Managing Coal Bed Methane Produced Water for Beneficial Uses, Initially Using The San Juan and Raton Basins as a Model

(Interim Progress Report)
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Allan Sattler, Mike Hightower, Tina Nenoff, Jason Pless, and Mark Phillips
Sandia National Laboratories,
Brian Brister
NM Bureau of Geology and Mineral Resources,
Rick Arnold
NM State University Agricultural Experiment Station,
Martha Cather and Brian McPherson
NM Tech Petroleum Recovery Research Center

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Abstract and Introduction

This report gives much of the progress of the second year (but essentially first year funding only) of the Managing Coal Bed Methane Produced Water for Beneficial Uses, Initially Using the San Juan and Raton Basins as a Model. The work is divided into two manor sections work that was accomplished last year and work that is planned this year with the fairly recent arrival of out second year's funding.

Work Done Last Year:

This report is primarily in two areas:

- Novel Desalination Research.
- Rangeland Improvement.

Novel Desalination Technologies (Sandia) reported here include:

- Ion Exchange/Ion Sorption
    - Including Laboratory Results
    - Cost Analysis
- Ultra, Nano Filtration Process for Desalinating and Removing Organics from Produced Water (Western Environmental)

Ion Sorption/Exchange (Sandia) results reported here include:

- Optimized procedures for synthesizing the artificial anion exchanger Hydrotalcite and cation exchanger, Permutite.
- Results showing that the ion exchange capacity of Permutite holds up rather well on regeneration processes.
- A result showing that regeneration of HTC is disappointing at low temperatures and becomes costly at higher temperatures.
- Two preliminary cost estimations to desalinate 3000 TDS CBM produced water using a Bureau of Reclamation Code (BOR). Costs are in the dimes/barrel range whereas the estimates with a Sandia–developed model are in the dollars/barrel range. More study needs to be done but possible reasons for the discrepancy are discussed.

Ultra/Nano Filtration (Western Environmental)

- Results showing that the performance of the ultra filtration membranes for removal of organic material was considered highly successful during this test run.
    - The ultra filtration unit was operated on a 24 hour per day basis. The ultra filtration unit operated a total of 1953 hours out of the potential 2412 hours of the test run or about 81%.
    - The unit was not flushed with fresh or processed water during downtime.
- Additional results showing that nano filtration is efficient for removal of divalent ions.

Capacitive Deionization and an Electro Chemical Process for Removal of Both Organic Contaminants and Total Dissolved/Suspended Solids

- This report contains both schematics and description of the principles of both desalination methods.

Rangeland Improvement Accomplishments (New Mexico State University, Ag Experiment Station) include:

- Results of two waterings of 5400 and 10600 TDS produced water on seedlings on the Williams Production Co land. The Sodium Absorption Ratio (SAR) and Electrical Conductivity (EC) Conductivity of the soil rose only slightly.
- Results of three waterings of CBM produced water in the high 3000, low 4000 TDS range on seedlings on Conoco Phillips land. Conductivity of the soil rose only slightly.

A Portion of the Work to be done this Following Year:

Novel Desalination Technologies

- Capacitive Deionization[1] (Biosource)
- An Electro Chemical Process for Removal of Both Organic Contaminants and Total Dissolved/Suspended Solids[1] (Alpha Omega)
    - Contracts were just recently put in place being written to vendors of the above two technologies

Ultra/Nano Filtration (Western Environmental)

- Unsolved Problems future project

Participation in other Technologies and Activities-This report briefly describes other technologies and activities that this project and its personnel are associated with.

1 FY 04 Funds did not arrive until August, 2004. Contracts are being put in place with appropriate vendors[1]

Section 1: Work Done Last Year:

Ion Exchange/Sorption Desalination Process
(Sandia)

In-situ Ion Exchangers for Desalination:

Brackish water, either groundwater or produced water, can be viewed as a collection of various solvated anions and cations. What has been studied is the use of various low cost oxide materials that have a preference to select the ions commonly found in brackish water. This is done with minimal extra energy due to the high selectivity of the ion exchange materials. Furthermore, because the ion exchangers are comprised of durable inorganic oxides (as opposed to resins, such as organic polymers), they are very stable over a large pH range. Overall, the favorable kinetics of ion exchange allow for easy desalination of the brackish water, resulting in potable water (Jason Pless et al, "Desalination of Brackish Ground Waters and Produced Waters Using In-situ Precipitation," Sandia Report 2004-3908, August 2004).

The process was tested on actual produced waters provided by Aztec Drilling of Farmington, NM. These waters had high concentrations of sodium and carbonate ions, a TDS of approximately 11,000ppm and a pH of 8.4.

<u>The anionic getters</u> we have developed provide significant anionic sequestration from brackish waters. We have synthesized *Hydrotalcites* (HTCs) with general formula $[Mg_6Al_2\ (OH)_{16}]^{2+}[A]^{-}_{2}\bullet nH_2O$ where A = Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-} and SO_4^{2-}. The synthesis of these materials is based on inexpensive starting chemicals, which react and precipitate at room temperature for a short time. The HTC is activated (involving the collapse of the structure) by calcination at 550°C. After calcination and immersion in saline water, the material recovers its initial structure. In the course of water treatment, each mole of regenerated HTC incorporates two anionic equivalents from the salt solution. Our experiments showed that the activated HTCs have an average anionic incorporation capacity of 2.5 mEq/g, measured with $Na_2(SO_4)$.

Once a bulk amount of HTC is synthesized, it can be either dumped or reused in a cyclic process. This method also allows for cost reduction - some of the side products of the synthesis and regeneration of HTCs could be either sold (NH_4NO_3) or used in the next steps of the technological process (HCl, H_2SO_4, HNO_3).

<u>The cationic getter</u> that was developed is amorphous silica, which provides significant cationic sequestration from brackish waters. It is nominally related to an aluminosilicate named *Permutite*, with general formula Si_3AlO_9. Various amounts of elements to the framework (i.e., Al; thereby incorporating a net negative charge) can be added to tailor the ion exchange ability; depending on the dopant amount, the ion exchange capacity is between 1.7- 2.7 mEq/g, measured with NaOH.

Other cation getters have been synthesized and tested as replacements for Permutite. They include Zirconium Phosphate and minerals such as Illite, Bentonite, and synthetic Montmorillonite. Though their ion exchange capacities and efficiency values of exchange are less than the permutite, they can in principle all be used in this process too.

The rest of this section involves the anion getter Hydrotalcite and the cation getter Permutite and their properties and characteristics.

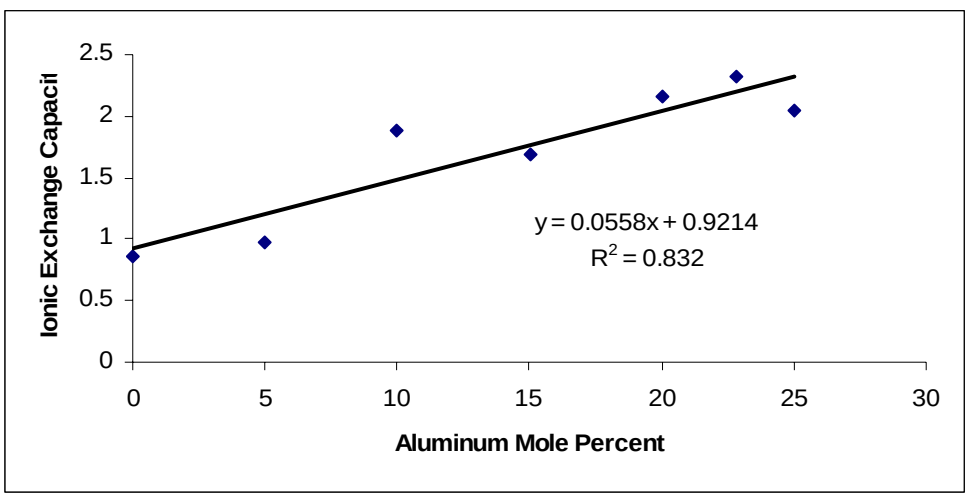
Synthesis Optimization, Scale Up, and Regeneration of the Artificial Ion Exchange Materials Hydrotalcite and Permutite

Results of Optimizing Synthesis of Hydrotalcite and Permutite

Procedures have been optimized for synthesizing the artificial anion exchanger Hydrotalcite and cation exchanger Permutite.

