are Offsite Commercial Disposal Facilities Located?

- 14 states have dedicated E&P-specific commercial offsite waste disposal infrastructure
  - AL, AR, CA, CO, LA, NE, NM, ND, OK, PA, TX, UT, WV, WY
  - Major differences from state to state
    - *Extensiveness of facility networks*
    - *Range of disposal options*
- 14 states show few or no disposal companies dedicated to E&P waste
  - AK, AZ, FL, IL, IN, KS, KY, MI, MO, MS, MT, NW, SD, VA
  - In many states, waste disposal facilities are owned by the operators on their respective leases
  - Operators who require offsite disposal send oil field wastes to a local sanitary landfill or out of state

Second Project Phase: Identify Disposal Methods and Costs at Offsite Commercial Disposal Facilities

- Second project phase – contact facilities
  - Used the lists provided by the agencies and made many phone calls

Develop Separate Tables

- Oil-based muds and cuttings
- Water-based muds and cuttings
- Produced water
- Contaminated soils
- Tank bottoms
- Naturally occurring radioactive material (NORM)

Data Elements in Tables

- State
- Disposal company name and contact information
- Type of E&P waste
- Disposal method
- Disposal costs
- Other comments

Preliminary 2005 Commercial Disposal Costs ($/unit)

Method	Oil-Based DW	Water-Based DW	Produced Water
Landspread	--	$0.50-2/bbl	$0.30-0.40/bbl
Landfill	$28/ton	$32/ton	
Treat/landfill	$28-70/ton	$2.50-70/ton	$2.30/bbl
Salt cavern	--	--	--
Injection	--	$0.50/bbl	$0.35-0.75/bbl
Treat/inject	9.50 – 14.50/bbl	$.50-12.50/bbl	$5-14/bbl
Evaporation	--	$4-20/bbl	$1.20-84/bbl
Incineration	$0.14-0.40/lb	$0.14-0.40/lb	--
Recycling	$5/bbl	$5/bbl	$0.65-5/bbl

Note: reflects first data from 11 states; includes just disposal fees

Preliminary 2005 Commercial Disposal Costs ($/unit) - continued

Method	Contaminated Soils	Tank Bottoms	NORM
Landspread	--	--	--
Landfill	$28-32/ton	$32/ton	$135/ton
Treat/landfill	$65-70/ton	$65-70/ton	$70/ton
Salt cavern	--	--	--
Injection	$50/yd	--	
Treat/inject	--	$10.50-14.50/bbl	--
Evaporation	$45/ton	$28.00-140.00/ton	--
Incineration	$35-800/ton	$35-800/ton	
Recycling	$15-35/ton	$35-200/ton	--
Other	--	--	$50/hr

Note: reflects first data from 11 states; includes just disposal fees

Next Steps

- Continue with Second Project Phase
  - Data collection effort impacted by the hurricanes
  - Work towards collecting data points from as many disposal companies as possible
- Begin Third Project Phase (Operators/Industry Associations)
  - Verify findings of phase II effort
- Prepare report in 2006

TRACE ELEMENT COMPOSITIONS OF BRINE IMPACTED SOILS AND PRODUCED WATER IN OSAGE COUNTY, OKLAHOMA

Dan Weber, Eleanor Jennings, Kerry Sublette, Kenneth Roberts, and Bryan Tapp
Center for Applied Biogeosciences
University of Tulsa
600 S. College Avenue
Tulsa, OK 74104

Abstract

Current brine remediation techniques focus on salt removal as the primary goal. However, residual disturbance to the vegetation is a common characteristic of remediated sites. The purpose of this research is to identify potential brine-induced, elemental phytotoxins that could persist in the soil after a successful removal of the sodium chloride salt. Awareness of these phytotoxins could lead to more thorough remediation techniques that draw impacted soils closer to a pristine state. Twenty soils, representing a variety of stages of brine contamination, and three brine samples were investigated. Of the elements identified in brine-impacted soils, most appeared to follow the trend of the salt component of brine in that higher concentrations were found in non-remediated soils than in remediated ones. Historic brine scars typically contained the highest levels of both salt and identified elements, while pristine prairie soils had the lowest. One identified element did not follow this trend. Boron levels remained significant in all soils other than those from unimpacted prairie. In other words, boron was resistant to standard brine remediation techniques. This is significant because boron is a known phytotoxin.

Introduction

Current produced water (brine) remediation techniques focus on salt removal as the primary goal. Brine impacted soils are typically remediated by increasing soil permeability with organic matter, and perhaps gypsum, to allow salt to wash out of the soil toward an appropriate receptor (a subsurface drainage system, for example) (Carter 2002). These methods have been shown to be effective in sufficiently reducing salinity to allow for re-vegetation of a contaminated area. However, this re-growth could be stunted or altered by the presence of

harmful compounds introduced by brine that are resistant to these practices. Ignoring such phytotoxins and the damage they could inflict may result in the long-term inhibition of growth of desirable plants. Furthermore, there may be a return of vegetation to a once-contaminated area but the plant community may not be as diverse, abundant, or healthy as in pristine areas (Ross 1994).

Produced water composes the largest volume of waste emitted from oil and gas production activities. For onshore oil production, over 90% of produced water is reinjected into subsurface formations while offshore, it is discharged into the surrounding seawater (Ray 1992). Due to the immense volume produced and the necessity of handling and disposing of it, research has been conducted to characterize the chemical makeup of produced water and its corresponding hazards (Jacobs 1992). Although the composition of produced water is dependent on location and the effectiveness of the oil/water separation process, brines can be expected to contain a mixture of complex inorganic and organic components. The majority of in-depth analyses of these components and their corresponding toxicities have dealt with offshore produced water as it poses the most immediate threat to the adjacent environment (Tibbetts 1992). However, there is a significant gap in the literature concerning the ecotoxicological potential of onshore produced water, especially with regard to native, non-agricultural plant communities.

The purpose of this research is to identify potential brine-induced, elemental phytotoxins that could persist in the soil after a successful removal of the sodium chloride salt. Awareness of these phytotoxins could lead to more thorough remediation techniques that draw impacted soils closer to a pristine state. The first goal of this project was to identify which components of brine were suspected of being phytotoxic. Secondly, the phytotoxins impervious to current remediation

techniques were determined by analyzing the concentrations of these suspect elements in soils with various degrees of impact from produced water. For the purpose of this research, the definition of a phytotoxin is any substance that inhibits plant growth (Ross, 1994).

The degree of toxicity of a given compound may differ between various plants (Ross, 1994). Additionally, some compounds are only harmful above a particular concentration, and again this concentration may be plant-specific. For example, trace amounts of Cu, Zn, Fe, and Mn are vital for plant development while high amounts are generally inhibitory to plant health. In short, different plant species possess different thresholds of tolerance to the presence of phytotoxins in the soil. The effect of phytotoxins at the cellular level may include obstructing, denaturing, or inactivating enzymes, displacing and/or replacing important metal ions, and disturbing the proper function of cell membranes and organelles. The symptoms associated with this phytotoxicity include reduced cellular photosynthesis and respiration, water stress, wilting, and reduced ion selectivity in roots as a result of an alteration of the cytoplasm and plasma membrane. Several factors can determine whether various symptoms result, including: the plant species itself, various environmental stresses, and the detection technique utilized (Ross 1994). The literature is relatively silent about the relative phytotoxicities of different elements on native plant species, with most attention being devoted to agricultural species. While this current work does not explicitly define any element as a phytotoxin, it is intended to contribute to a growing awareness of the response of native plant communities to environmental contamination.

Materials and Methods

Site History:

All samples used in these experiments were obtained from throughout the Tallgrass Prairie Preserve, a 39,000-acre nature preserve located in Northeastern Oklahoma. The Nature Conservancy purchased the former oil field in 1989 for the purpose of restoring what was previously rangeland to the native tallgrass ecosystem which was once predominant in the Flint Hills region of northeastern Oklahoma and central-eastern Kansas. The primary means The Nature Conservancy accomplishes this goal is through a management plan consisting of bison grazing and prescribed burning. This plan is meant to mimic what would have been the natural occurrences of the historic tallgrass prairie as closely as possible. However, active petroleum production still continues on the Preserve. Accommodating both resource extraction and ecosystem restoration has been the impetus of a great deal of research between the University of Tulsa and the Nature Conservancy in the last decade.

Sampling Protocol:

A total of twenty sites were sampled, and these sites fall into four classifications (Table 1). The first classification applies to unimpacted pristine prairie sites used as the controls for the experiment. These produce a model of what an uncontaminated tallgrass soil should be composed of and what remediated sites should ideally return to. Seven of such sites were sampled. The second classification applies to historic brine scars, which are areas of non-remediated spills dating back as far as the early 20th Century. These sites are often the result of multiple contamination events. Five of these historic brine scars were sampled. The third classification applies to recent brine spills that have been remediated. These provide information as to which potential phytotoxins are carried away with salt during remediation and which

remain. Three of these sites were sampled. The fourth classification applies to recent brine spills that have not been remediated. Five of such sites were sampled.

In addition to soils samples, three liquid brine samples were taken directly from pump jacks at locations distributed across the Tallgrass Prairie. These samples provide the elemental makeup of the brine prior to contaminating the soil.

Soil Preparation

Sampling proceeded with five-fold composite samples taken at each research site. For each site, five holes were dug 15 cm deep at random locations, yielding roughly 60 kg (total) of sub-sample soil for each site. These sub-samples were then combined to form the composite sample that was then subjected to further testing. Each sub-sample was bagged, labeled and refrigerated at 4 C after sampling until use (no more than 4 days). Because the composite samples were composed of varying soils from each site, the soil had to be first homogenized before determining overall soil composition. Each soil sample was dried at 150 C for six hours to facilitate better grinding. Each was initially ground to a fineness of $\leq$150 microns using an automatic soil grinder (Cole-Parmer® Analytical mill, 110 VAC/60 Hz EW-04301-00). Due to mechanical malfunctions, a manual grinder was used for remaining samples. Grinding creates more surface area for future dissolution of the soluble components of the soil. From each homogenized sample, 25 grams of soil was dried at 150 C for four hours in order to remove any moisture that may have accumulated during the grinding process.

