April 28, 2000

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Dear Sir or Madam,

As specified in the Milestones Reporting Requirements Checklist for Contract No. DE-AC26-99BC15221, "Treatment of Produced Oil and Gas waters with Surfactant-Modified Zeolite," enclosed please find five copies of the semi-annual Progress Report for the period 28 September 1999 – 30 April 2000.

Sincerely,

Lynn E. Katz
Assistant Professor and Project Manager

cc: Nancy Comstock

CONTRACT TITLE: Treatment of Produced Oil and Gas Waters with Surfactant-Modified Zeolite

REPORT TYPE: Semi-Annual Progress

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Lynn E. Katz
Project Manager

Abstract

Whereas most water produced from onshore oil and gas operations is disposed via reinjection, some waters, such as those from offshore production platforms, coastal production, and some onshore wells, must be treated to remove organic constituents before the water is discharged. Current methods for reducing residual free phases and dissolved organic carbon are not always fully effective in meeting regulatory limits. In addition, cost, space requirements, and ease of use are important factors in any treatment system. Surfactant-modified zeolite (SMZ) has been used successfully to treat contaminated ground water for organic and inorganic constituents. This research will use laboratory batch and column studies to design a field system that will be used to treat produced waters to reduce dissolved and free-phase organic constituents. The system will be designed to operate simply and to have low operating costs. Methods for regeneration of the spent zeolite will also be tested, as will the treatment system at a field production site in the final project task.

Research over the past six months has focused on the selection and characterization of the surfactant modified zeolite and the produced waters. The zeolite to be used in this work has been obtained from St. Cloud Mine near Winston, New Mexico. The primary surfactant to be used to modify the zeolite is hexadecyltrimethylammonium (HDTMA). Current contacts for selection, and ultimately, testing of example oil field waters include Phillips Petroleum Corp. (offshore location, Gulf of Mexico); Amoco production in Farmington, New Mexico; Devon Energy in Houston, Texas, and the New Mexico Bureau of Mines and Mineral Resources (mining operators for coal bed waters from the Farmington area).

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Introduction

Oil and gas produced waters are the largest waste-stream sources in the United States. These waters contain many pollutants, including substantially high concentrations of volatile organic compounds (VOCs) benzene, toluene, ethylbenzene, and m-, o-, and p-xylenes (collectively known as BTEX). While reinjection is the most commonly used method of wastewater management for onshore facilities, it is not always feasible because of geographic and cost considerations. In the case of offshore waters, discharge is the most practical and cost-effective means of treatment. In these situations it may be desirable, and often necessary from a regulatory viewpoint, to treat produced water before discharge to remove organic compounds. It also may be feasible to treat waters that slightly exceed regulatory limits for re-use in arid or drought-prone areas, rather than losing them to re-injection.

Surfactant-modified zeolite (SMZ) has been shown to be effective at removal of both organic and inorganic constituents in aqueous systems. The objectives of this study include the use of SMZ in laboratory batch and column studies to design a field-scale treatment system for the removal of BTEX from oil-field produced water. Methods for regeneration of spent SMZ will also be tested to determine the cost-effectiveness of the process. Pre- and post-treatment needs will also be studied. In the final phase of the research, a pilot plant system will be tested.

Results and Discussion

Task 1. Laboratory Batch Testing

1. Selection of co-produced waters and SMZ to be used in batch and column testing

Literature review has revealed that produced waters from various sources differ greatly in composition. Produced water can originate during natural gas generation, coal production, and from both onshore and offshore oil production facilities. Each of these sources creates characteristic produced waters, but even within the same source-type, the wastewater can differ substantially. The following tables demonstrate the variance that exists both between different source-types and within each source-type. The large variation in produced water characteristics indicates that selection of example oil-field waters will be important and may affect the field-scale treatment system to be designed later in the project.