- The best results were synthesis with metal chloride salts and Na_2CO_3/NaOH for the scale up of Hydrotalcite because of the high ionic exchange capacity and "best" (i.e. quickest) filtering properties.

- The best ion exchange of Permutite is with 23% Aluminum loading of Permutite (Figure 1).



Ion Exchange Capacity of Permutite vs. Aluminum Mole Percent
(Best results for enhanced ion exchange capacity with ~23% loading)

Results of Scale Up and Subsequent Production, Batches of Hydrotalcite and Permutite

Production of batches of Hydrotalcite and Permutite were scaled up to get some idea of how much ion exchange capacity (IEX) could be lost in scaling up production. Results

are shown below. These materials hold their ion exchange capacity rather well, especially Permutite where the ion exchange capacity actually increased. The ion exchange data for the scale up in production (mid-size) follows:

HTC, Hydrotalcite: A nominal, starting ion exchange capacity, (IEX) 3.182

(**A**) Mid-size scale-up - 8X amounts of baseline conditions

- IEX = 2.523 mEq/g, (ave of 4)

(B) Mid-size scale-up - 3X concentrated metal salts over baseline conditions

- IEX = 2.343 mEq/g, (ave of 8)

Permutite: A nominal, starting ion exchange capacity of 2.318**

- mid-size scale-up at 10X amounts of baseline conditions
  - IEX = 3.026 mEq/g, (ave of 10)**

**note: value is higher than any previously synthesized sample.

Ion Exchange Capacity of Permutite and Hydrotalcite during Regeneration

<u>Attempts at Regeneration of the Ion Exchange Capacity</u>

The ion exchange capacity of Permutite holds up rather well on regeneration processes. IEX decreases with H_2SO_4 regeneration because of reaction between H_2SO_4 and Al but holds up better with the use of acetic acid which however is more costly. Regeneration of HTC however is disappointing at low temperatures and becomes more costly at higher temperatures. Results follow below:

Regeneration of HTC: (Initial IEX~ 3.182)

- Heating ~5g, (**A**) at 350C for 1h
  - IEX = 0.063 mEq/g, (ave of 4)*
- Heating ~5g (**B**) at 550C for 1h
  - IEX = 0.036 mEq/g, (ave of 4)*

* Low values because the regeneration temperatures are not high enough

Regeneration of Permutite: (Initial IEX = 2.94 mEq/g)

- Washing with H_2SO4
  - IEX = 1.20 mEq/g, (ave of 3)

4th Regeneration of Permutite

- Washing with $H2SO_4$
  - IEX = 1.03 mEq/g

Regeneration of Permutite (Initial IEX = 3.11 mEq/g)

- Washing with acetic acid
  - IEX = 2.46 mEq/g, (ave of 4)

9th Regeneration of Permutite

- Washing with acetic acid
  - IEX = 2.12 mEq/g

Nano Filtration for Pretreating CBM and Oilfield Produced Water
(Western Environmental)

Introduction

The use of membrane technology in the purification of produced water has been limited by the inability to cost effectively remove the oil and hydrocarbons in the produced water. The removal of the oils required non-membrane treatment procedures before membrane technology could be applied. This treatment step has been considered as potentially the most difficult and economically – one of the most costly in the overall purification of produced water. Western Environmental has been collaborating with Sandia, informally and formally, in its approach of using nano filtration to remove (mostly) divalent ions and some monovalent ions and more recently the removal of organic matter from produced water (Western Environmental Management Corp. Ltd and GE Osmonics, Inc. "Interim Report: Membrane Technology for Purification of Produced Water").

Operation Description

The Membrane Research Pilot Plant (MRPP) of Western Environmental was operated from July 5, 2003 through October 11, 2003 (100 Day Test) demonstrating membrane technology in the purification of produced water. The membranes used during this demonstration were developed by GE Osmonics, USA of Minnetonka, Minnesota. This system was evaluated for analytical and initial operational performance relative to defined performance goals needed for full-scale implementation of this technology.

The ultra filtration membrane process uses a hydrophilic membrane to remove the undissolved hydrocarbons from the produced water to be treated. Previous testing has shown that removal efficiencies to a level of less than 0.1 ppm had been accomplished based on the EPA Oil and Grease analytical procedure. If this system can operate without fouling of the membranes from the iron, dissolved solids, and organic compounds in the produced water, this system would significantly reduce produced water pretreatment costs over previously tried technologies. In addition, because the oil is de-emulsified in the membrane process and the salt content of the produced water is not rejected by this (ultra filtration) membrane process, the reject water/oil stream can be recycled back to the inlet oil separation equipment to recover the oil and allow the produced water to be reprocessed resulting in zero waste water discharge from this ultra filtration system.

The demonstration provided analytical and operational data to initially evaluate the performance of the ultra filtration membrane. Initial tests indicated that the oil and grease contaminant removal efficiencies greater than 99% could be accomplished with the membrane system. Continuous mode operation allowed produced water with a 20-30 ppm oil level as feed combined with recycle water to provide an actual oil and grease

operating gradient across the membranes of 50 – 115 ppm to be reduced to a non-detectable level of less than 5.0 ppm in the permeate.

Operation Results

The ultra filtration membrane unit operated with an available on-stream efficiency of 97.6 percent and an actual on stream efficiency of 81.0 percent. The major on-stream efficiency problems were related to support equipment and facilities unrelated to the operating membrane unit. The membrane process showed no fouling based on the normalized flux and pressure drop. The unit did not require cleaning during the 100 day demonstration test. A limited cost analysis of field operational costs for the ultra filtration membrane system shows the use of the system may provide cost-effective produced water pretreatment, with a direct energy operating cost of $0.020/barrel of pretreated produced water.

The nano filtration and reverse osmosis units were operated during brief periods only. The minimal operation was due to the design capacity of the pumps provided on these units. Large recycle streams were required to maintain mechanical stability of the pumps. The large flow rates of these streams caused large pressure drops in the system which is believed to be detrimental to the membranes.

The performance of the ultra filtration membranes was considered highly successful during this test run. The primary objective of operating the membranes on produced water that contains oil and hydrocarbons without fouling was accomplished. The ultra filtration unit was operated on a 24 hour per day basis. The unit was not flushed with fresh or processed water during downtime. During shutdowns, the unit was flushed with the inlet produced water and allowed to sit in this condition. This is anticipated to be the highest potential fouling condition for the membranes.

The ultra filtration unit operated a total of 1953.75 hours out of the potential 2412.5 hours of the test run or about 81%. The total downtime hours attributed to the ultra filtration unit was 58.0 hours representing 2.4% downtime or a potential on stream time of 97.6%. The remaining hours of downtime were attributed to several other factors such as – water return system failure, raw material availability (sulfuric acid), produced water availability, operating personnel not available. A graph showing the downtime hours for all causes is shown in Figure 1.

The produced water used during this test was received from the Devon Gas Well Lever 2 Federal 1 in the New Mexico Permian Basin. The water analysis of this well is provided in Tables 1 and 2.

The water produced by the ultra filtration unit was clear as compared to the cloudy opaque coloring of the concentrate water discharged from the unit. Pictures depicting the water quality from the ultra filtration unit are shown in Figure 2.

The analysis of the hydrocarbons from water streams inlet and outlet of the ultra filtration unit are provided in Tables 2 and 3. The data confirms UF technology that only hydrocarbons are removed by this membrane. This data shows the oil and grease levels in the permeate to be non-detectable and based on the analysis and the flow rate data. The quantity of oil and grease found in the concentrate would equate to the calculated level in the feed water. This supports the analysis that essentially no oil and grease remained in the permeate. The analytical work was performed by Assaigai Analytical Laboratories, Albuquerque, NM.

The operating data was normalized to evaluate any changes in the UF membrane flux and pressure drop during the operation of the pilot study. Both variables were essentially constant during the entire test period. These results would support the conclusion that the membranes performed with a minimum or extremely low fouling during this 100 day test run. This performance was obtained with the membranes seeing an average oil and grease level of about 50 ppm inlet and 115 ppm outlet. This oil and grease level was calculated based on the actual analytical values and the internal water recycle rates. A concentrate recycle rate of about 7 - 8 gpm was returned to the inlet of the UF unit and combined with the makeup water, thereby raising the actual oil and grease level in the water being processed by the membranes.

Energy Consumption, Preliminary Cost Analysis

The energy consumed by the ultra filtration unit consisted of operating the pumps indicated below.