Extraction Procedure

The first step in the extraction procedure was to create a soil solution consisting of 5.0 grams of soil combined with 50.0 mL of high purity de-ionized water in a 50.0 mL plastic centrifuge tube. These solutions were sonicated at high power for one hour in a warm water bath (Branson 8210 Sonicator) in order to disperse the water-soluble components of the soils throughout the solution (Brady and Weil, 1999) . The insoluble components of the soil extracts were removed through a process of centrifugation and syringe filtration. Samples were centrifuged at 2,205 x g for 30 minutes. The supernatant was decanted and 15.0 mL were filtered through 0.45 micron filters (Acrodisc 37, Gelman Sciences). Ten mL of the resulting material were filtered a second time. This second filtration utilized 0.20 micron filters (Acrodisc 13 CR, Gelman Sciences) .

Preparation of the brine samples followed the same steps as above with the exception of an initial pipetting step. The brine samples contained a mixture of both crude oil and produced water. Therefore, the residual oil had to first be removed from the surface of the brine sample before further extraction steps could occur. The oil/brine mixture was allowed to settle at room temperature for approximately one hour to allow for phase separation. The oil was then gently hand pipetted from the surface. If phase separation was proceeding slowly, gentle centrifugation was applied to the mixture in order to encourage the segregation of the hydrocarbon from the accompanying produced water. The collected hydrocarbon was discarded and the produced water was diluted in a similar fashion as the soil samples. Initial brine dilutions were made by adding 5.0 mL of produced water to 45.0 mL of doubly de-ionized water.

The resulting brine and soil solutions were analyzed using inductively coupled plasma mass spectrometry (ICP-MS; Perkin-Elmer DRC II). Due to the sensitivity of the machine, coupled with the high concentrations of sodium and chloride in the samples, 1:1,000 dilutions

were required for the soil extracts and refined brine samples. Dilutions were made using high purity doubly de-ionized water. Salt concentrations were also measured indirectly by determining the conductivity of each solution. Given the small volume of the solution, a handheld conductivity probe was used.

Discussion

The goal of this project was to discern which components of produced water may be responsible for the recalcitrant phytotoxic effects found at sites of brine contamination. This study involved 20 sites and represented soils ranging from historic brine scars to remediated recent spill sites. Pristine, unimpacted soils were also analyzed. Three raw brine samples provided a comparison to the soils, in order to determine which residual soil elements were considered suspect of phytotoxicity.

The initial stage of this study involved the analysis of the components of raw brine. Seven major and eight minor elements were isolated from produced water samples (Tables 2 and 3). Elements were classified as “major” based on concentrations greater than 100 mg/L in the produced water and “minor” elements on concentrations less than 100 mg/L. Of the major elements, Mg gave the highest range of concentrations (5834-7882 mg/L) and Ti and Ba the lowest (0-104 and 37-103 mg/L, respectively). Of the minor elements, Li gave the highest range of concentrations (8.1-15.4 mg/L) and As the lowest (0.1-0.5 mg/L). There was no apparent pattern of element distribution in that no one brine sample consistently had more or less of the identifiable elements in comparison to the other two samples.

The concentrations of the various brine elements then had to be compared to concentrations of elements extracted from soils that were recently brine-impacted (both

remediated and non-remediated) and historic brine scars. Unimpacted prairie soils would provide the comparison soil composition that would allow us to determine whether remediation had lowered potentially phytotoxic compounds to near normal levels.

Certain elements, such as magnesium and calcium, were detected at relatively high concentrations in the brine samples (Table 2). However, these elements are common in non-contaminated soils as well as in the biomass of plants (Brady 1999). Therefore, these elements were not primary suspects as the causative agents of phytotoxicity. Other elements that are not found in great abundance in the soil, such as strontium and bromine, appeared at relatively high concentrations in brine (Table 3). When compared with their soil concentrations (data not shown), though, most of these elements displayed the trend established by soil conductivity. That is, their concentration is related to the presence of the brine salt. As salt levels decreased, so did the levels of strontium and bromine. The conclusion is that their introduction is clearly associated with the presence of brine and they respond to salt removal remediation.

Measuring the conductivity of the soil samples was meant to provide a relative measure of soil ions. By comparing this model to the trends of individual elements within the soil, we could determine whether these elements responded to or resisted salt-removal remediation techniques. The model we generated for soil conductivity shows a progressive increase in soluble salts from least to greatest beginning with unimpacted sites followed by recent remediated spills, recent non-remediated spills, and historic brine scars (Figure 1). It is not surprising that a historic brine scar (which is often the result of multiple contamination events) would contain higher concentrations of soluble salts than more recent spill sites that are often the result of a single release event. It also is not surprising that a recent, non-remediated spill site would contain more soluble salts than a remediated one. Therefore, for an element to be considered brine-induced it

should demonstrate relatively high concentrations in historic brine scars and non-remediated brine spills as compared to pristine soils. Further, for an element to show a response to salt-removal remediation, the element should demonstrate relatively low concentrations within a remediated, recent brine spill site in comparison to its concentration in brine scars or non-remediated brine spills.

An analysis of bromine in soils displayed a trend very similar to that of salt (Figure 2). The levels of the element in historic brine scars and recent, non-remediated brine spills were comparatively higher than those in pristine areas and remediated brine spills. Thus, Br concentrations in the soils were likely a result of brine exposure. Non-remediated sites, both historic and recent, also exhibited greater variation in concentrations compared to remediated and pristine sites. In contrast, the levels of Br in remediated sites approached those of pristine areas. This trend indicates that Br had a positive response to salt-removal remediation efforts.

Strontium displayed the same concentration pattern as Br (Figure 3). There were extremely high concentrations in historic scars. The concentration in recent, non-remediated sites was four times that of unimpacted soils. Greater variation in these concentrations was also found in the contaminated sites, following the pattern observed with Br. Again, remediation of the recent brine spill reduced levels of Sr close to levels found in unimpacted prairie. Furthermore, there was more consistency in Sr concentrations among remediated sites. Increased consistency of element concentrations between soil samples was also indicative of a generally positive response to salt-removal remediation.

Using bromine and strontium as examples, it can be deduced that most elements showing a significant concentration in both brine and brine-impacted soils would return to near-normal levels following remediation. This means that potentially phytotoxic elements that showed a

decrease in concentration after remediation were removed by current remediation protocols. Each such element showed a clear signature of the brine in historic and recent spills, with elevated levels compared to unimpacted sites. These elements also showed significantly diminished concentrations following remediation. Therefore, we do not feel that these types of elements are responsible for the negative effects on vegetation that linger at remediated sites.

In contrast, boron was the one element analyzed that did not follow the above pattern established by the other elements (Figure 4). Boron showed the signature of the brine, with elevated concentrations in both historic and recent brine spills. Historic scars showed a wide range of values peaking at nearly 3 mg/kg. In contrast to the other analyzed components of brine, boron persisted at high levels in remediated sites (soil classification "3"). Whereas soil washing was able to reduce the concentration of other brine elements, boron concentrations were not decreased in response to the salt-removal techniques.

The apparent recalcitrant nature of boron is interesting because the element is known to be phytotoxic to some plants. Boron is toxic to rice at soil concentrations greater than 4mg/kg (Dobermann, 2000). Soil levels of boron in remediated sites approached this concentration. While phytotoxicity thresholds vary from plant to plant, residual NaCl from brine contamination may weaken the defense mechanism in plants growing in salt-affected areas (Salisbury and Ross, 1992). This may make them more susceptible to the toxic effects of boron when the element is present at lower concentrations than would normally cause a negative response. It is for this reason that boron is suspected of being a significant phytotoxic component of brine.

Conclusions

Brine spills introduce a number of various compounds into the soil. Some of these compounds are introduced in significantly higher amounts than levels found in unimpacted soils. Salt remediation works to diminish the presence of many of these elements. However, there are exceptions to this trend. Such elements show no response to current remediation techniques. Some of these recalcitrant compounds, such as boron, are known to be toxic to plants. Their toxic effects could be compounded by the presence of any sodium chloride persisting in contaminated soils.

Deconstructing produced water exposed its composition to be far more than simply sodium chloride-impacted water. Contamination by produced water introduces a myriad of elements into the soil. However, boron is the only element detected thus far that resists current salt-removal remediation techniques. This element is known to be phytotoxic at levels found within the test samples. Thus, boron will be the focus of future research attention.

Future Work

Future work will require additional trials of the previous experiment to identify other suspect elements. Additional testing will also reinforce our initial findings. If further experimentation uncovers new compounds of interest, element-specific extraction procedures will be implemented to enhance the recovery of them for analysis. Future work would include determining how much of a suspected phytotoxin is available for uptake by plants. Additionally,

investigations will be performed to discern the specific effects of the identified elements on tallgrass prairie climax grasses and salt-stressed grasses.

Acknowledgements

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Table 1. Classification of Sample Sites

Classification	Description	# of Sites
1. Pristine	Areas unimpacted by oil production	7
2. Historic Brine Scars	Areas subjected to long-term contamination with brine without clean-up efforts	5
3. Remediated Brine Spills	Areas affected by recent brine spills that have been successfully remediated	3
4. Non-remediated Brine Spills	Areas affected by recent brine spills that have not been remediated	5

Table 2. Major Elements in Produced Water (mg/L). The following elements were detected in the produced water samples at concentrations ≥100 mg/L.

