Hydrophobic Membranes for Removal of Organic Impurities in Production Water

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Summary: We propose to develop hydrophobic aerogel technology to remove organic compounds from drilling and production waters on oil production platforms. We envision the aerogel will be used in a granular or membrane form, be in direct contact with the waste water, removing the offending organic compounds, yielding a water that can be disposed of easily, economically, and in compliance with environmental regulations. The aerogel will be design in such a way that the organic can be extracted, allowing reuse of the aerogel. This technology will be available for use on drilling platforms, but also will be suitable to land-based production and refinery applications, as well as DOE contaminated water issues.

Statement of the Problem: Offshore oil production in the US faces environmental regulations dealing with disposal of drilling and production waters. A large percentage of these waters cannot be returned directly into the surrounding environment because of their high concentrations of free oil, dissolved organics and metals, such as crude oil and drilling fluids.[1] Treatment technology is available that removes the free oil, but it is slow and not efficient. New methods that are more efficient have less space demands, and better address dissolved organics, are necessary because of the volume of the produced water and the current cost of disposal.

Application and Benefits of the New Technology: Produced water is an integral part of oil production. Worldwide daily production in 1999 was 210 million barrels, three times the oil production. About 50% the water is re-injected and the other 50% discharged. Most discharged water requires treatment because of the concentrations of free oil, heavy metals and dissolved organics (such as BTX, carboxylic acids, and polynuclear aromatics). Treatment and disposal in the US is estimated to cost $0.6/bbl.[2] Unless treatment can reduce the content of organics to an environmentally acceptable level, the water cannot be disposed of into the ocean, and must be transported from the platform. The aim of this project is to develop a commercially viable adsorbing or membrane material that can be used in remediation and removal of organic materials, such as dissolved organics, in high-ion content aqueous media, rendering a reusable or releasable water stream. The primary focus will be on the treatment and removal of dissolved organics, and possibly free oil, in production waters. Other applications will include oil-spill and fuel-spill clean-up and refinery stream clean-up. LLNL will provide the membrane technology and the Industrial Partner will provide the scale-up, large scale testing towards commercial application. The end result is a cost effective technology that allows for direct treatment of contaminated water at the source, whether production or other, reducing the need for alternative costly disposal methods.

Background Technology: Current methods of treatment of include skimmer vessels, plate separators, gas flotation systems and static hydrocyclones. These can remove free-oil impurities to some extent but are limited for dissolved organics. New technologies, such as advanced gas strippers, biotreatment, adsorption, wet air oxidation and membranes show promise towards a more complete treatment process. In particular, adsorption and membrane technologies show superior potential because of the possible variety and flexibility of the materials used in the processes. New materials are being developed that can be tailored to target specific problems, such as removal of free oil, dissolved organics, or a specific metal.[3]

Technical Approach: The aim of this project is to develop a system to separate organics from water. The approach is to use membranes or adsorbants to do the separation and use in a continuous flow system that can be installed at a remote location such as a drilling platform. The materials to be used for this are inorganic/organic composites known as hydrophobic sol-gels or aerogels. These materials already have been shown in laboratory testing to be effective for separations of oil and organics from water. The challenge here is to bring this material technology to commercial use as membranes or adsorbants in real, remote applications such as ocean located drilling platforms.

Materials Development. Aerogels are very porous light materials made from sol-gels. They have densities that are less than 0.5 g/ml, very high surface areas and porosities that approach 95^{+}%. As a result, aerogels can be very good absorbers. Through classical aerogel processing techniques, aerogels can be made with a variety of densities, porosities and surface areas to fill many applications. Recently elucidated synthesis techniques also allow variation in the chemical properties of the aerogels. From this synthesis approach, we have recently developed new hydrophobic silica sol-gel materials that can effectively separate organics from water through adsorption. A specific material that has been very effective is a hydrophobic aerogel formed through incorporating a fluorinated material into the silica sol-gel matrix. This material has been shown, tested as a powder in the laboratory, to absorb crude oil from a salt-water mixture up to 237 times its weight.[4] It has been demonstrated as a membrane to continuously separate diesel fuel from water.[5] It has also been shown to greatly outperform activated carbon in absorbing organic solvents from water such as trichlorethylene.[6] The value of this material is that after adsorption, the oil can be extracted and the aerogel can be reused. The material can also be formed into a membrane, and that it can be used in a continuous flow process, separating the organic from the aqueous phase. As a result, aerogels that absorb crude oil, diesel, and organics in the presence of an aqueous phase are now attainable.