Feed Water Pump--3/4 Horsepower
UF Feed Pump1--1/2 Horsepower (Variable Frequency Drive)
UF Booster Pump--3 Horsepower

The amps measured at the power supply to the ultra filtration unit indicated an average operating load of about 3.2 amps at 442 volts. This power supply is for the three pumps indicated above. Based on these numbers and a unity power factor, the calculated energy usage by the ultra filtration unit is 2.45 kilowatts per hour. Based on the average permeate or production rate of 5 gallons per minute, the projected energy usage for the ultra filtration unit was 0.34 KWH per barrel or 8.16 KWH per 1000 gallons. At an electrical energy cost of $0.06 per kilowatt, the energy operating cost of the ultra filtration process is $0.020 per barrel or $0.49 per 1000 gallons.

Table 1
Feed Water Analysis to Ultra filtration Unit
Devon Well Levers 2, Fed #1

Cations	
	milligrams/liter
Sodium	**3,434**
Calcium	**600 (Calcium Hardness 1500mg/l $CaCO_3$)**
Magnesium	**171 (Magnesium Hardness 700 mg/l $CaCO_3$)**
Anions	
Chlorides	**4,456**
Sulfate	**2,658**
Carbonate	**132**
Bicarbonate	**488**
Total Dissolved Solids	**11,939**
Other Properties	
pH	**8.64**
Hydrogen Sulfide	**270 ppm**
Iron	**0.1 ppm**
P-Alkalinity	**110 ppm $CaCO_3$**
M-Alkalinity	**620 ppm $CaCO_3$**

Table 2
Devon Well Levers 2, Fed #1
Oil & Grease Analysis

Oil & Grease Analysis

Date	Feed Water	Permeate	Concentrate
8-13-03	25.9 ppm	N/D*	115 ppm

*N/D – None Detected

Table 3
Water Analysis
Nano Filtration Unit

	Feed Mg/L	Permeate Mg/L	Concentrate Mg/L
Cations			
Sodium	3,201	2,524	3,750
Calcium	578	98	1,160
Magnesium	148	16	304
Anions			
Chlorides	4,118	3,976	3,976
Sulfate	2,944	50	6,217
Carbonate	0	0	0
Bicarbonate	171	171	281
TDiSs	11,158	6,835	15,687
Other Properties			
pH	6.64	6.43	7.48
Iron	0.1 ppm	N/D	N/D

Figure 1
Ultra-Filtration Pilot Study
100 Day Test, July 7 - October 14, 2003
Downtime Summary

Total On-Line Hours	1,953.75
UF System, Downtime Hours	56.00
Return Water System, Downtime Hours	247.00
Raw Materials Availability, Downtime Hours	86.75
Water Source Not Available, Downtime Hours	36.00
Operating Personel Not Available, Downtime Hours	33.00
Total In-Service Hours	2,412.50

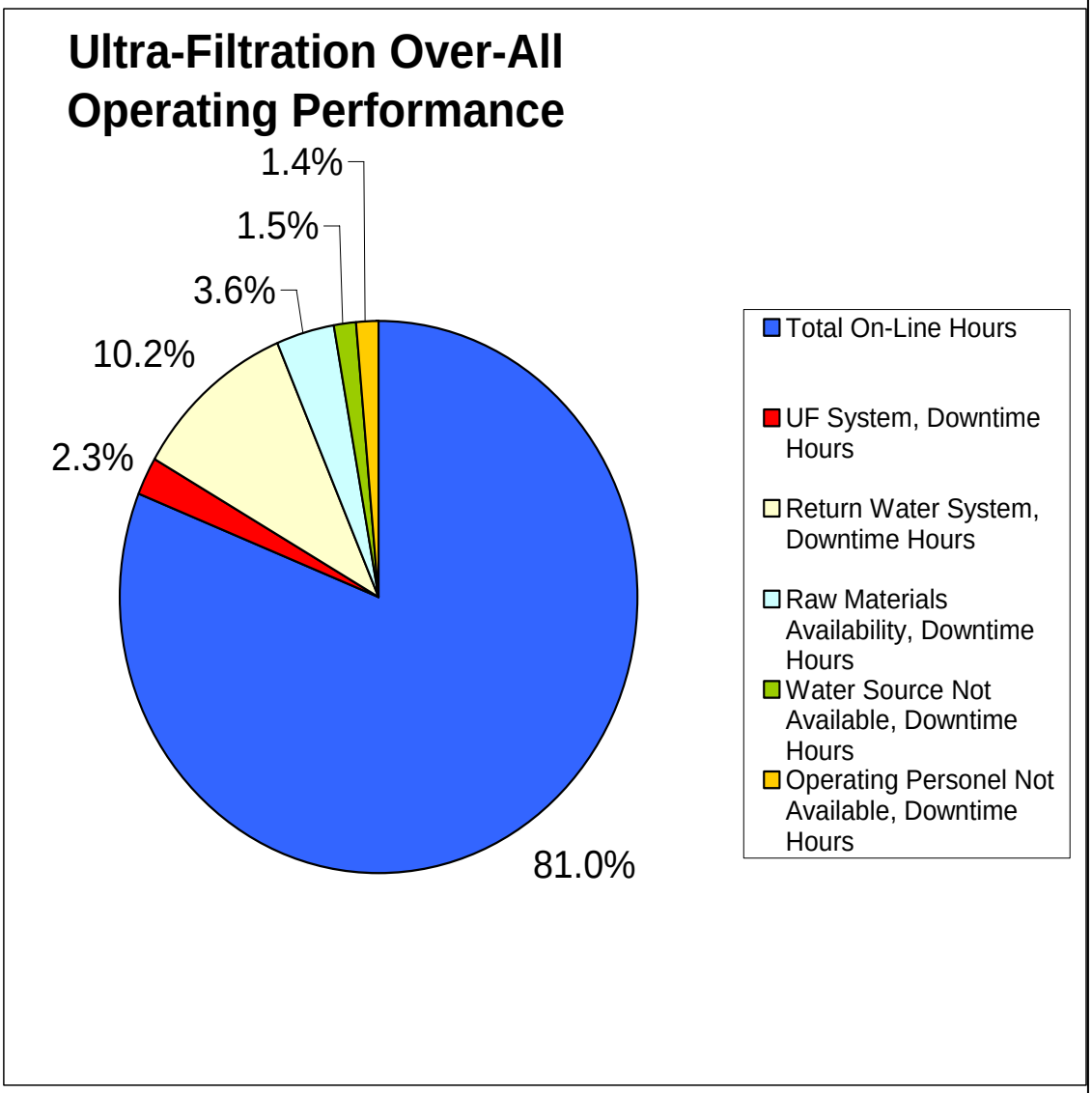
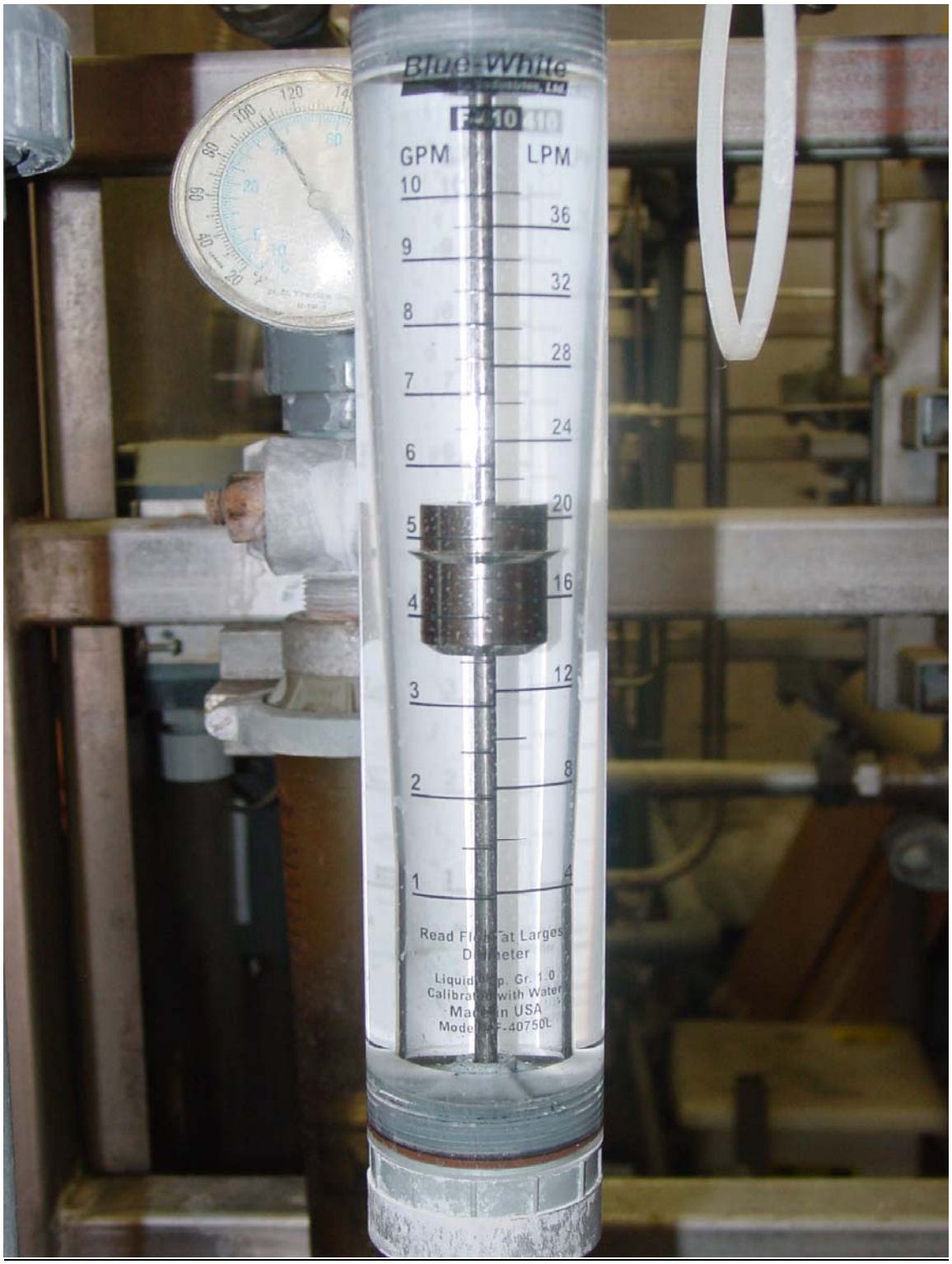