Brine Sample	Mg	K	Ca	Ti	Sr	Ba	Br
SW	5834	336	2588	84	1115	103	1860
E	7882	362	2977	104	2136	37	2662
NW	6106	509	2349	0	1037	80	1597

Table 3. Minor Elements in Produced Water (mg/L). The following elements were detected in the produced water samples at concentrations ≤100 mg/L.

Brine Sample	Li	V	Mn	Se	Rb	B	I	As
SW	10.6	0.3	1.6	0.4	0.8	3.6	1.0	0.1
E	8.1	0.4	1.5	0.5	0.8	1.7	1.3	0.5
NW	15.4	0.3	2.3	0.3	1.2	7.0	0.9	0.1

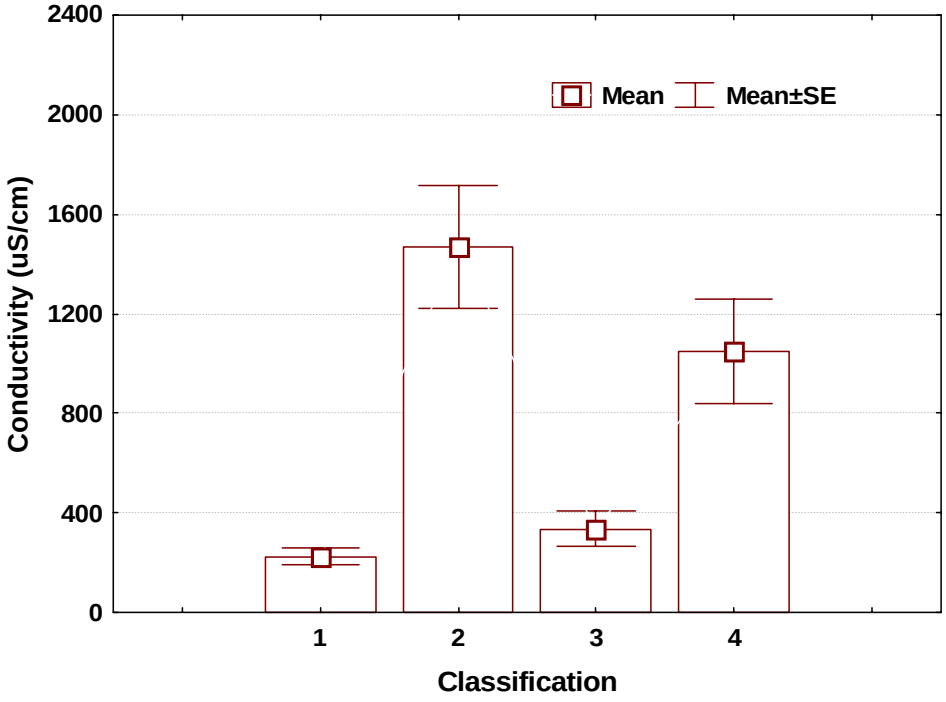

Figure 1. Conductivity of Soil Extracts. Measurements are on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
2= historic brine scars
3= recent, remediated brine spills
4= recent non-remediated brine spills

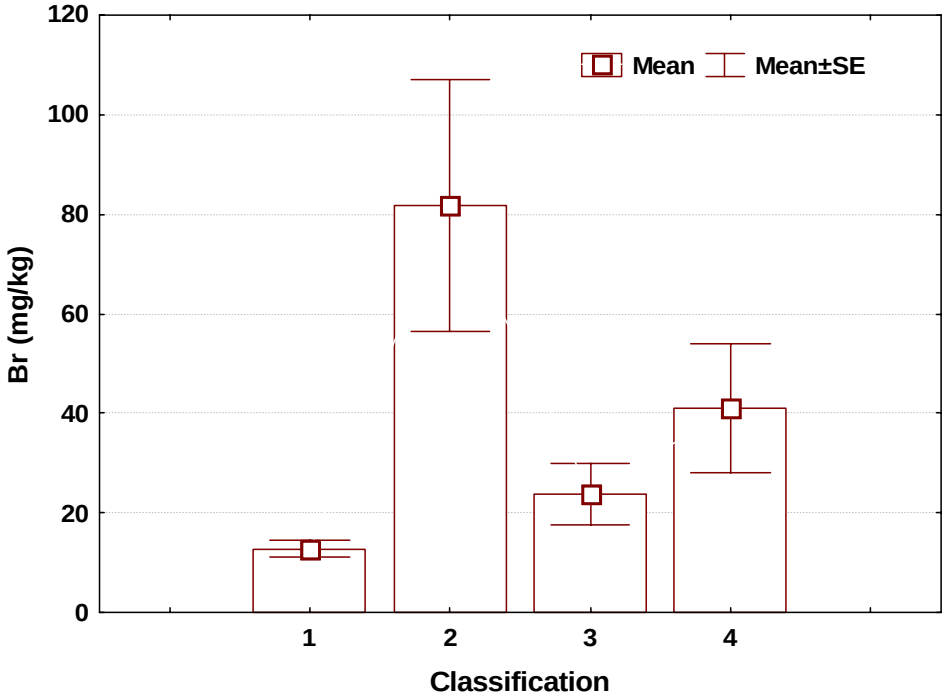

Figure 2. Bromine Concentration in Soils based on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
2= historic brine scars
3= recent, remediated brine spills
4= recent non-remediated brine spills

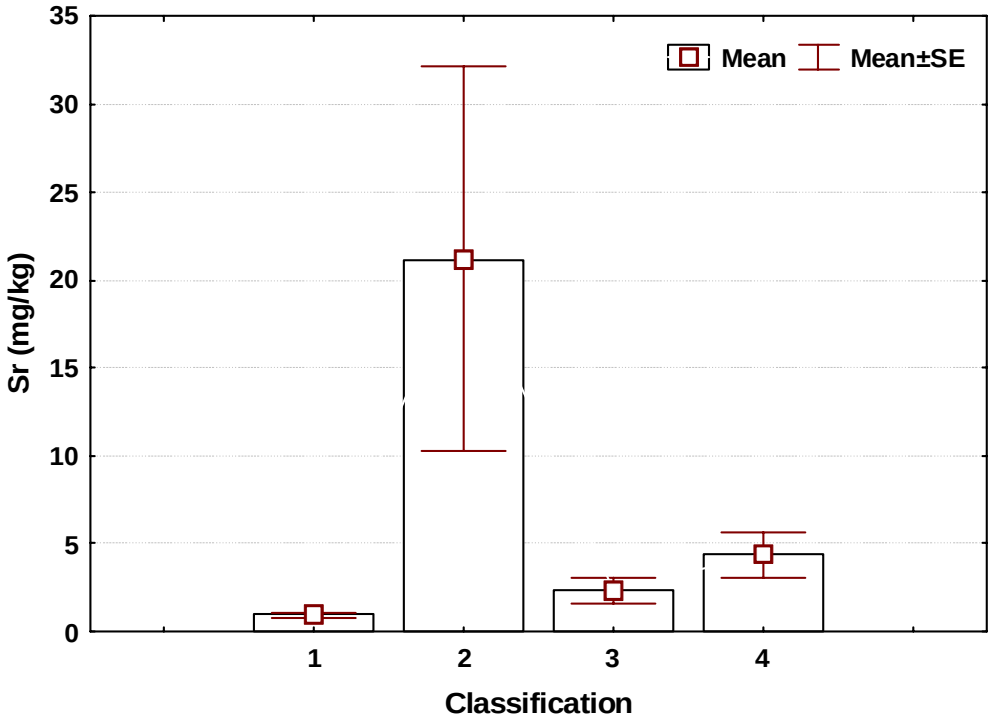

Figure 3. Strontium Concentration in Soils (based on dry weight). Measurements are on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
2= historic brine scars
3= recent, remediated brine spills
4= recent non-remediated brine spills

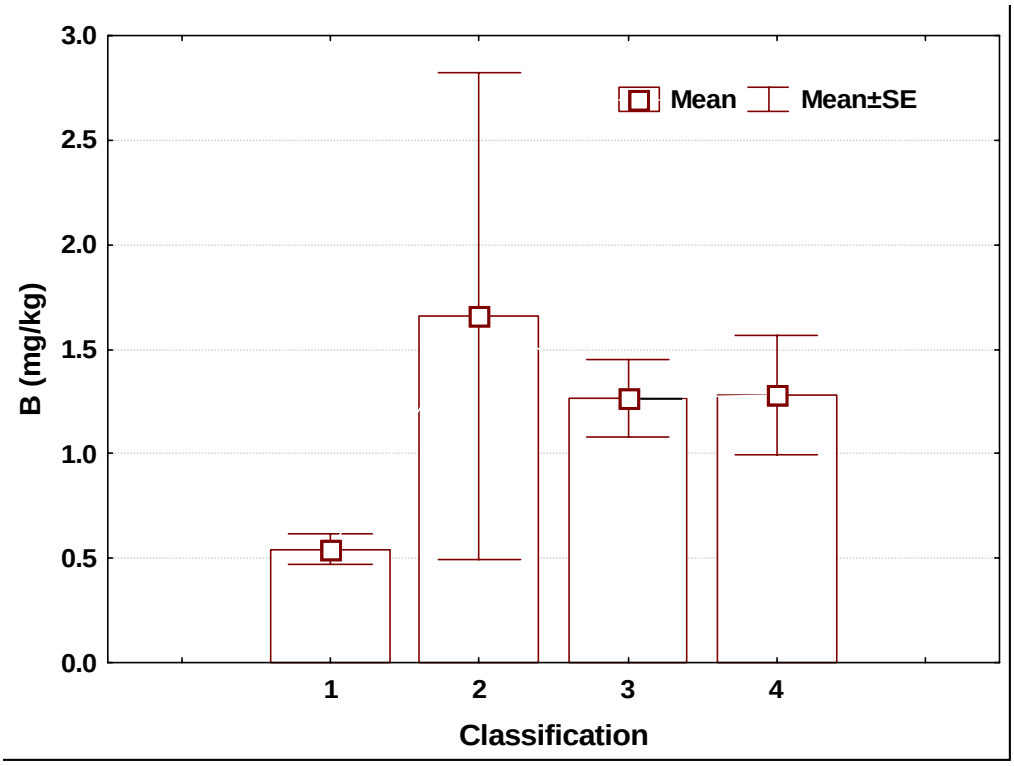

Figure 4. Boron Concentration in Soils (based on dry weight). Measurements are on a per gram of dry soil basis.

