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STRATEGIES FOR PRODUCED WATER HANDLING IN NEW MEXICO

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 with

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Abstract

New Mexico produces about 454 million barrels of brine annually as a byproduct of oil and gas operations. As a result of the state's diminishing water resources, there is much attention focused on the possibilities of economically utilizing this brine for beneficial uses. The New Mexico Petroleum Recovery Research Center (PRRC) at New Mexico Tech (NM Tech) is the research arm of the petroleum industry in New Mexico. The four focus areas of produced water studies at the PRRC/NM Tech to be discussed are (1) *Water shutoff and conformance improvement*: We develop strategies for diagnosing and solving excess water production problems.

Particular emphasis is on strategically placed gels to reduce water production and channeling through fractures and other high-permeability features; (2) *Inventory mapping*: In this project, produced water data, including chemistry information, are being collected from various oil and gas companies to establish a summary dataset of produced water. We will make the data available to the public via a website with GIS capability; this is a joint effort with the New Mexico Oil Conservation Division (NMOCD); (3) *Optimal process identification*: Five existing water treatment processes have been proposed to the Industrial Advisory Board for this project. Two of the five processes will be chosen and pilot plants will be constructed in Lea County, New Mexico as a joint effort with the Sandia National Laboratories. In another arm of this project, together with industrial partners, we are examining optimal pretreatment methods of coalbed methane (CBM) produced water in the San Juan area; (4) *Brine treatment innovations*: This long-term study includes testing various brine treatment concepts in the laboratory. We are currently evaluating different clay membranes for their ability to reject salt. This is a joint effort with University of Missouri-Rolla.

Introduction

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Water Shutoff and Conformance Improvement

On average in the United States, more than seven barrels of water are produced for each barrel of oil. Worldwide, an average of three barrels of water is produced for each barrel of oil. The annual cost of disposing of this water is estimated to be 5-10 billion dollars in the US and around 40 billion dollars worldwide.

Many different causes of excess water production exist (see Fig. 1). Each of these problems requires a different approach to find the optimum solution. Therefore, to achieve a high success rate when treating water production problems, the nature of the problem must first be correctly identified. Many different materials and methods can be used to attack excess water production problems. Generally, these methods can be categorized as chemical or mechanical (see Table 1). Each of these methods may work very well for certain types of problems but are usually ineffective for other types of problems. Again, for effective treatment, the nature of the problem must first be correctly identified.

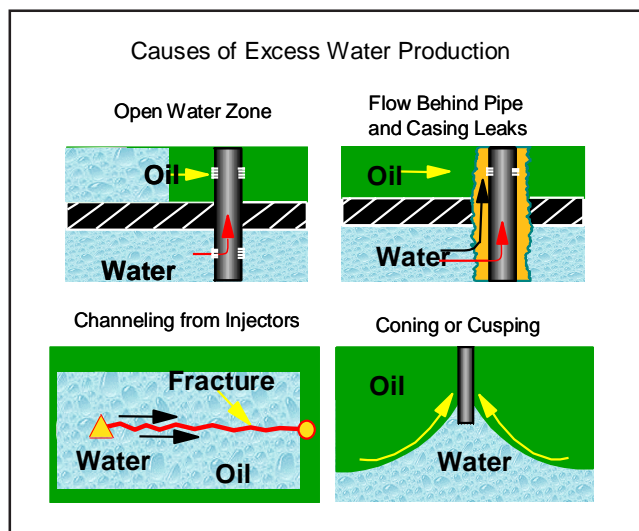


Figure 1. Causes of Excess Water Production

Table 1. Water Shutoff Materials and Methods

CHEMICAL	MECHANICAL
cement, sand, calcium carbonate	packers, bridge plugs
gels, resins	well abandonment, infill drilling
foams, emulsions, particulates, precipitates, microorganisms	pattern flow control
polymer/mobility-control floods	horizontal wells

Logically, identification of the excess water production problem should be performed before attempting a water shutoff treatment. Unfortunately, many (perhaps most) oil and gas producers do not properly diagnose their water production problems. Consequently, attempted water shutoff treatments frequently have low success rates. Several reasons exist for the inadequate diagnosis of excess water production problems. First, operators often do not feel that they have the time or money to perform the diagnosis, especially on marginal wells with high water cuts. Second, uncertainty exists about which diagnostic methods should be applied first, where perhaps 30 different diagnostic methods could be used. In the absence of a cost-effective methodology for diagnosing water production problems, many operators opt to perform no diagnosis. Third, many engineers incorrectly believe that one method (e.g., cement) will solve all water production problems or that only one type of water production problem (e.g., three-dimensional coning) exists. Finally, some service companies incorrectly encourage a belief that a “magic-bullet” method exists that will solve many or all types of water production problems.

We propose a straightforward strategy for diagnosing and solving excess water production problems. The strategy advocates that the easiest problems should be attacked first and diagnosis of water production problems should begin with information already at hand.