Figure 2
Ultra Filtration Clear Permeate Water



Cost/Economic Evaluation of Desalination and Preliminary Design of Produced Waters Using *In-Situ* Precipitation via Ion Sorption/Ion Exchange (Sandia-Developed Formalism)

Introduction

Preliminary design and cost estimates are presented for fabrication of hydrotalcite and permutite, two novel ion-exchange materials used in a proposed patent-pending ion-exchange desalination process. Water treatment costs using this process are considered for treatment of produced water from coal-bed methane sites using a portable water treatment unit mounted on a flatbed trailer. Economy of scale for ion-exchange material production is calculated. Water qualities and flow rates treatable using a single portable unit is estimated (Donahe et al". Preliminary Design and Economic Evaluation of Desalination of Produced Waters Using *In-situ* Precipitation, preliminary Sand report, August 18, 2004).

The patent-pending process proposed for desalination of water [i] is an ion-exchange (IX) process possessing many technical advantages over RO. Among these are:

1) No high-pressure pumps are required, thus lowering energy cost;
2) No expensive membranes are required;
3) Brine waste is sequestered on the ion-exchange materials, allowing spent ion-exchange material to be potentially reapplied as filler in building material or simply land filled as non-hazardous waste;
4) Process has a wide range of applicability, with uses ranging from existing water treatment plants to RO pretreatment to portable and/or in-situ treatment of brackish groundwater sources.

Figures 1a, 1b, and 2 show schematically how this ion exchange sorption process works.

Results

Because determining the effect of flow rate and other variables on plant total cost and average unit cost is an integral part of this analysis, and because many unit operations in the process cannot be readily specified without detailed experimental study, no single set of unit specifications or cost results is included here. Instead, trends in cost and performance are presented and analyzed to determine overall technical and economic feasibility of the process. For suggestions on required experimentation and other avenues of investigation, consult the *Recommendations* section. For a discussion of specific process concerns, consult the *Discussion* section. A qualitative process description and analysis of economic trends follows.

Economic and factor space constraint results indicate that the portable unit may be competitive with current disposal costs of $1-4 per barrel for produced water in the San Juan and Raton basins if TDS is sufficiently low (3,000 mg/L or less). Use of ores instead of bulk specialty chemicals wherever possible appears to cut the cost of manufacturing IX materials by 50% or more.

A tradeoff exists between significant cost savings associated with lime softening pretreatment of produced water prior to ion exchange and the increased footprint associated with lime treatment equipment (Figure 3). Lime pretreatment appears to be preferred as a means of lowering treatment cost, especially for bicarbonate-dominated waters; however, if increased throughput is required, lime treatment equipment may be omitted in exchange for larger ion-exchange columns for an added cost dependent on bicarbonate content. Cost estimates derived from these assumptions are $85/1000 gal ($3.57/BBl) with lime softening and 125/1000gal ($5.25/ BBL) without lime softening.

In carrying out further design and experimental work on the process, care should be taken to ensure that:

1) The ion-exchange products can be engineered into a palletized form for use in a packed bed; if not, availability of other water treatment measures should be assessed, such as slurry contact filtration.
2) The ion-exchange products may be flocculated or coagulated to provide good filterability and processability.
3) Saline waste from ion-exchange material manufacture can be reformed and reapplied as either a commercially useful product or as a feedstock to another process. Barring this, waste disposal using evaporation ponds or biodegradation should be evaluated. However, disposal may not be an option for some waste streams because of their volume.

Fig. 1a: How Ion-Exchange Desalination Works

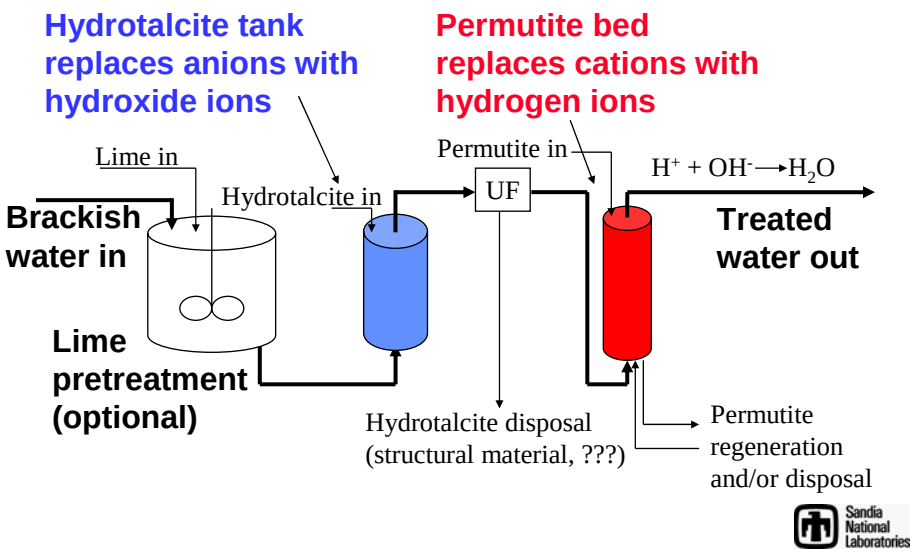
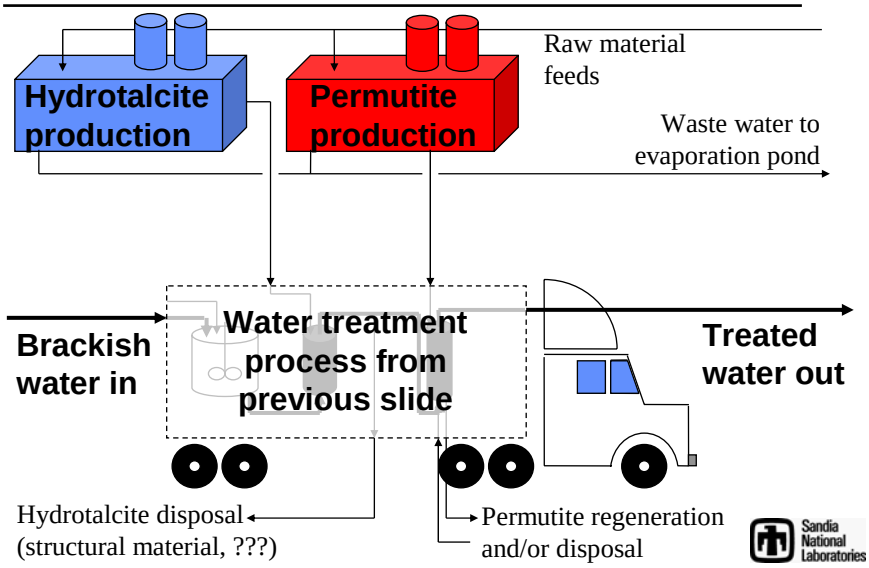