Classification code: 1= unimpacted prairie
2= historic brine scars
3= recent, remediated brine spills
4= recent non-remediated brine spills

Magnetite Nanoparticles as Adsorbents for Arsenic Removal and Magnetic Separation

Yean, S.[1], Cong, L.[2], Yavuz, C. T.[3], Mayo, J. T.[3], Kan, A. T.[1], Colvin, V. L.[3], and Tomson, M. B.[1]

[1]Department of Civil and Environmental Engineering and Chemistry, Rice University, Houston, TX 77005
[2]Champion Technologies, Houston, TX 77098
[3]Department of Chemistry, Rice University, TX 77005

ABSTRACT

Magnetic magnetite nanoparticles are potential sorbents for arsenic removal in drinking water. The adsorption and desorption of arsenite and arsenate using magnetite nanoparticles and the effect of dispersion of the nanoparticles were investigated. Laboratory-synthesized magnetite nanoparticles can remove approximately two hundred times more arsenic than larger commercial materials. Moreover, arsenic is not readily released from the magnetite nanoparticles, presumably because the binding of the adsorbed arsenic results in the formation of highly stable iron-arsenic complexes. The effectiveness of arsenic removal is strongly influenced by the dispersion of magnetite nanoparticles. Magnetic separation was possible using rare earth magnets.

INTRODUCTION

The arsenic-rich groundwater has been a significant water quality problem in many parts of the world; particularly Bangladesh, West Bengal, India, South Asia, and western U.S. Chronic exposure to arsenic in drinking water could lead to health problems thus the WHO guideline value for arsenic in drinking water has been provisionally decreased from 50 to 10 µg/L (1). Also, U.S. EPA has lowered the standard to 10 µg/L for arsenic in drinking water (effective Jan 23, 2006). Both arsenite and arsenate have a high affinity for iron oxides (2-4). The sorption behavior of arsenic is dependent on pH and its oxidation state. It is reported that arsenate adsorption decreases with increasing pH (3); however, there is conflict about arsenite adsorption versus pH. Arsenite adsorption increases with increasing pH, with maximum adsorption at approximately pH 9 (3, 4), while Dixit and Hering (5) observed that the arsenite adsorption was independent of pH from 4 to 10. Considerable research has been done on arsenic adsorption on iron oxides; however, little has been done on the desorption of adsorbed arsenic and even less on sorption/desorption hysteresis.

Due to small particle size and large surface area, nanomaterials have considerable potential for use in environmental engineering. Nanomaterial properties may not be predictable from observations on larger-sized materials since nanomaterials might have different physical, chemical, and biological properties. Little is known about the relationship between the adsorptive property of oxides and the nano-particle size. In the current study, the sorption and desorption behavior of arsenic to magnetite nanoparticles were evaluated. It was demonstrated that the magnetite dispersion was of considerably importance with respect to decreasing the arsenic level. Also, magnetic separation was performed.

MATERIALS AND METHODS

Sorbents and chemicals

Two different sizes of commercially available magnetite with nominal particle sizes of 20 and 300 nm were used. A limited quantity of monodisperse (11.72 nm) magnetite was synthesized in the laboratory, following the procedure of Yu et al. (6).

Adsorption and desorption experiments

An electrolyte solution containing 0 to 45 µmol/L of As was prepared. Then 40 ml of the electrolyte solution was reacted with 0.011g/L of 11.72 nm magnetite, 0.1g/L of 20 nm magnetite, and 2.5 g/L of 300 nm magnetite. Adsorption studies were conducted at pH 4.8, 6.1, and 8.0. Desorption studies were performed on 20 and 300 nm magnetite. Arsenic-free electrolyte solutions were added to the aliquot, following a 24-h adsorption. The samples were tumbled for 24 h, centrifuged, and then filtered through a 0.2 µm Nalgene syringe filter for the 20 and 300 nm magnetite samples. A magnetic field column separator was used to separate the solid from the liquid phase for 11.72 nm magnetite particles.

Effect of aggregation

To test the effect of magnetite aggregation on arsenic removal, three methods were used: without sonication, with a sonication bath, and with a sonication probe. The solution of As(III) or As(V) containing 1.33 μmol/L of As was added to 1g/L of 20 nm magnetite nanoparticles suspension. Samples were manually shaken for 1 minute. Upon completion of As adsorption on magnetite nanoparticles, rare earth magnets were utilized to separate the solid from the liquid.

RESULTS AND DISCUSSION

Adsorption isotherms

All adsorption data were fitted with Langmuir adsorption isotherms. Table 1 lists the weight and surface-area based Langmuir parameters at pH 4.8, 6.1, and 8.0. The adsorption of As(III) to 20 nm and 300 nm magnetite nanoparticles is independent of pH. The maximum adsorption capacities of As(V) on 20 and 300 nm magnetite nanoparticles decrease with increasing pH. At each pH condition, surface-area based As(III) and As(V) adsorption capacities (q^{max}, μmol/m^2) are similar for 20 nm magnetite and 300 nm magnetite nanoparticles, but each shows a systematic decrease in maximum adsorption capacity (μmol/m^2) with increasing pH. Arsenic adsorption on 11.72 nm magnetite appears to be bimodal. The adsorption capacities for both As(III) and As(V) to laboratory prepared (11.72 nm) magnetite increase significantly compared to the commercially prepared magnetite. This observation may be due to more adsorption sites being exposed to arsenic by the 11.72 nm magnetite, which was completely dispersed in solution. We have shown that when prepared in a nanocrystalline form, magnetite can remove two hundred times more arsenic than the larger commercial materials, on a wt/wt basis. On a wt/wt basis, the amount of arsenic removed by 11.72 nm magnetite is comparable to or greater than that removed by other Fe(III) hydroxide minerals. Additionally, nano-magnetite effectively removed both As(III) and As(V).

Desorption

Hysteretic desorption was observed with As(III) and As(V) from 20 nm and 300 nm magnetite samples (Figure 1). After three steps of the desorption, each taking 24 hours, only 20 to 25 % of adsorbed arsenic is desorbed from the 300 nm magnetite. Desorption of both As(III) and As(V) from 20 nm magnetite nanoparticles shows almost complete desorption hysteresis. After three steps of desorption, each taking 24 hours, approximately 1 % of adsorbed As(III) and As(V) are released from the 20 nm magnetite nanoparticles. Regarding desorption, smaller particles tended to show stronger desorption hysteresis, presumably because the binding of the adsorbed arsenic results in the formation of highly stable iron-arsenic complexes uniformly over the surface. Thus, once loaded these nanoparticles resist arsenic desorption and bleed-off, a significant advantage in disposal at common environmental pH ranges.

Effect of aggregation

We observed the effect of dispersion of magnetite nanoparticles on the concentrations of iron and arsenic (Table 2). Throughout the current study, the aggregation of magnetite nanoparticles was one of the central issues of magnetite application as a means of arsenic removal. In our study, sonication was used to break magnetite nanoparticles aggregates. Arsenic concentration decreased with increasing the dispersion of magnetite nanoparticles. When filtration was used, the iron concentration was below 0.3 mg/L, which is the guideline value for drinking water proposed by World Health Organization (WHO). The use of sonication is indicative of the significance of de-aggregation of nanoparticles for further practical purposes. Additionally, methods of de-aggregation are being investigated.

Table 1. Weight based and surface-area based Langmuir adsorption isotherm parameters.

Arsenic	Magnetite	pH	b (L/µmol)	q^{max} (µmol/g)	q^{max}·b (L/g)	q^{max} (µmol/m^2)	q^{max}·b (L/m^2)
As(III)	300 nm	4.8 - 8.0*	0.05	20.8	1.04	5.62	0.28
As(III)	20 nm	4.8 - 8.0*	0.04	388.9	13.98	6.48	0.23
As(III)	11.72 nm	8.0	0.02	1532	31.79	15.49	0.32
		8.0	0.02**	1800	37.40	18.22	0.38
As(V)	300 nm	4.8	0.08	14.4	1.12	3.89	0.32
		6.1	0.10	10.0	0.98	2.70	0.26
As(V)	20 nm	4.8	0.82	152.3	125.49	2.54	2.09
		6.1	0.54	101.3	54.71	1.69	0.91
		8.0	0.48	79.4	38.07	1.32	0.63
As(V)	11.72 nm	8.0	0.11	622.7	66.63	6.3	0.67
		8.0	0.11**	2300	24.61	23.28	2.49

* Arsenite adsorption is independent of pH.
** b values for the second maxima were assumed to be the same as that for the first maxima.

Table 2. Effect of magnetite aggregation on reductions of arsenic and iron.