Laboratory Examination—Intrinsic Adsorption Properties. The above developments have been made in the laboratory, testing organic separations for demonstration of proof-of-principle only. For examples, the crude oils and solvents were tested in batch form with powdered materials; continuous separation was performed with a hand-fabricated device. For the first phase of this proposal, the hydrophobic aerogels will need further laboratory testing using target organics typically found in production waters, as well water mixtures of high saline and other salt concentrations, such as K, Ca and Mg. The performance of the aerogels will be first tested in a batch application as powdered materials to establish capacity and fundamental kinetics of adsorption. For example, surrogate salt-water solutions with target organics at various levels (most likely ppm and ppb) will be mixed together and the amount of removal will be measured on the solutions by typical organic environmental analysis techniques such as gas chromatography-mass spectrometry. The solids will also be analyzed to determine mass balances. Once the surrogate solutions are tested, real production waters with high saline and ion concentrations will then be tested to establish capacity and kinetics of adsorption. Particular detail will be given to adsorption suppression effects by ions and other components, if any are observed. In addition, because production waters differ, depending upon location in reservoirs and types of produced oils, variations in adsorption based on water origin will also be determined.

Laboratory Examination–Flow Systems. Once the intrinsic adsorption properties are determined, and optimum conditions are established from that data, the hydrophobic aerogels will be tested in flow systems, both granular and membrane form. The first will be testing the aerogel in granular form in a packed bed. This will establish the use of the material in common treatment hardware such as ion-exchange columns or activated carbon canisters. Again, absorption capacities, flow conditions and mass balances will be determined with surrogate solutions and real production waters. This will result in parameters necessary for scale-up.

The other testing will be using the aerogel as a membrane. The hydrophobic aerogel can be formed into various shapes, including thin, flat surfaces. It also can be used to coat porous devices, such as carbon sponge and NASA tiles. These surfaces will be tested for permeation barriers for separating organics from water. Again, parameters necessary for scale-up will be determined as well a competition effects from ions and other impurities. The potential commercial use of the material as a ceramic membrane will be determined from these experiments.

Scale-up and Commercialization. The true utilization of these new adsorbing materials will be in the commercialization, as either column adsorber or a membrane. These particular approaches invested into will be determined by laboratory testing above. To illustrate this, assume the material will be used in the granular form as an exchange column packing. A large-scale column system pilot plant will be designed, potentially utilizing water purification system hardware. For example, most oil fields have water retention and treatment systems after settling tanks. With modifications of the hardware, field tests could be performed on the hydrophobic aerogels with minimum cost and effort. This should lead to information allowing engineering and design of commercializable systems.

Another aspect of the technology that will be needed is scale-up of production of the hydrophobic aerogel. There are companies that produce aerogels on a commercial large-scale basis. Although these companies have specific formulations, the IPAC office at LLNL is working with these companies on producing aerogels from custom formulas on a large scale. The hydrophobic aerogels above should fall into this realm.

1. S. Patin, Environmental Impact of Offshore Oil and Gas Industry, EcoMonitoring Publishing, http://www.offshore-environment.com/discharges.html. 2. Z. Khatib, P. Verbeek, Society of Petroleum Engineers, paper 73853, (2002), SPE, Richardson TX. 3. D. Hadfield, Environmental Protection Bulletin, 33, 13-24 (1994). 4. J. G. Reynolds, P. R. Coronado, L. W. Hrubesh, Energy Sources, 23(9): 831–843 (2001); 5. J. G. Reynolds, P. R. Coronado, L. W. Hrubesh, LLNL Invention Disclosure (2001). 6. P. R. Coronado, L. W. Hrubesh, J. H. Satcher, Jr., J. Non-Cryst. Solids, 285 (1–3): 328–332 (2001).

Why DOE Funding is Required. The current state of this technology is in the laboratory discovery phase. A material has been identified to potentially solve a costly and environmentally significant problem, but that needs to be proven for the exact application. Until this is accomplished, industrial investment is unlikely because of the risk. However, if the material is successful, industrial participation is necessary to make the material commercially viable for use. The Industrial Partner has issued a letter of commitment of participation. This material, if commercialized, has a much broader application, addressing some environmental clean-up issues at many DOE sites.

Critical Decision Points: Verify aerogels can efficiently absorb or separate target dissolved organic compounds relevant to production waters; verify aerogels can operate in real conditions without fouling; determine deployment method as adsorbant or membrane or both; verify aerogels are physically strong enough; scale-up of aerogel production.