Fig. 1b: How The Desalination Process Works



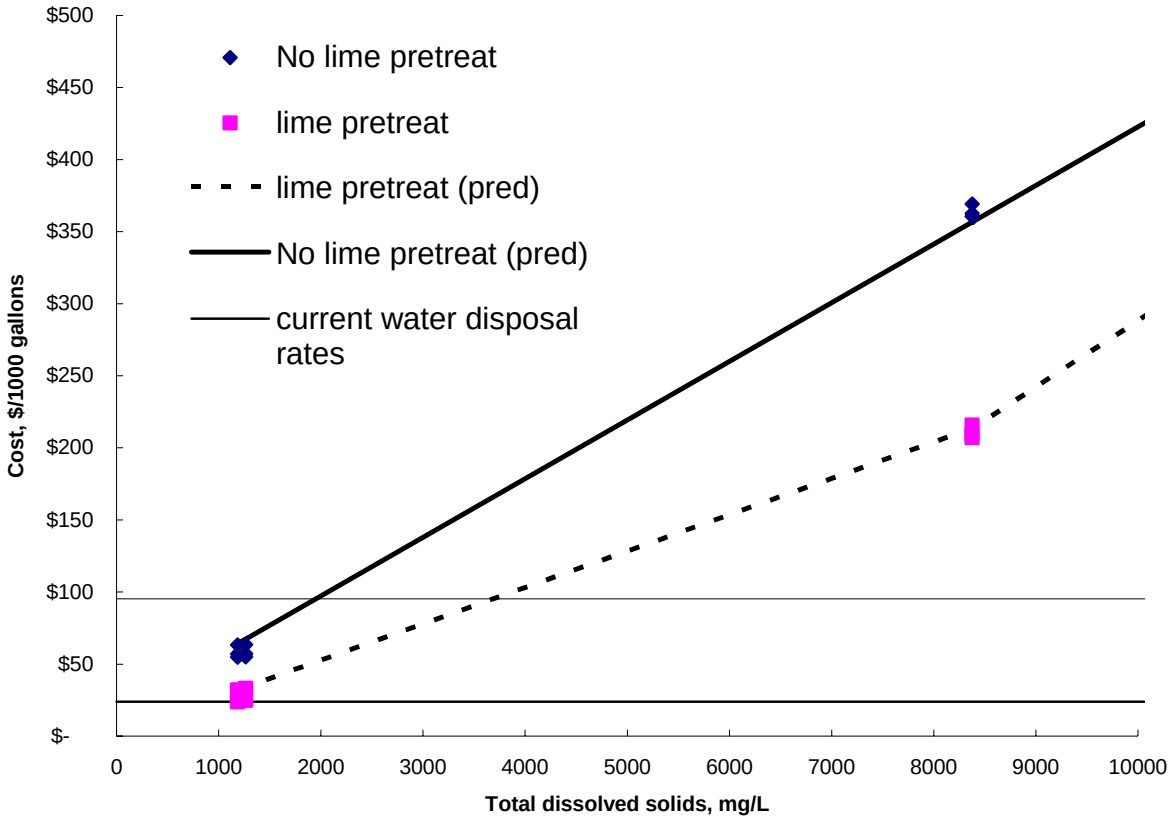


Figure 2: Cost of Ion Excahnge Methods versus Water Quality

Cost Estimation of the Ion Exchange/Ion Sorption Process (U. S. Bureau of Reclamation Formalism)

Cost estimation was made of a scale up of the ion exchange /ion sorption process using the Bureau of Reclamation (BOR) cost estimate model[1] (Lindsay Evans and Jim Miller internal Sandia Report June 2004). This was done because the BOR model is an accepted model in the industry. This approach lacked the fine detail of the other estimate. The ion exchange desalination approach, while more expensive than accepted Reverse Osmosis technology, may be viable in areas there the disposal costs are already high and where an alternative process may be appropriate due to the isolation of the CBM wells. The approach taken for the cost estimation through the BOR formalism and a brief description of the BOR formalism are briefly presented. Results are presented in tabular form for two cases: one with chemical regeneration and one with thermal and chemical regeneration of the Permutite and Hydrotalcite. Costs with chemical generation alone are approximately $3.75/100gal ($.16/BBl) and with chemical and thermal regeneration is$2.34/1000gal ($ .10/bbl). The TDS of the produced water associated with these cost estimates is approximately 3000. These results are presented in Figures 1using chemical regeneration and Figure 2 using thermal regeneration as well as chemical regeneration.

Summary (Approach Taken for Preliminary Cost Estimation)

- Used the Bureau of Reclamation cost estimate model to derive system costs
- Best case conditions for evaluating each system
- Systems evaluated for similar conditions (i.e., same type of BW (brackish water), same plant capacity and similar operating constraints)
- Evaluate a 5 MGD (5 x 10^6 gallons/day) plant treating BW similar to the Tularosa Basin water
- Waste disposal not considered unless specifically mentioned
- Waste disposal expected to be similar for all options

Bureau of Reclamation's Water Treatment Estimation Routine (WaTER)[1]

- WaTER is a cost estimation model developed in the late 90's for water treatment processes that is based on plant capacity and a given water condition
- Adapted from the U.S. EPA 1979 report Estimating Water Treatment Costs, Vol.2, Cost Curves Applicable to 200 mgd Treatment Plants (EPA-600/2-79-1626, August 1979)

- Update costs to current dollars using either Engineering News Record (ENR) or Bureau of Labor Statistics (BLS) cost indices

- System sizing calculations based on user input parameters

- Estimates unit water cost based on annual O&M (operation and maintenance) and capital costs for a given interest rate over a defined project life

1 - Water Treatment Estimation Routine (WaTER), Water Desalination Research & Development Program Report No. 43, U.S. Department of the Interior.
Bureau of Reclamation Technical Service Center, Environmental Resources Services, Denver Colorado, August 1999