Method	As Concentration (µg/L)	Fe Concentration (mg/L)
No sonication	> 35	N/A
Sonication bath	~ 23	> 3
Sonication probe without filtration	< 10	1 ~ 6
Sonication probe with filtration	< 10	< 0.3

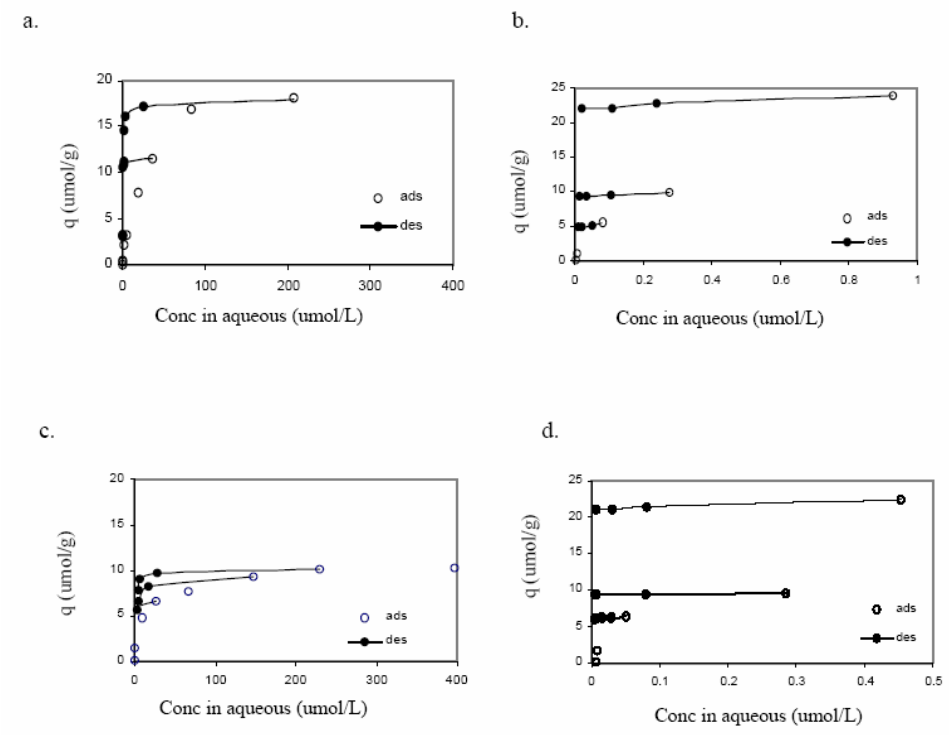

Figure 1. Plot of the adsorption and desorption of As(III) and As(V) to 300 and 20 nm magnetite samples at pH 6.1. (a) As(III) to 300 nm magnetite; (b) As(III) to 20 nm magnetite; (c) As(V) to 300 nm magnetite; and (d) As(V) to 20 nm magnetite. The open symbols are data from adsorption approach and the closed symbols are desorption data for selected adsorption points.

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Effective Storm Water and Sediment Control During Pipe Line Construction Using New Filter Fence Concept

S.Yeri[1], B.Barfield[2], E.Stevens[3], K.Gasem[4], A.Jeyarathan[5], and J.Hayes[6]

[1] Biosystems and Agriculture Engineering, Oklahoma State University, 111 Ag. Hall, Stillwater,OK 74078; PH (405) 744-5289; FAX (405) 744-6059; email: yeri@okstate.edu
[2] Biosystems and Agriculture Engineering, Oklahoma State University, 111 Ag. Hall, Stillwater, OK 74078; PH (405) 744-8398; FAX (405) 744-6059; email: bill@okstate.edu
[3] Biosystems and Agriculture Engineering, Oklahoma State University, 111 Ag. Hall, Stillwater, OK 74078; PH (405) 744-2877; FAX (405) 744-6059; email: stvnsel@okstate.edu
[4] Chemical Engineering, Oklahoma State University, 423 EN, Stillwater, OK 74078; PH (405) 744 5280; FAX (405) 744 6338; email: gasem@okstate.edu
[5] Chemical Engineering, Oklahoma State University, 423 EN, Stillwater, OK 74078; PH (405) 762 6543; FAX (405) 744 6338; email: jeyarat@okstate.edu
[6] Environmental Conservation, Clemson University, 109 Barre Hall, Clemson, SC 29634; PH (864) 656 4042; FAX (864) 656 0338; email: jhayes@clemson.edu

ABSTRACT

Sediment has recently become an emphasis in the EPA NPDES storm water rules due to its impact on habitat in stream channels. Currently silt fence is commonly used as BMP for linear construction. A recent national study and limited evaluation of silt fence in the field has showed a very low percentage of sediment trapped.

Modification to current silt fence technology is required that will replace current ineffective silt fence with a workable silt fence that is effective in trapping sediment and is also economically feasible. We are working under an IPEC-funded grant to develop such a system.

A consistent problem with silt fence is failure at the toe, allowing release of sediment through undercutting. A geotextile apron, an integral part of fence, placed in front of the fence can control the lateral flow and resulting undercutting. The lateral flow is further restricted by incorporating flow barriers that will facilitate impoundment of flow thus increasing detention time and trapping efficiency.

Our initial field test results indicate that the new design is effective in reducing off-site sediment release, with a high trapping efficiency of over 90% in most cases. A new pilot model has been developed to evaluate the effectiveness of polyacrylamide in combination with silt fence in trapping the fine silt and clay particles. We will follow up the pilot-scale with field-scale tests at our Silt Fence Test Facility.

RATIONALE

Studies have shown that construction operations disturbing the parent soil material increase the sediment yield by as much as 10,000 times when compared to undisturbed sites (1). Ongoing research by the ARS showed that the reduction in species diversity is strongly related to the number of hours sediment load exceeds 1000 mg/l, a sediment concentration that is frequently two orders of magnitude greater in runoff from most construction sites (2). Clearly methodologies are needed to reduce sediment loads to levels that maintain habitat and species diversity. Currently silt fence is the only best management practice for linear construction which causes very little or no significant disruptions to landscape during installation and removal. A recent national study (2) and limited evaluation of silt fence in the field have shown that a very low percentage of sediment is trapped (3) and silt fence may be totally ineffective under some conditions.

Field inspections conducted by Barfield and Hayes (4) in which more than 50 construction sites were visited in South Carolina and Kentucky revealed that silt fence was seldom installed according to standards and specifications. The conventional silt fence installation procedure specifies that the fence must be buried in a 6 inches by 6 inches trench, backfilled and compacted. Due to high cost and labor the compaction is rarely up to standards. With current installation practices silt fence can transform shallow overland flow into concentrated flow down slope of the fence causing increased erosion. Some laboratory studies with controlled conditions have cited trapping efficiencies between 40 to 100 percent (3, 5, 6, 7), but similar results have not been obtained in field tests.

With current silt fence technology trapping of clay, fine and medium silts will not occur. The time for a particle to settle out of the flow will be on the order of 0.1 to 0.2 days, with 0.05 to 0.1m depths behind the fence. Hence, detention times are inadequate to trap small and fine particles. Due to low strength of polypropylene material used in silt fence, concentrated loadings cause excessive stretching, resulting in concentrated flow, overtopping of fence at low spots, increased erosion down slope and failure of the fence. The solution called for in many guidelines (2) is seldom used in practice due to the expense and cost of installation. Also inadequate strength of support posts leads to failure of silt fence and fence post. Due to cost of installation, expense of material and expense of removal for reuse, using large posts and burying them deeper seems impractical, as called for by EPA (2). The advantages for continued use of silt fence would be low labor for installation, low cost, durability, some potential for reuse and popularity. Contractors have used silt fence extensively and its visibility advertises to the public that erosion and sediment control structures are being used.

OBJECTIVE

The objective of this work is to turn currently inadequate silt fence design and installation technology into highly effective sediment control system which we call Failure Avoidance and Effective Silt Fence Technology (FAEST). The FAEST design intended to solve problems of flow concentration at low spots resulting in undercutting along the fence, overtopping, low strength and efficiency of fence and failure of fence posts. Field test studies at OSU show that it

should be possible to accomplish this. Specific objectives are to prove the new silt fence design and implementation concept under laboratory and field conditions where current silt fence fails due to 1) Flow concentrations, 2) Undercutting of fence, 3) Overtopping of fence 4) Failure to trap silt and clay particles, 5) Excessive stretching of silt fence and 6) Insufficient stability of support posts.

METHODOLOGY

Design of FAEST

In-order to develop an effective silt fence technology three main failure modes of the current silt fence design i.e., undercutting at the toe of the fence, overtopping of the fence and flow concentrations at low spots was addressed. Construction site visits and field testing indicated that due to contoured installation and poorly compacted toe trench, the flow along the fence eroded the toe trench often exposing the anchored fence. Hence, to overcome this failure mode a non erodible material along the toe of the fence, known as apron, was spread on the ground. The apron was made up of the same material as the fence and was fabricated as an integral part of the fence. Also, due to increased erosion along the fence due to disturbed parent soil material the toe installation in a trench was eliminated. Instead, a narrow slit was made along the fence, with the help of a straight edged shovel, and the toe of apron was tucked into the slit and compacted. The apron and the new installation technique eliminated undercutting of fence.

The overtopping of the fence, with current design was often observed due to irregular impoundments and flow concentration at low spots. In-order to control lateral flow along the fence, flow barriers were installed at regular intervals along the fence. These flow barriers were made up of the same material as fence, with scalene right angled triangular shape and curved base. The base and the vertical side of the flow barrier were attached to the apron and the fence respectively. The flow barriers intercepted the flow along the fence and impounded the flow behind the fence at regular intervals. This eliminated the flow concentration and excessive stretching of the fence at low spots and increased the detention time for better trapping.

The time required for fine particles to settle out of flow behind the fence will be in the order of 0.1 to 0.2 days. Although flow barriers in the new design improved the detention time and impoundment behind the fence, it will still not yield enough detention time to trap fine particles. A possible solution to this would be to introduce Polyacrylamide (PAM) into the runoff and flocculate the fine particles and reduce detention time. Work is currently in progress to enhance the fence strength and post stability to minimize stretching due to increased trapping. A schematic diagram of the FAEST is shown in Figure 1.