Produced Water Characteristics

Natural Gas Produced Waters - "Low TDS"

	Units	Gas - Sample 1	Gas - Sample 2	Average
pH	Units	7.6	7.4	7.5
TDS	mg/L	8,620	9,350	8,985
Oil & Grease	mg/L	86.7	97.6	92.15
Benzene	mg/L	2.6	3.2	2.9
Toluene	mg/L	5.8	4.9	5.35
Ethylbenzene	mg/L	<.500	<.500	<0.500
Xylene	mg/L	5.0	3.4	4.2

Note: Samples 1 and 2 were taken from produced waters in Wyoming.

Reference: Lawrence, A. W., J. A. Miller, D. L. Miller, T. D. Hayes *Regional Assessment of Produced Water Treatment and Disposal Practices and Research Needs* SPE 029729. 1995.

Produced Waters from Onshore Oil Production - "High TDS"

	Units	Snyder Field, TX Sample 1	Snyder Field, TX Sample 2	Average
pH	Units	8.23	8.08	8.155
TDS	mg/L	54,085	56,102	55,093
Oil & Grease	mg/L	Not Reported	Not Reported	-
Benzene	mg/L	12.3	11.5	11.9
Toluene	mg/L	6.46	4.25	5.355
Ethylbenzene	mg/L	1.91	1.04	1.475
Xylene	mg/L	0.827	0.541	0.7

Permian Basin oil-producing region samples taken from Snyder oil field - Howard County in Texas
Both samples analyzed September 3, 1998, (unpublished data)

Produced Waters from Offshore Oil Production

	Units	Krisna Oil Platform - Java Sea, Indonesia	Cinta A Oil Platform - Java Sea, Indonesia	Cinta B Oil Platform - Java Sea, Indonesia	Average
pH	Units	Not Reported	Not Reported	Not Reported	-
TDS	mg/L	Not Reported	Not Reported	Not Reported	-
Oil & Grease	mg/L	15	15	15	15
Benzene	mg/L	4.4	3.0	2.7	3.4
Toluene	mg/L	1.2	1.1	1.3	1.2
Ethylbenzene	mg/L	0.11	0.10	0.11	0.11
Xylene	mg/L	0.86	0.73	0.74	0.78

Reference: Smith, J.P., A.O. Tyler, M.C. Rymell, H. Sidharta *Environmental Impact of Produced Waters in the Java Sea, Indonesia* SPE 37002. 1996.

Selection of Example Oil-Field Waters

This task has been delayed due to the difficulties we encountered in finalizing a subcontracting plan with Los Alamos National Laboratory (LANL). This difficulty has recently been resolved by allowing LANL to obtain funding directly from DOE. Funding for LANL is anticipated to become available in mid-May.

Current contacts for selection, and ultimately, testing of example oil field waters include Phillips Petroleum Corp. (offshore location, Gulf of Mexico); Amoco production in Farmington, New Mexico; Devon Energy in Houston, Texas, and the New Mexico Bureau of Mines and Mineral Resources (mining operators for coal bed waters from the Farmington area). Work is continuing on improving small producer contacts in east Texas, which would be the most accessible location for a long-term supplier of larger volumes of waters. An emphasis is being made on testing a variety of produced waters of various compositions, as well as searching for low salinity waters because they tend to be more often reused for watering of stock or for irrigation.

Selection and Laboratory Testing of SMZ Properties

Most of the laboratory testing of SMZ has been conducted at New Mexico Institute of Technology (NMIT) under the supervision of co-PI R. Bowman. However, testing of hydraulic conductivity for the material is currently being performed at the University of Texas at Austin (UT).

- SMZ Background

  The chemistry of natural zeolite is similar to that of smectite clays, although zeolites do not display shrink-swell characteristics. Total cation exchange capacities (CEC) for natural zeolites have been found to range from 250 to 3000 meq/kg and total surface areas up to 800 m^2/g have been measured (Ming and Mumpton, 1989). Natural zeolites have not shown significant affinity for adsorption of dissolved organic compounds; however, once treated with cationic surfactants, these dissolved organics are readily sorbed. This surfactant-modified zeolite (SMZ) is still able to sorb heavy metals and sorption of target organics not greatly affected by the presence of other organics (Neel and Bowman, 1992). Because of its ready availability and low cost, hexadecyltrimethylammonium (HDTMA) has been chosen as the primary surfactant to be used in this study.