Figure 1

DESAL System Layout and Cost Summary Using Chemical Regeneration

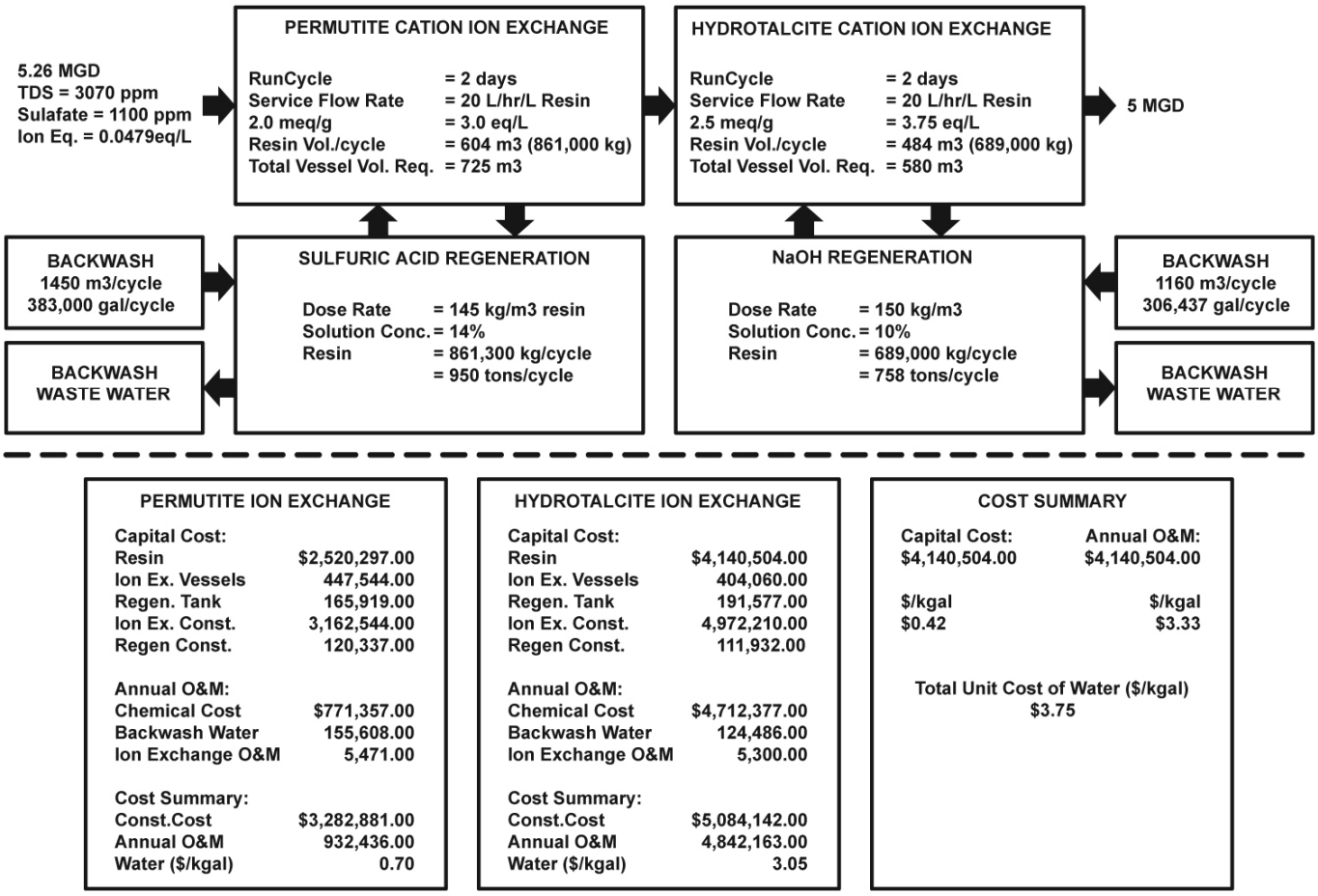
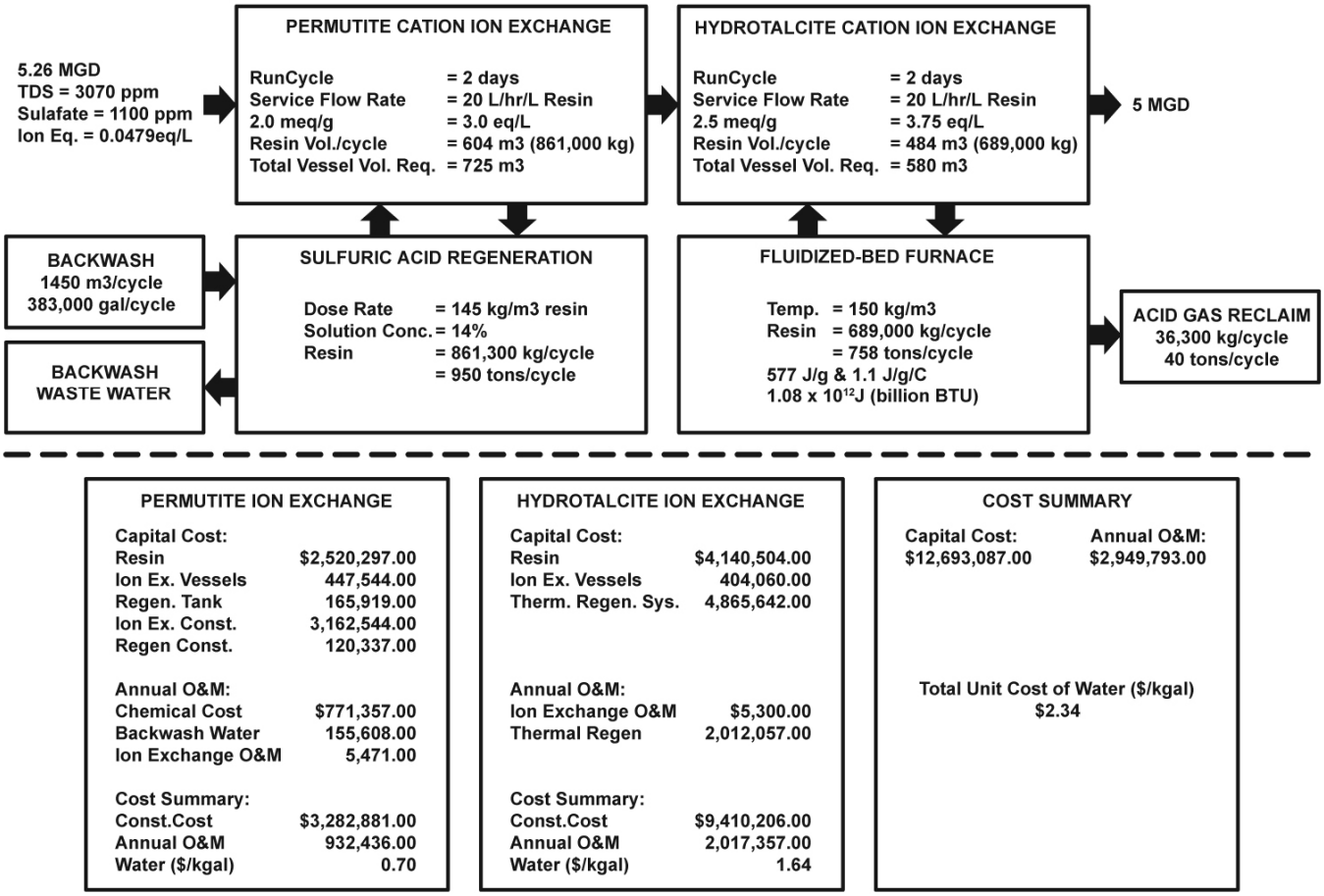


Figure 2

DESAL System Layout and Cost Summary Using Chemical and Thermal Regeneration



Comment on Comparison of the Preliminary Predictions of Both Models

There is a large disparity between the two estimates that cannot be reconciled at this time. It is our opinion that the predictions of the BOR model are low and perhaps the formalism is more suited for membrane processes rather than a process that takes a raw material, almost from the mine. The other prediction, the in house generated formalism preceding this section, is rather high such as the ion exchange capacities. On the other hand, the in-house generated model made a more thorough, exhaustive investigation of the raw material processing. Little is known about these materials and assumptions of the Sandia-developed model seemed to be made on the conservative side. Finally, this report is more in the nature of a progress report, not a final report.

Rangeland Improvement
(New Mexico State University Agricultural Experiment Station, Farmington, NM)

Beneficial uses for CBM-treated waters (e. g. stock tank, agriculture, rangeland improvement, wildlife refuge, cooling water for power plants, oilfield operations, etc) are being examined. The water treated will be made available for agricultural, industrial, and ecological interests initially in the Four Corners and Raton area.

The very first step was to find out what seedlings would be appropriate in the arid southwest climate which was accomplished earlier. The next step being accomplished is to water a matrix of seedlings with produced water on a spot basis (not steady state watering) to sprout the seedlings. The watering is only to get them started. The degree of germination and the soil characteristics (especially the sodium absorption ratio and the electrical conductivity) is to make sure the soil was not harmed. The BLM has approved this temporary watering. Use of desalinated produced water on these seedlings with corresponding lower TDS would further minimize chances for soil disruption

Two metrics of soil damage are soil conductivities (EC) greater than 15 and sodium absorption ratios (SAR's) of greater than 25. Watering with produced water has the potential of greatly enhancing both of these values. These quantities for the CBM produced water itself are far higher than the metrics for conductivity and the sodium absorption ratio mentioned above. On the one hand the soil is in effect a buffer and it turns out that these quantities for the soil itself do not appear to increase greatly. On the other hand the quantities end up below the value represented by the metrics above.

Tables 1, 2 and 3 show the relevant parameters for watering the seedlings with ~5,000 and ~10,000 TDS produced water on Williams Production Company land. Table 1 indicated amount of produced water, Table 2 indicates produced water parameters and Table 3 shows the soil parameters both before and after watering. Figure 1a shows the results of some of the planting in the fall of 2003. The sprouting is encouraging.