Field Tests

Field evaluation of FAEST was done at specially constructed Silt Fence Test Site (SFTS) at USDA Hydraulics Lab, Stillwater, Oklahoma. Details of the test plot specifications and sampling techniques are described by Stevens et al., (8). A test grid was formed with a total of

nine simulations with three different slopes (10, 13 and 20 percent) along the fence and three type of soil (Sandy Loam, Loam, Silt Clay). All nine simulations have been completed and the results of first six simulations are presented in results section. In addition to the nine simulations, field tests were conducted for qualitative evaluation of FAEST and observe the performance of various flow barrier configurations. Figure 2 shows the picture of the SFTS with FAEST installed at the downstream end of the source area.

Flocculation Tests

Field test results indicated that the FAEST design was effective in trapping coarse and medium particles but a large percentage of fine particles passed through the fence. One possible solution to this would be to flocculate the fine particles into larger aggregates that can be trapped by FAEST. Flocculation by using Polyacrylamide (PAM) is soil specific and suitable formulation and concentration of PAM has to be identified by Jar Test Experiments. The jar test apparatus employed in our study consisted of six gang stirrers and six jars of one liter capacity. The mixer speed could be varied from zero to 300 rpm and up to five different speeds could be preset by a switching mechanism. Figure 3 shows the picture of the jar test apparatus with the dosing module. Due to limitation in time and resources only Loam type soil and three PAM formulations were chosen for flocculation tests. We selected anionic polyacrylamide with charge densities of 10, 20 and 30 percent. A sequence of jar test experiments were developed considering the factors affecting the flocculation process and the flocculation efficiency was calculated in each case. The flocculation efficiency is defined as:

$$\text{Flocculation Efficiency} = \frac{\text{Initial Turbidity - Final Turbidity}}{\text{Initial Turbidity}} \text{.....} Eq.1$$

Several factors affect the flocculation process of which PAM concentration, exchangeable ion concentration, sediment concentration, dosing time, dosing intensity and the time duration between the end of dosing stage to the beginning of sampling stage. These factors are also known as control parameters. Other parameters such as temperature and pH were selected as fixed parameters to simplify the experimental process. The qualitative factor here would be the three PAM formulations with different charge densities. The response variables that were measured are the flocculation efficiency and percentage reduction in suspended solids concentration (SSC). In order to simplify the process we decided to choose appropriate values for some of the control parameters by conducting preliminary tests. The sediment concentration was set to the average runoff concentration observed during FAEST field tests with the same soil. This concentration was equal to 25000 ppm. We further decided that the evaluation would be more conservative if all of the soil particles employed in the jar test were silt or clay particles. Hence the soil from the field was dried, ground and sieved with 53 microns sieve and the soil particles passing through this sieve were used for the tests. Keeping all other control parameters constant, jar tests were conducted to study the effect of dosing time on flocculation efficiency. The results indicated that the flocculation efficiency remained fairly constant with dosing time ranging from 10 to 120 seconds. Also similar results were obtained by varying time interval for sample collection from 10 to180 seconds. Hence 30 seconds of dosing time and 30 seconds interval time for sampling were selected for the tests. The dosing intensity which is the mixer speed at the time of dosing PAM largely controls the floc size formed. We decided to keep this parameter constant in our initial set of jar tests until a suitable PAM formulation and

concentration was identified. Later on we will evaluate the effect of dosing intensity on floc size for a given formulation and concentration of PAM.

Three sequences of experiments were developed to evaluate the flocculation process and identify a suitable PAM for the soil in this study. With the first sequence only PAM was used as flocculant and tests were conducted with the three PAM formulations by varying the PAM concentration from zero to sixty parts per million, keeping all other control parameter constant. Here we intended to study the effect of PAM formulation and concentration on flocculation efficiency as increasing the PAM concentration will initially increase the efficiency and then the efficiency decreases after a threshold limit is reached. The second sequence tests were conducted with calcium chloride, an exchangeable cation source, as flocculant by varying the calcium chloride concentration from zero to 25 mM. Finally tests were conducted with PAM and calcium chloride as flocculants and selecting three concentration levels for each PAM formulation and calcium chloride. A high medium and low concentration levels for the PAM were selected based on the minimum and maximum threshold concentration and flocculation efficiency results from the first sequence of tests. Similarly the three concentration levels for calcium chloride were selected based on the impact of calcium chloride concentration on flocculation efficiency from the second sequence tests.

The experimental procedure was developed for the jar test experiments and the same procedure was followed for each sequence of tests. Approximately 25 grams of loam soil with particles less than 53 microns is weighed and transferred to each of the jars. The jars are then filled with unprocessed lake water up to the one liter mark. The mixer paddles are lowered into the jar and the sediment solution is prepared at 300 rpm. The temperature, pH and turbidity of the sediment solution are measured. The type and required amount of flocculant, as per experimental grid, is drawn in syringes and mounted on the dosing module for each jar. The mixer speed is changed to a dosing intensity of 100 rpm and immediately the flocculant is dosed into the jar. Simultaneously two timers are set at 30 and 60 seconds to indicate the end of dosing time and beginning of sampling time respectively. At the indication of the first timer the mixer is stopped and the brass sampling tubes are mounted on the dosing module. In order to keep the time interval before sampling and the actual sampling time constant between the jars a special sampling device was fabricated. The device consisted of a total of twelve sampling bottles with six 250ml bottles and six 500ml bottles each arranged in row with 500ml bottles behind the 250ml bottles. A stopper with two openings was mounted on each of the bottles. Respective bottles of 500ml and 250 ml in the sequence were interconnected with plastic tubing. The brass sampling tubes mounted on the dosing module of the jar test apparatus was connected to the respective 250ml sampling bottle with plastic tubing. The sequence of 500ml bottles were further connected in series with one end connected to a vacuum source and other end closed. By applying vacuum the supernatant sample from respective jar would be first drawn into the 250ml bottle and once it is full, it would flow into the 500ml bottle. Figure 4 shows the picture of the sampling apparatus employed here. At the indication of the second timer vacuum is applied to the sampling device for approximately eight to ten seconds until enough samples are drawn into the sampling bottles. The temperature and pH of the supernatant solution is immediately measured. Samples collected in 250ml bottles are processed for suspended sediment concentration and turbidity of the supernatant solution is measured with the samples collected in the 500ml bottles. Flocculation efficiency for each jar is calculated using equation 1 and the reduction in SSC is calculated using the initial and final SSC.

RESULTS

Field Tests

A total of eleven simulations have been completed to date. Two simulations were conducted to observe the working of samplers, performance of various flow barrier configurations and conduct qualitative observation of FAEST. The tests indicated that the rainfall simulator, gauges and sampling devices all functioned well. Also a variety of configurations of flow barriers were tested and the results indicated that a scalene right angle triangular shape with curved base was efficient in trapping more sediment. Nine simulations were conducted by developing a grid from three types of soil and three slopes along the fence. The samples from the last three simulations are in the analysis stage and hence the results presented here refer to the six simulations with three types of soil and two slopes along the fence. Table 1 shows the simulation parameters for the six field tests.

In general it was observed that the undercutting, overtopping and flow concentration problems of the current design were eliminated. The performance of the fence depended on the soil type. With silty clay soil, the clay particles tended to form a coat on the fence, plugging the openings on the fence. Hence impoundments filled rather quickly and flowed around the barriers when compared to the sandy loam soil. Whereas scouring along the toe of the apron was considerably higher for sandy loam soil when compared to silty clay soil. The problem of scouring along the toe of the apron partially prevented the runoff water from entering the impoundment and thus limiting the performance of the fence. This problem will be addressed later with design modifications. However the scouring was significantly less when compared to the toe trench scour with conventional silt fence design. Also it was observed that the flow through the apron increased with increased slope along the fence with mild scouring below the apron which was predominant with the sandy loam soil.

Samples were collected from source area runoff, flow passing through the fence and flow overtopping the barriers and were designated as EP, DF and UF respectively. These samples were weighed at the end of the test to determine the flow rate and volume and are presented in Table 2. It was observed that the flow passing through the fence was lower for silty clay soil as the clay particles formed a coat on the fence. The sum total runoff volume at DF and UF was not equal to runoff volume at EP due to losses in the system. This included the infiltration through the section between the toe of the apron and upslope soil, seepage through the apron and impounded runoff behind the fence at the end of the test. During the fourth simulation, due to strong north winds much of the rainfall simulation water bypassed the source area samplers and hence it can be noticed that the flow at UF is more than flow at EP.

Grab samples were collected from the samples collected at the three sampling locations and were processed in the lab to determine suspended sediment concentration (SSC), settleable solids concentration and eroded size distribution. Table 3 shows the SSC and settleable solids data for samples collected for the first six simulations. It was observed that there was a significant reduction in the concentration of the sample collected passing through the fence when compared

to samples collected at the source area. Few of the samples at EP and DF from the first simulation were lost due to malfunction on an oven and also the samples from UF were accidentally discarded. Also during the fifth simulation the soil was very wet due to heavy rains and the area between the apron toe and upslope soil could not be compacted well. As a result runoff water seeped below the apron and soil particles below the apron mixed with the flow passing through the fence and increased the DF sediment concentration.

Eroded size distribution was done by wet-sieve analysis and microscan particle size analyzer and Figure 5 shows the pictorial of the size distribution for the first six simulations. Here the large and medium aggregates were separated by wet-sieving with a stack of 300, 150 and 75 micron sieve. Grab samples were collected from the wet-sieve tank of the particles passing through the 75 micron sieve and the size distribution of small aggregates were evaluated with the particle size analyzer. Results indicated that the percentage of eroded silt and clay particles was higher at DF when compared to EP with all six simulations.