Breakdown of First Year Activities–Accomplishments, Milestones, and Changes to Proposal

Proposed: 1) Synthesis of hydrophobic aerogels for testing. Accomplished: 1). Synthesized several different hydrophobic and hydrophilic aerogels by different methods ready for testing (30%, 10%, and 1.5 % by weight formulation propyl-CF_3 hydrophobic aerogel, hot methanol extraction; 30 wt % propyl-CF_3 hydrophobic aerogel CO_2 extraction; 30 wt % ethyl-NH_2 hydrophilic aerogel CO_2 extraction, heptadecafluoro hydrophobic aerogel CO_2 extraction).

Proposed: 2) Measurement of powdered hydrophobic aerogel adsorption properties with surrogate solutions. Accomplished: 2) Parameters for absorption for 30% propyl-CF_3 hydrophobic aerogel, ethyl-NH_2 hydrophilic aerogel were measured on surrogate solutions at different conditions and were compared to granulated activated carbon. Several trends were observed depending upon the organic compound absorbed, including that the absorption activity parallels the K_{ow} of the target compound. The surrogate solutions consisted of benzene, toluene, xylene, phenols, and naphthenic acids. Surrogate waters containing biocides and lubricants were not yet tested. These are proprietary materials that are still being obtained from the industrial sponsor. One talk at a professional meeting was presented and one manuscript to a technical journal was submitted for publication on these results. Although the absorption data is good at higher concentrations, the uncertainty in the data at lower concentrations was sufficient that we are changing to column testing for a wider range of parameters.

Proposed: 3) Selection of production water for testing. Accomplished: 3) Type of production water based on our targets of interest has been selected in concert with the Industrial Sponsor. Full compositional analysis has been and will continue to be supplied by the Industrial Sponsor when the waters are shipped.

Proposed: 4) Determination of intrinsic adsorption kinetics for surrogate water solutions. Accomplished: 4) Kinetic parameters for absorption for 30% propyl-CF_3 hydrophobic aerogel were measured under selected conditions. Initial results at higher concentrations of targets, indicate the adsorption kinetics are relatively fast. However, at lower concentrations, the statistical scatter in the data was sufficient that good kinetic parameters could not be obtained. The issue appears to be the high hydrophobicity of the aerogels inhibits good contact with the aqueous solutions containing the target compounds when working in batch conditions. Because batch studies are necessary for intrinsic kinetics, we are redesigning the batch reactor system to accommodate lower concentration experiments. Testing will resume within 2 months.

Proposed: 5) Obtaining production water preserved (special handling) for testing. Accomplished: 5) Enough production waters from Wyoming and Gulf of Mexico have been obtained from Industrial Sponsor to do initial testing. North Sea productions water will be available when we are ready to test them. Because production waters separate quickly, only small amounts are obtained at a given time, and the composition can be variable. These will be provided on an as needed basis.

Proposed: 6) Measurement of adsorption properties with production water. Accomplished: 6) Pending column testing of surrogate solutions. Not yet time for milestone. However, substantial analytical progress has been made in adapting UV-vis and purge and trap GC-MS, and LC-MS techniques required to analyze complex mixtures, necessary for analysis of production water treatments.

Proposed: 7) Comparison of capacities and kinetics of surrogate solutions and selected production water. Accomplished: 7) Pending development of column testing. Not yet time for milestone.

Changes in Milestones and Deliverables:

1) Column testing of surrogate solution milestone was proposed for second year of work. Because the batch testing was not as useable as thought when proposed, see 4) above, this milestone is being shifted to this year. Columns have been purchased and flow hardware has been constructed. Testing will commence when synthesis of larger batch of 30% propyl-CF_3 hydrophobic aerogel is completed.

2) Determining the intrinsic adsorption kinetics for surrogate water solutions, 4) above, Measurement of adsorption properties with production water, 6) above, and Comparison of capacities and kinetics of surrogate solutions and selected production water, 7) above, have been postponed because the batch testing method under the current experimental design is being modified. This is being reconfigured and the effort will commence within 2 months, and will extend into the second year. However, Column testing of surrogate solution and production water, scheduled for next year, has been started this first year.

Publications and Presentations

Hydrophobic Aerogels for Removal of Organic Impurities in Aqueous Phase by Adam H. Love, M. Leslie Carman, Paul R. Coronado and John G. Reynolds presented at 13^{th} Symposium on Separation Science in Energy Applications, Gatlinburg, TN in October 2003.

Engineering surface functional groups on silica aerogel for enhanced cleanup of organics from produced water by Adam H. Love, M. Leslie Hanna and John G. Reynolds. Manuscript submitted for publication in Nov 2003 to *Separation Science and Technology.*