Tables 4, 5, and 6 show the relevant parameters for watering the seedlings with ~5000 and ~10,000 TDS produced water on Conocophillips land. Table 4 indicates the amount of produced water, Table 5 indicates produced water parameters and Table 6 shows the soil parameters before and after watering.

Figures 1a and 1b show some of the sprouting of the seedlings. The results are generally encouraging. Table 1 indicates the varieties of grasses planted. In both cases the conductivity and Sodium absorption ratio (SAR) values of the soil are within reasonable limits. For the the Conocophillips planting and watering, the conductivity and SAR values increased only slightly, in spite of the relatively high TDS of the produced water.

Table 1:Williams Prod Rosa 159-A Produced Water Schedule Fall 2003

Date	Amount of Produced Water Applied		
8-13-03		1.12 in	160 bar
8-19-03		1.12 in	160 bar
9-17-03		1.12 in	160 bar
9-23-03		1.12 in	160 bar
Total		4.48 in	640 bar

Table 2: Produced Water Analysis for W. Rosa 159-A Fall 2003

Date	pH	TDS mg/l	SAR	EC (mmhos/cm)
8-19-03	8.5	5440	71.1	16.1
9-17-03	8.0	10682	122.4	17.4
AV.	8.25	8061	96.7	16.8

Table3: Produced Water Williams 159-A (Soil) Fall 2003

	pH	EC (mmhos/cm)	Ca (ppm)	Mg (ppm)	Na (ppm)	SAR	Tex
Before Sample	7.32	3.39	291	66.8	533	7.32	loam
After Sample	7.53	5.12	341	79.7	725	9.17	loam
Spring Sample	7.86	2.52	36	6.8	540	21.6	Silt loam

Table 4: Williams Prod Rosa 159-A Produced Water Schedule Fall 2003

Date	Amount of Produced Water Applied		
8-13-03		1.12 in	160 bar
8-19-03		1.12 in	160 bar
9-17-03		1.12 in	160 bar
9-23-03		1.12 in	160 bar
Total		4.48 in	640 bar

Table 5: Produced Water Analysis for W. Rosa 159-A Fall 2003

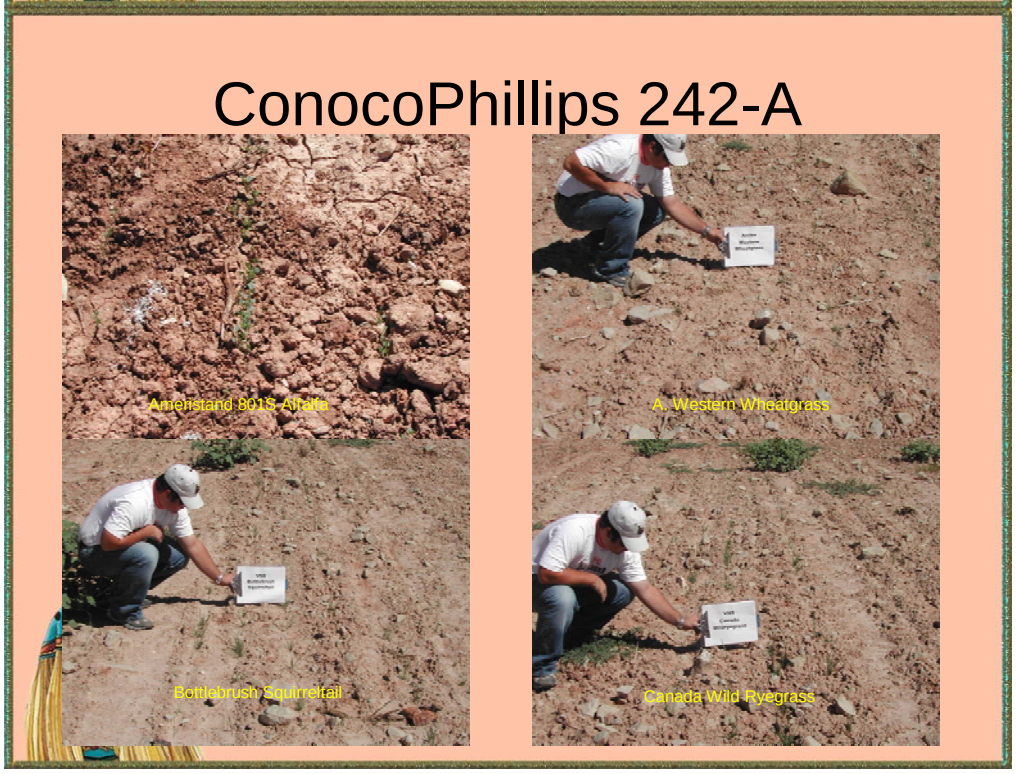
Date	pH	TDS mg/l	SAR	EC (mmhos/cm)
8-19-03	8.5	5440	71.1	16.1
9-17-03	8.0	10682	122.4	17.4
AV.	8.25	8061	96.7	16.8

Table 6: Produced Water ConocoPhillips 242-A Soil, 2004

	pH	EC (mmhos/cm)	Ca (ppm)	Mg (ppm)	Na (ppm)	SAR	Tex
Before Sample	7.67	3.37	324	75	422	5.49	loam
After Sample	7.76	3.59	282	61	526	7.4	loam

Table 7: Varieties Planted

Arriba Western Wheatgrass	Chief Inter. Wheatgrass	Luna Pubsc. Wheatgrass	Hy Crest Crested Wheatgrass
Canada Wild Ryegrass	Bozoisky Russian Wild Ryegrass	Critana Thickspike Wheatgrass	Bottle Brush Squirreltail
Redondo Arizona Fescue	Paloma Indian Ricegrass	Anatone Bluebunch Wheatgrass	Junegrass
Four-wing Saltbush	Covar Sheep Fescue	San Luiz Slender Wheatgrass	Needle and Threadgrass



Figures and 1a and 1b

Figure 1a-Results of Planting Seedlings at Williams, Fall 2003Figure 1b-Results of Planting Seedlings at Conoco Phillips, Spring 2004

Section 2: A Portion of the Work to be Done this Following Year

An Electro Chemical Process for Removal of both Organic Contaminants and Total Dissolved/Suspended Solids (Alpha Omega Environmental Inc)

Sandia is contracting with Alpha Omega Environmental Inc in the second year of the project to test an electro chemical process to both remove organics and dissolved solids. A "scale-up" R&D unit will test the ability of Vapor Ion Plasma & Ion-Separation Technology to agglomerate, "electro-coalesce" and remove both suspended and dissolved solids (TSS & TDS) from water. A bench-scale flow system diagram from the manufacturer is shown in Figure 3.

A 30 gallon recycling /contact tank is filled with produced water from a hydrocarbon producing well, probably a coal bed methane well. The brackish water will be saturated with ionized peroxides, hydroxides, and single oxygen ions from a cell, creating a large number active, reactant gas molecules in the water filled tank. The vapor ion reactants are air generated and agglomerate the dissolved and suspended solids (both organics and inorganics) into large particulate clusters, colloidal coagulations, and other electrically active solids.

The electrically active agglomerated solids and ionized water particulates then gravity flow to a cell where the coagulated inorganics, carbonates, and clustered organic/inorganic complexes are electro-precipitated by adjustable and "reverse polarity" direct current on the anode/cathode plates of the cell. Ion-tagged agglomerated solids are attracted to the cell plates for collection. They are discharged by polarity reversal.

The partially treated water flows to a second recirculation tank where additional ionized reactants from air are injected into the water during recirculation. The addition of these "second stage" ionized gas reactants results in increased removal efficiency of TDS & TSS particulate agglomerations.