The trapping efficiency of the FAEST for each simulation was estimated and is presented in Table 4. For real construction sites, it will be recommended that the FAEST installation at the downstream end of the fence, after the last flow barrier, be extended towards upstream side with a large curvature a few feet in length. Thus runoff flow around the barriers will be intercepted by this downstream extended section of the fence and trap all the sediment. In order to facilitate sampling of the flow around the barriers for size distribution data the extended part of the fence could not be installed in our field simulations. Hence trapping efficiency calculations are based on the sediment load thorough the fence and at the source area and assuming that all of the sediment flowing around the barriers will be trapped by the extended section. Results indicated that the performance FAEST was highly effective in trapping sediment when compared to the conventional silt fence design. Stevens et al., (9) study indicates that with some of the simulations conducted with conventional silt fence design and installation, more sediment was discharged at upstream of the fence than was discharged at the source area. Also it was noticed that the trapping efficiency varied with the soil type.

Flocculation Tests

Several jar test experiments were completed following the three sequences of tests. With the first sequence, tests were conducted with the three PAM formulations and varying the concentration of PAM from zero to 60 ppm. The flocculation efficiency and percentage reduction in SSC are presented in Table 5. It can be noticed that the efficiency of all three PAM formulations were same after a threshold minimum concentration. The efficiency decreased at about 40 ppm for all three PAM's indicating the threshold maximum concentration. Thus the results indicated that within the threshold concentration range the flocculation efficiency is constant. Also, we observed that very small concentrations (0.5 ppm) of PAM can achieve high flocculation efficiency.

Tests were also conducted with Calcium Chloride as flocculant, and the results are presented in Table 6. The flocculation efficiency and percentage reduction in SSC did not follow the same trend and this can be attributed to the fact that calcium chloride, which is a desiccant,

absorbs moisture quickly during the weighing operation and introduces error. No particular trend was observed in flocculation efficiency as the concentration was increased.

Our last sequence of tests was conducted with both PAM and calcium chloride as flocculant. We anticipated that calcium chloride will act as bridging agent with PAM and will enhance the flocculation process. Three concentration levels for each PAM formulations and calcium chloride were chosen. The results are presented in Table 7. The results indicated that there was no significant difference in flocculation efficiency when compared to tests with PAM only. However, the effect of calcium chloride in combination with PAM, on the floc size formed still needs to be evaluated.

CONCLUSIONS AND RECOMMENDATIONS

Nine field simulations with three types of soil (sandy loam, loam, silty clay) and three slopes (10, 13 and 20 percent) along the fence with Nilex 2130 fabric have been completed. Results indicate that the first generation FAEST represents a significant improvement over the conventional design in eliminating failures and increasing sediment trapping. The smallest slope employed in this study was equal to the steepest slope in Stevens et al., (9) study with conventional silt fence. At this slope the conventional fence failed and in five out of six tests discharged more sediment along the toe than was discharged from the source area. Erosion along the toe of apron at very steep slopes and especially with sandy loam soils needs to be addressed. Work is in progress to modify the design and installation process to overcome this problem.

Several jar test experiments have been completed with PAM and calcium chloride as flocculant. Results have indicated a promising solution to flocculate fine particles and trap them with FAEST design. Also very little PAM is required to make a significant difference in trapping of fine particles. Testing is continuing to study the effect of dosing intensity and calcium chloride on floc size. Techniques for introducing PAM into the surface runoff at appropriate concentrations are currently being developed.

Work is in progress to optimize the fabric strength and post spacing to minimize the bulging and sagging of the fence due to increased sediment storage. Field tests are currently in progress to study the effect of using a non-porous apron with very steep slopes and sandy loam soil. Also a unique settling column apparatus is developed to measure the settling velocity of the flocs for given flocculation parameters.

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TABLES

Table 1. Simulation parameters for test grid.

Simulation	Soil Texture	Slope along Fence (Percent)	Rainfall Rate (cms/ hr)	Test Duration (hrs)
1	Silty Clay	10.1	6.18	1.0
2	Sandy Loam	9.5	6.00	1.3
3	Loam	9.4	5.69	1.6
4	Loam	13.2	7.40	0.7
5	Sandy Loam	13.2	6.66	1.0
6	Silty Clay	12.2	5.12	1.1

Table 2. Total discharge volume and flow rate.

Simulation	**1**	**2**	**3**	**4**	**5**	**6**
Soil Texture	Silty Clay	Sandy Loam	Loam	Loam	Sandy Loam	Silty Clay
Flow Volume(m^3) at EP	3.71	3.58	4.57	1.61	2.46	2.28
Flow Volume(m^3) at UF	0.94	0.80	2.51	2.09	0.79	1.68
Flow Volume(m^3) at DF	0.44	0.48	0.76	0.43	0.58	0.23
Flow Rate (m^3/hr) at EP	4.28	3.57	3.16	2.34	2.55	2.55
Flow Rate (m^3/hr) at UF	1.32	1.12	2.14	3.26	1.32	1.94
Flow Rate (m^3/hr) at DF	0.51	0.51	0.61	0.61	0.71	0.31

Table 3. Suspended sediment concentration and settleable solids data.

Simulation	**Soil Type**	**EP**		**UF**		**DF**	
		SSC	**SS**	**SSC**	**SS**	**SSC**	**SS**
1	Silty Clay	28567	120	-	-	6396	23
2	Sandy Loam	7657	29	3207	24.5	5329	17.5
3	Loam	24615	122.5	16285	78	8907	4.5
4	Loam	50274	187.5	66530	152.5	23687	56
5	Sandy Loam	31488	185	95596	282.5	63990	70
6	Silty Clay	12154	21	7370	21.5	6271	16.5

Table 4. Sediment load and trapping efficiency.

Simulation	**Total Sediment at EP (kg)**	**Total Sediment at UF (kg)**	**Total Sediment at DF (kg)**	**% Trapping Efficiency**
1	108.0	0.0	2.8	97.4
2	27.5	2.6	2.5	90.8
3	114.8	41.4	6.8	94.1
4	83.6	145.2	10.2	87.8
5	79.0	79.8	38.6	51.1
6	28.1	12.4	1.4	94.9

Table 5. Flocculation efficiency and % SSC reduction for PAM only tests.

	PAM 10			PAM 20			PAM 30	
Conc. (ppm)	**% Floc. Efficiency**	**% SSC Reduction**	**Conc. (ppm)**	**% Floc. Efficiency**	**% SSC Reduction**	**Conc. (ppm)**	**% Floc. Efficiency**	**% SSC Reduction**
0	8.96	52.14	0	8.96	52.14	0	8.96	52.14
0.05	50.85	79.73	0.05	26.52	69.01	0.05	44.58	76.35
0.1	77.88	92.34	0.1	66.86	88.76	0.1	69.30	88.38
0.25	79.77	92.87	0.25	76.44	92.31	0.25	77.63	92.36
0.5	94.71	97.01	0.5	89.08	96.11	0.5	90.21	96.77
1	95.84	97.70	1	91.68	96.66	1	93.28	97.47
1.5	93.68	97.30	1.5	94.66	97.47	1.5	95.40	98.24
2	96.21	95.78	2	95.35	97.26	2	95.77	97.21
2.5	96.36	97.57	2.5	95.35	97.72	2.5	96.43	97.23
3	96.77	97.48	3	95.10	97.51	3	96.02	97.41
3.5	96.88	97.89	3.5	96.80	98.91	3.5	97.05	98.55
4	97.02	97.66	4	96.53	97.69	4	96.49	97.95
4.5	97.45	97.93	4.5	96.96	97.76	4.5	97.14	97.21
5	97.11	97.74	5	96.74	98.40	5	96.65	97.78
7	96.62	98.12	7	96.40	97.89	7	96.75	98.84
10	96.73	98.53	10	96.65	98.00	10	96.63	98.02
15	93.96	97.44	15	95.40	97.74	15	93.55	97.08
25	95.13	98.82	25	95.09	97.90	25	93.73	97.14
40	89.90	95.61	40	89.73	96.46	40	88.45	95.82
60	87.93	94.94	60	85.98	94.98	60	87.54	94.32

Table 6. Flocculation Efficiency and % SSC reduction for Calcium Chloride tests.

$CaCl_2$ Conc. (ppm)	**Flocculation Efficiency (%)**	**Percentage SSC Reduction (%)**	**$CaCl_2$ Conc. (ppm)**	**Flocculation Efficiency (%)**	**Percentage SSC Reduction (%)**
0	5.73	42.44	7.5	6.42	45.27
0.5	11.45	43.63	8	7.37	41.65
1	9.44	32.22	8.5	7.36	40.18
1.5	8.53	50.74	9	13.73	22.55
2	13.30	33.67	9.5	13.11	39.80
2.5	12.10	46.30	10	9.63	22.37
3	14.28	31.78	10.5	9.24	21.32
3.5	17.09	37.27	11	12.41	34.45
4	16.94	33.64	11.5	13.51	35.84
4.5	15.67	29.80	12	6.42	23.74
5	17.61	44.21	14	8.45	32.12
5.5	18.28	41.64	16	5.91	15.71
6	8.60	37.57	18	9.04	31.44
6.5	9.47	44.32	20	7.37	26.03
7	7.12	26.79	25	8.57	24.09

Table 7. PAM and Calcium Chloride combination test results.