- Properties and Preparation of SMZ

  The SMZ being used for the project originated from the St. Cloud Mine near Winston, New Mexico. With XRD analysis, the natural zeolite was determined to consist of 74% clinoptilolite, 5% smectite, 10% quartz plus cristobalite, 10% feldspar, and 1% illite. Using a method modified from that of Ming and Dixon, the internal CEC for this zeolite was found to be 800 meq/kg and the external CEC to be 100 meq/kg (Li and Bowman, 1997; Ming and Dixon, 1987). Through nitrogen adsorption, the external surface area was 15.7 m^2/g (Sullivan et al., 1997). Porosity for zeolite aggregates was 0.6 and dry bulk density was 1 kg/L.

  An existing batch plant at the St. Cloud mine was used to produce the SMZ. Raw zeolite and an HDTMA solution were quantitatively added to a mixing chamber. The mixture was further homogenized and fed by a screw-auger into a rotating dryer heated by a propane burner. The mixture exited the dryer onto a conveyor belt leading to a 1-m^3 "supersack" storage container. Two sizes of SMZ were produced in bulk at the mine. The smaller 14-40 mesh aggregate (1.4-0.4 mm) has undergone hydraulic conductivity testing to determine the material's permeability and will be used in the batch and column studies. The larger 8-14 mesh SMZ (2.4-1.4 mm) is currently undergoing hydraulic conductivity testing described below. If possible, the smaller aggregate will be used because of its larger surface area and correspondingly larger adsorption capacity.

- Hydraulic Conductivity Testing

  Constant head permeability tests are being conducted to determine the hydraulic conductivity (K) for both the 14-40 and 8-14 SMZ at different sample densities. The hydraulic conductivity of the SMZ must be determined because

this value will have a substantial impact on the hydraulics of the column reactors. The constant head permeability test apparatus is being used because the hydraulic conductivity of the SMZ was considered to be too large to obtain accurate results with other equipment. Results have been obtained for two densities of the 14-40 SMZ and tests are currently being performed for the 8-14 material. For each density of the 14-40 SMZ, multiple tests were run at different hydraulic gradients. As shown in Figures 1 and 2 below, a limiting value for the hydraulic conductivity was reached in every test. When the SMZ had a density of 0.905 g/cm^3, the hydraulic conductivity approached 0.11 cm/sec. With a density of 0.961 g/cm^3, the hydraulic conductivity neared 0.080 cm/sec.

Figure 1: Experimental Values of Hydraulic Conductivity for SMZ Density = 0.905 g/cm^3