The initial stages are strongly oxidizing and may remove organics as well as ions from the feed water. This combines ion removal with what is considered a very necessary pretreatment step, removal of organics. **The oxidation of organic material and the ion removal efficiency is a critical question in the use of this technique.**

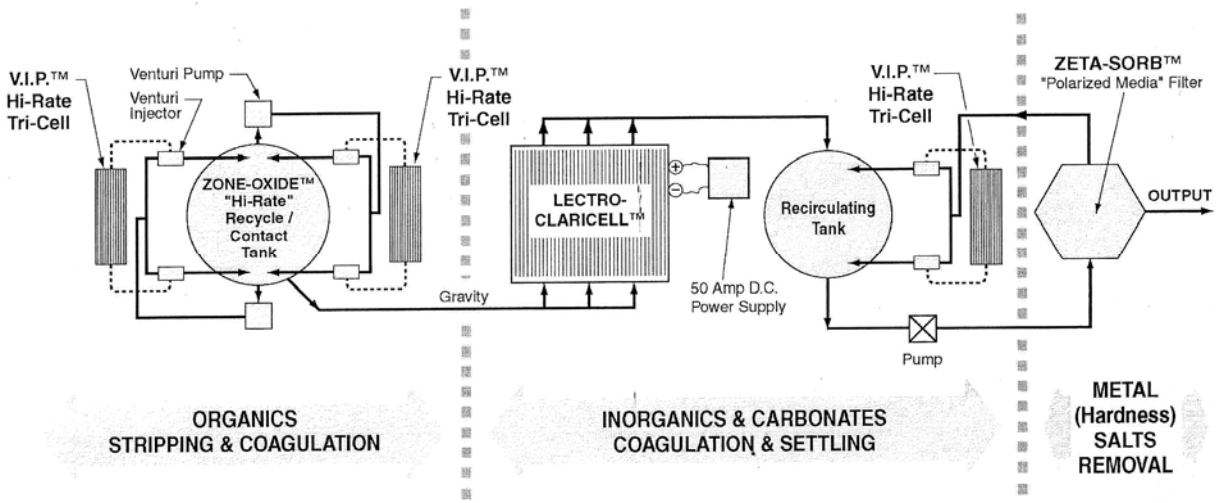
A portion of the recirculation water is separated and conducted to the final polishing (ultra) filter where additional TDS & TSS are removed. Here the water goes through a

D.C. activated "polarized" mechanical and electro-ion filtration stage that provides final removal of the reacted, ion tagged, agglomerated solids from the water.

The process may be expected to remove as much as 30-50% of the TDS as well as the TSS. The removal rate would be sufficient to allow the treated water to be used for rangeland applications. This is to be investigated.

Figure 1 Bench Scale Flow Diagram

Alpha Omega Electro Chemical Desalination Process



Capacitive Deionization
(Biosource, Inc.)

Preliminary contractual arrangements are being made with Biosource Inc. to obtain the use of a Capacitive Deionization Unit for laboratory testing for a limited time period. The unit is centered around a multi layer capacitor.

The electric double layer capacitor is made from alternating electrodes of activated carbon in a salt solution. Activated carbon is conductive and has enormous surface area. Carbons with areas up to 3000 meters/gram are available. When a voltage is applied to this system, enormous capacitance results. The dielectric is a minutely thin layer of water that exists between the conductive surface and the absorbed ions As long as the charging voltage does not exceed the so called Nernst potential for electrochemistry to occur, ions in the salt solution absorb electrostatically to the charged surface. Some carbons provide as much as 150 Farads capacitance per gram. That is a big number. In contrast, film type capacitors are typically measured in pico Farads.

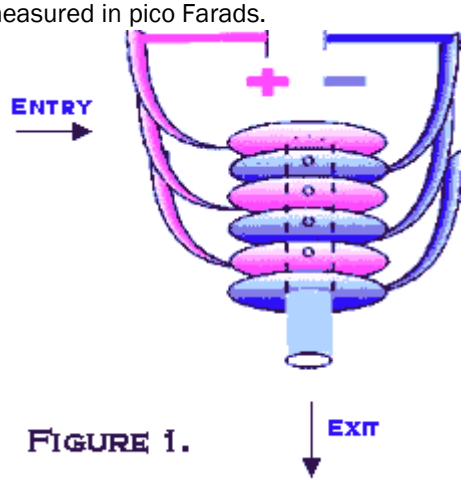


FIGURE 1.

The flow through capacitor is simply a capacitor of the electric double layer type designed to provide a flow path for water. Due to the capacitance, a very strong field gradient exists right at the conductive surface. This allows for design of filters with short flow channels and virtually no pressure drop. The ionic contaminants are pulled perpendicular to the flow path, down into the carbon. Any geometry with facing electrodes will do, including spiral wound, stacked disk, flat plate, or bundles of polygonal electrodes. Figure 1 shows a typical, stacked disk configuration.

Upon applying a DC voltage, ionic contaminants electrostatically absorb to the conductive high surface area carbon, with an equivalent amount of electronic charge. The flow through capacitor holds a charge and stores energy when disconnected from the power source, just like an ordinary capacitor.

The flow through capacitor is analogous to ion exchange. To put it another way, an ion exchange resin is also a capacitor. The only difference is that the solid support charge is a fixed ionic charge. The electronic charge of the flow through capacitor is not fixed. It can be turned on and off, or modulated electronically. The FTC is regenerated by short circuiting its leads through a load. This neutralizes the charge, and releases the absorbed contaminants into a concentrated waste stream, shown in Figure 2.

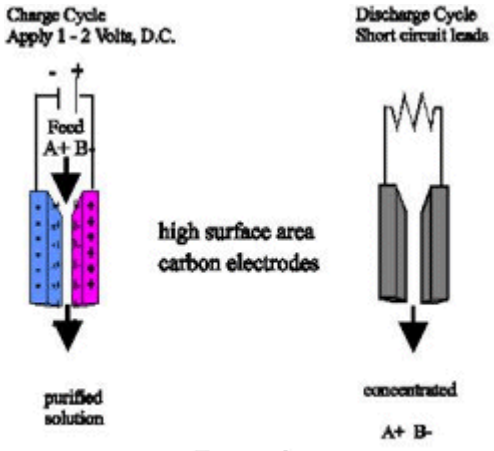


FIGURE 2.

Simultaneously, stored energy is released as DC current. The ability to turn the surface charge off electronically allows for chemical free regeneration. Waste water is simply the bed volume. In fact, the waste water can be less than bed volume by the simple artifice of saving the waste stream. This can be re-introduced on subsequent discharge cycles in order to concentrate it further. Saturated Gypsum has been supersaturated this way. The supersaturated solution was triggered to precipitate with a slight thermal shock, in order to recover a solid waste product.

To prevent fouling, the polarity of the flow through capacitor electrodes can be reversed every charge cycle. This tends to drive off foulants that might tend to favorably attract on one polarity electrode. The solid surfaces are "alive" and operate differently than pushing water through a static membrane. Relatively inert ions such as Na, K, Li, Cs, Mg, Ca, Sr, NO3, SO4, Cl, Al, BO4, PO4 etc., reversibly and electrostatically absorb to the carbon surface. Electrochemically active ions, such as copper, do not absorb electrostatically to the carbon, but tend to plate out on the carbon. In this case, the metals can be etched off with acid or base in order to regenerate the capacitor. This is no worse than ion exchange, and may prove to be more stochiometric, as opposed to the excess required by ion exchange thermodynamics. A further advantage is that metals seem to be preferred against background ions. It is also possible that the high voltage gradient of the carbon surface can be used to electrochemically destroy absorbed organic molecules or to sterilize microbes.

Nano Filtration for Pretreating CBM and Oilfield Produced Water
(Western Environmental)

Unsolved Problem/Future Work

There must be more rigorous organic analysis for each membrane process. Moreover, the final produced water will require a stripping of any hydrogen sulfide prior to agricultural uses. (**Oilfield** produced water was used here not CBM water which often does not contain perceptible amounts of hydrogen sulfide) A combination of organics and hydrogen sulfide could eventually foul the next membrane say nano filtration or reverse osmosis foul. Even though organics were not detectable downstream from the ultra filtration membrane, if the system is run long enough run long enough into a tighter membrane, such as nano filtration or reverse osmosis, some fouling could result in the downstream membrane. This NGOTP project will participate in this next stage.

Project Participation in Other Technologies

Preliminary contractual arrangements are being made to have a CBM sample tested by a newer technology named **Zero Liquid Discharge Desalination**. This is the name of a proprietary novel application/combination of a new electrodylasis membrane desalination fostered by the University of South Technology and ZDD Corporation. This technology has been applied to seawater and will be extended to terrestrial sources including a source of CBM produced water.

Sandia will be a principal contributor on produced water initiatives in the **ZERO NET Initiative**, a water/energy sustainability program in the State of New Mexico. EPRI is cooperating with the DOE National Laboratories to create a federal water/energy nexus research program. Public Service Company of New Mexico is also a major player on this program. Independent of this program, Sandia and Public Service Company of New Mexico have been collaborating and exchanging data on the use and treatment of produced water in the San Juan Basin for well over a year.