	Combination		Flocculation	% SSC
PAM Type	**PAM Conc. (ppm)**	**CaCl2 Conc. (mM)**	**Efficiency %**	**Reduction**
10	0.05	0.50	10.83	40.20
10	0.05	2.50	6.80	48.18
10	0.05	5.00	13.46	27.09
10	5	0.50	97.44	97.90
10	5	2.50	98.25	99.18
10	5	5.00	98.97	98.42
10	10	0.5	96.71	98.50
10	10	2.5	98.34	99.36
10	10	5	98.69	98.82
20	0.05	0.50	11.45	39.36
20	0.05	2.50	13.25	47.33
20	0.05	5.00	14.86	27.66
20	5	0.50	97.15	98.25
20	5	2.50	97.91	98.39
20	5	5.00	98.55	98.36
20	10	0.5	95.88	97.05
20	10	2.5	97.02	97.71
20	10	5	98.37	99.78
30	0.05	0.5	8.52	46.76
30	0.05	2.5	12.94	48.44
30	0.05	5	8.49	46.01
30	5	0.5	96.37	97.86
30	5	2.5	97.36	98.68
30	5	5	98.44	99.43
30	10	0.5	95.88	98.33
30	10	25	97.17	97.85
30	10	5	98.24	98.22

FIGURES

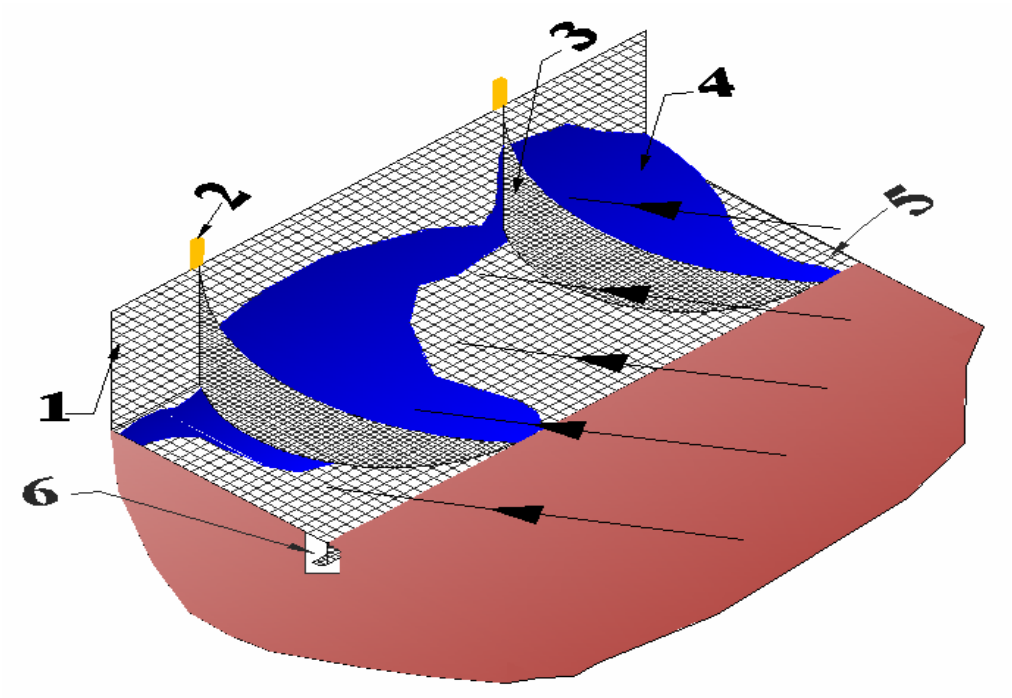

Figure 1. Schematic of Modified Silt Fence Design: 1. Fence, 2. Support Post, 3. Flow Barriers, 4.Impounded Water, 5.Apron, 6. Section showing installation of apron in a trench, (Arrows indicate runoff flow direction).

Figure 2. Picture of silt fence testing site with FAEST.

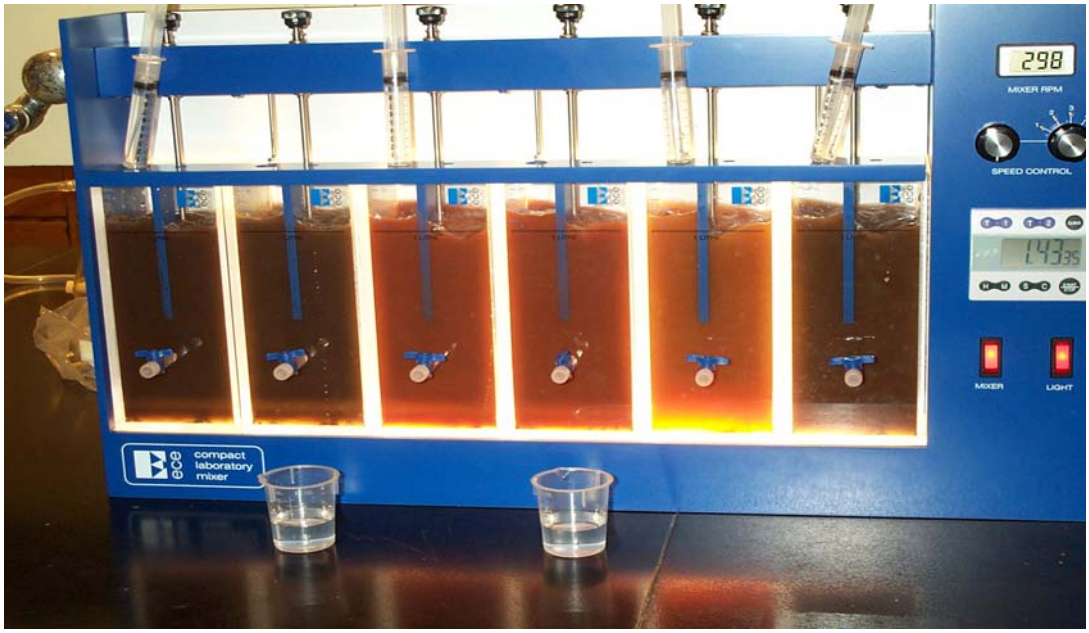

Figure 3. Jar test apparatus.

Figure 4. Sampling device for jar test apparatus.

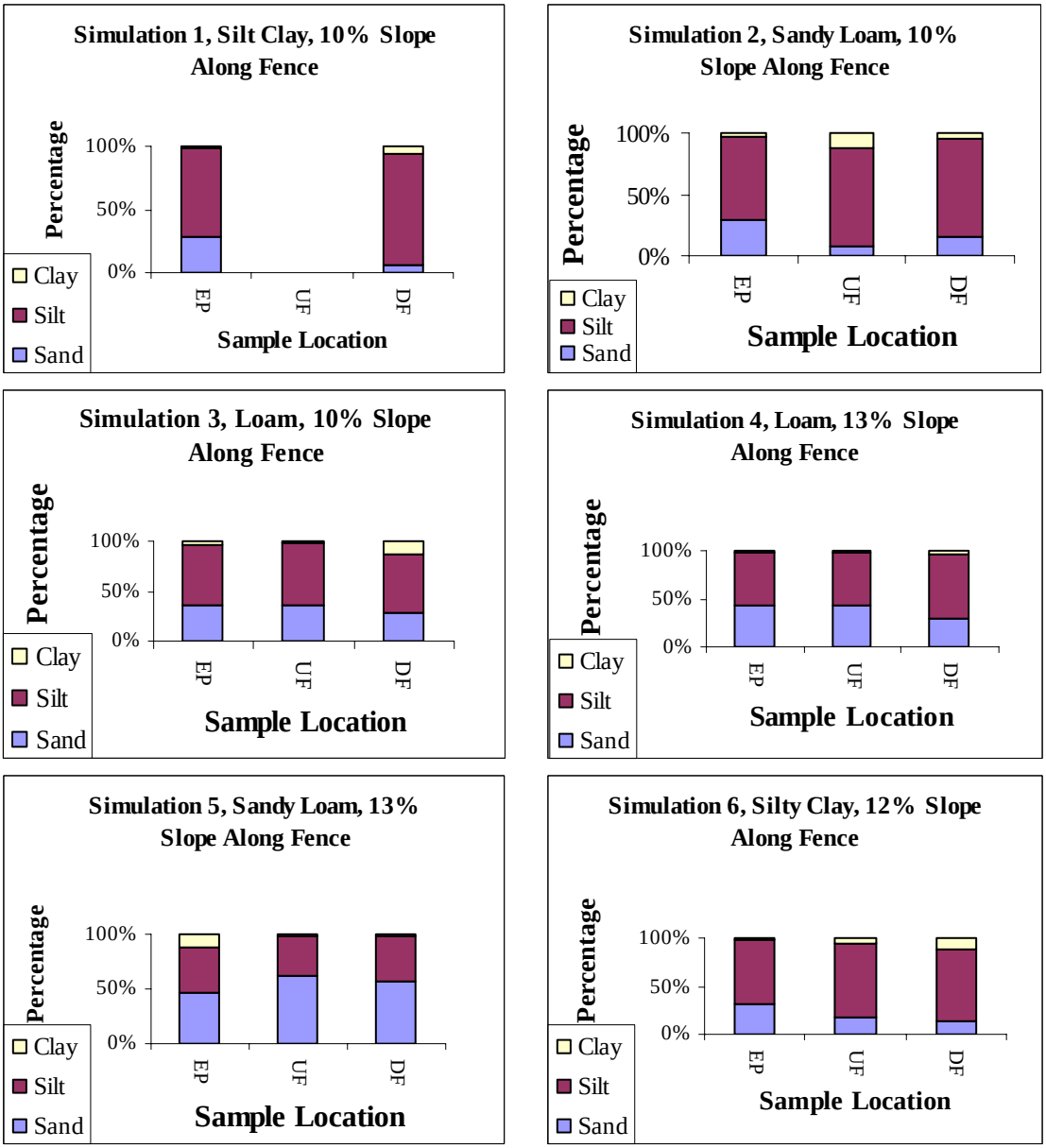

Figure 5. Chart of eroded size distribution data.