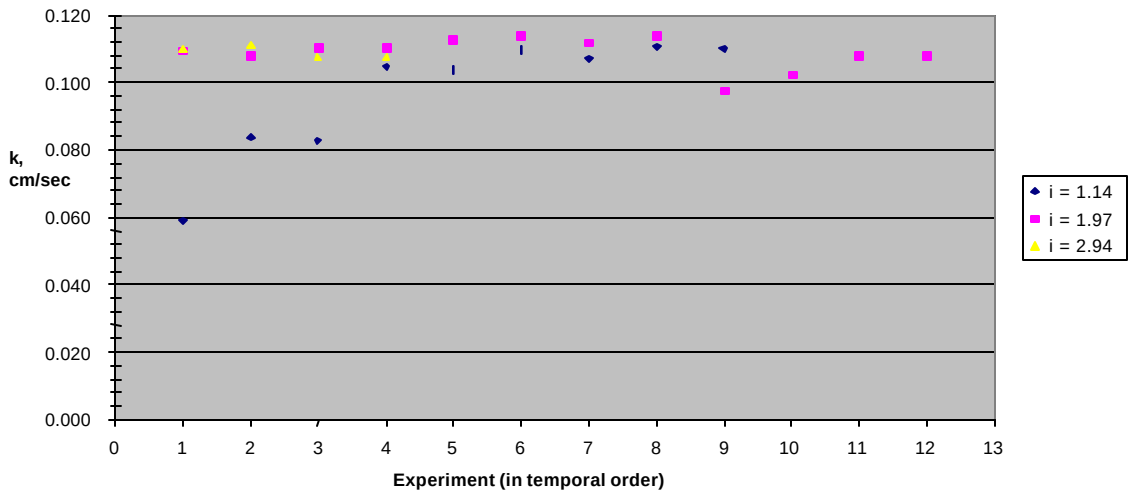
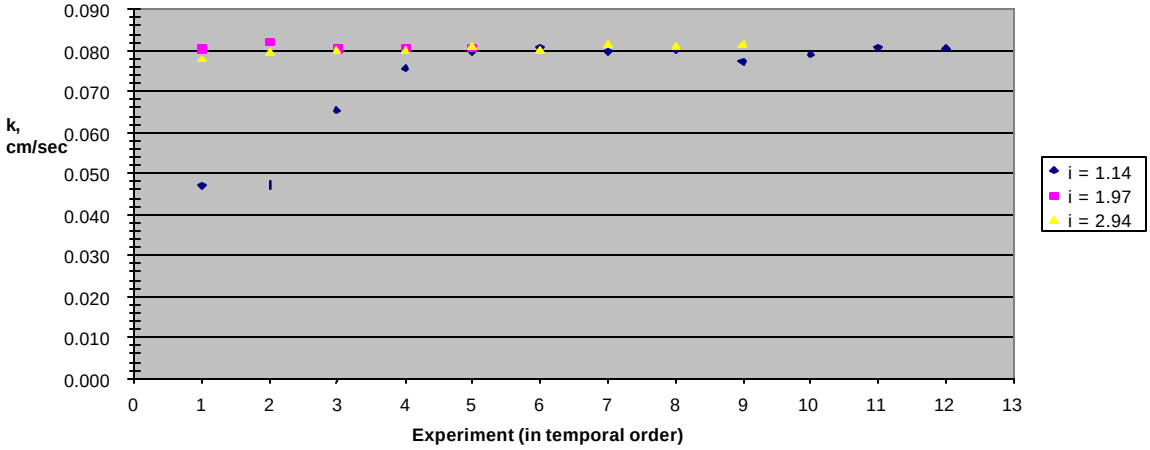


Figure 2: Experimental Values of Hydraulic Conductivity for SMZ Density = 0.961 g/cm^3



2. Demonstration that organic constituents are removed from selected oil-field waters in batch systems.

Research addressing this milestone has focused on the development of analytical methods for BTEX that will allow analysis of a large number of samples. As a result, we have elected to use a headspace/gas chromatography method for BTEX analysis. A new headspace sampler was purchased for this project by the University of Texas and a gas chromatographic method has been developed based on a previous method used in our laboratories.

- Analytical Method
  The Tekmar headspace analyzer 7000 maintains the samples at a temperature of 80°C and the injection line at 115°C. Samples from the headspace analyzer flow into a Hewlett Packard 5890A Gas Chromatograph containing a RESTEK 30m, 0.53 mm id, DB-3 column. The oven temperature initially remains at 40°C for one minute and is then ramped at 20°C/minute until a temperature of 85°C is reached. Ramping continues at 0.5^{o}C/minute until a temperature of 90°C is achieved. This temperature, 90°C, is then held for one minute. A Flame Ionization Detector is used for detection of the analyzed samples and this is held at a temperature of 250°C. Standard curves have been prepared using this method and we are currently assessing the method detection limits.

Conclusions

The major accomplishments to date are the selection of the SMZ to be used in the produced water adsorption experiments, measurement of hydraulic properties, and analytical method development. Selection of the produced water to be used in this work will be completed during the next quarter. Delays in this aspect of the work, due to contract negotiations, have limited our ability to make progress on subsequent milestones.

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