Conventional methods (e.g., cement, mechanical devices) normally should be applied first to treat the easiest problems—that is, casing leaks and flow behind pipe where cement can be placed effectively and for unfractured wells where impermeable barriers separate water and hydrocarbon zones. Gelant

treatments normally are the best option for casing leaks and flow behind-pipe with flow restrictions that prevent effective cement placement. Both gels and preformed gels have been successfully applied to treat hydraulic or natural fractures that connect to an aquifer. Treatments with preformed gels normally are the best option for faults or fractures crossing a deviated or horizontal well, for a single fracture causing channeling between wells, or for a natural fracture system that allows channeling between wells. Gel treatments should not be used to treat the most difficult problems—that is, three-dimensional coning, cusping, or channeling through strata with crossflow.

A key element of the proposed strategy is to look for and solve the easiest problems before attempting to attack the more difficult problems. In many cases, engineers initially assumed that three-dimensional coning caused the problem, whereas a small amount of subsequent diagnosis and analysis revealed the true source of water production was either flow behind pipe or “two-dimensional coning” through a fracture. This knowledge could have substantially reduced the cost of solving the problem. Also, by correctly identifying the problem first, the most appropriate method can be identified and the probability of successfully treating the problem increases significantly.

To help implement the proposed strategy, the following questions should be addressed in the order listed:

- 1) Is there a problem?
- 2) Is the problem caused by leaks or flow behind pipe?
- 3) Is the problem caused by fractures or fracture-like features?
- 4) Is the matrix-flow problem compounded by crossflow?

Further information of the study can be obtained at <http://baervan.nmt.edu/randy/> or contact Randy Seright at (randy@prrc.nmt.edu or 505-835-5571).

Inventory mapping

At present, New Mexico produces about 454 million barrels of water annually as a byproduct of oil and gas production. Some of this water is reinjected at the site, but much of it goes through flowlines to handling or separating facilities. As a result, produced water is almost always present in oil pipelines and handling facilities, and can cause a number of

problems. Although produced water in itself is not necessarily corrosive, in the presence of other gases and chemicals, it can become highly corrosive. This corrosivity is one of the major causes of leaks and spills in the oilfield. Obtaining data on the produced water quality to make decisions on a variety of issues from corrosion management to treatment decisions is very difficult. Produced water can also have high concentrations of undesirable substances such as salts and organic chemicals. Spills of produced water may cause surface and groundwater damage, and a spill of produced water requires reports to be filed with regulatory agencies. The necessary data for these reports, things like nearby wells or water bodies, depth to groundwater, and others, can be difficult and time-consuming to find for both the reporting operator and the regulatory agency in charge of verification. Information on location of water handling facilities, wellhead protection areas, surface water resources, or other vulnerable resources is often scattered among various offices and locations, yet this information is becoming increasingly important.

This NETL/DOE-funded project, "New Mexico Water and Infrastructure Data System (NM WAIDS)," seeks to alleviate a number of produced water-related issues in southeast New Mexico. The project is for the design and implementation of a Geographic Information System (GIS) and integral tools that will provide operators and regulators with necessary data and useful information to help them make management and regulatory decisions.

The major components of this system are: 1) databases on produced water quality, cultural data, and groundwater data, oil pipeline and infrastructure data, and corrosion information; 2) a web site capable of displaying produced water and infrastructure data in a Geographic Information System or accessing some of the data by text-based queries; 3) a fuzzy logic-based site risk assessment tool that can be used to help assess the relative seriousness of a spill of produced water based on proximity to water sources and other parameters deemed essential by the NM OCD; and 4) a corrosion management toolkit that will provide operators with data and information on produced waters that will aid them in deciding how to address corrosion issues.

The various parts of NM WAIDS will be integrated into a website with a user-friendly interface that will provide access to previously difficult-to-attain data and information. The benefits of this

project will be multiple. Savings in time and labor needed to look up data for regulatory purposes will be significant. An even greater benefit will be realized by operators who implement best practices corrosion management plans based on information provided by the program.

Work on the project to date includes:

1. Creation of a water quality database with a web-based data entry system,
2. Acquisition of groundwater data from the New Mexico Office of the State Engineer, including chloride content and TDS,
3. Creation of a scale prediction tool that uses two common scaling indices (Stiff-Davis and Otto-Thomson) to predict the likelihood of scaling, again with a web-based interface,
4. Creation of a map-based fuzzy logic tool that enables the user to select a location and assess the relative level of spill response based on current OCD criteria,
5. Compilation of corrosion information from operators in the southeast New Mexico area,
6. Qualitative assessment of produced water from various formations regarding corrosivity,
7. Efforts at corrosion education in both the northwest and southeast parts of New Mexico through workshops and operator visits.

Future work on this project will include the development of a web and GIS interface for the information collected in this effort, improvement of the fuzzy logic risk assessment tool, mapping of produced and groundwater quality where sufficient data is available, improvements to the produced water quality data entry and querying system, and compilation of an online corrosion toolkit. The preliminary results are shown in Figure 2. This study is a joint effort between PRRC/NM Tech and OCD. Further information can be obtained from Martha Cather at (martha@prrc.nmt.edu, 505-835-5685).

Optimal Process Identification

A consortium of New Mexico oil and gas producers is partnering with New Mexico Tech, New Mexico State University and Sandia National Laboratories to examine, compare, and optimize several produced oilfield brine pretreatment processes. One project is being undertaken in northwestern New Mexico, targeting coalbed methane produced water, and one in the southeast for the oilfields of Lea County. Ultimately, commercial implementation

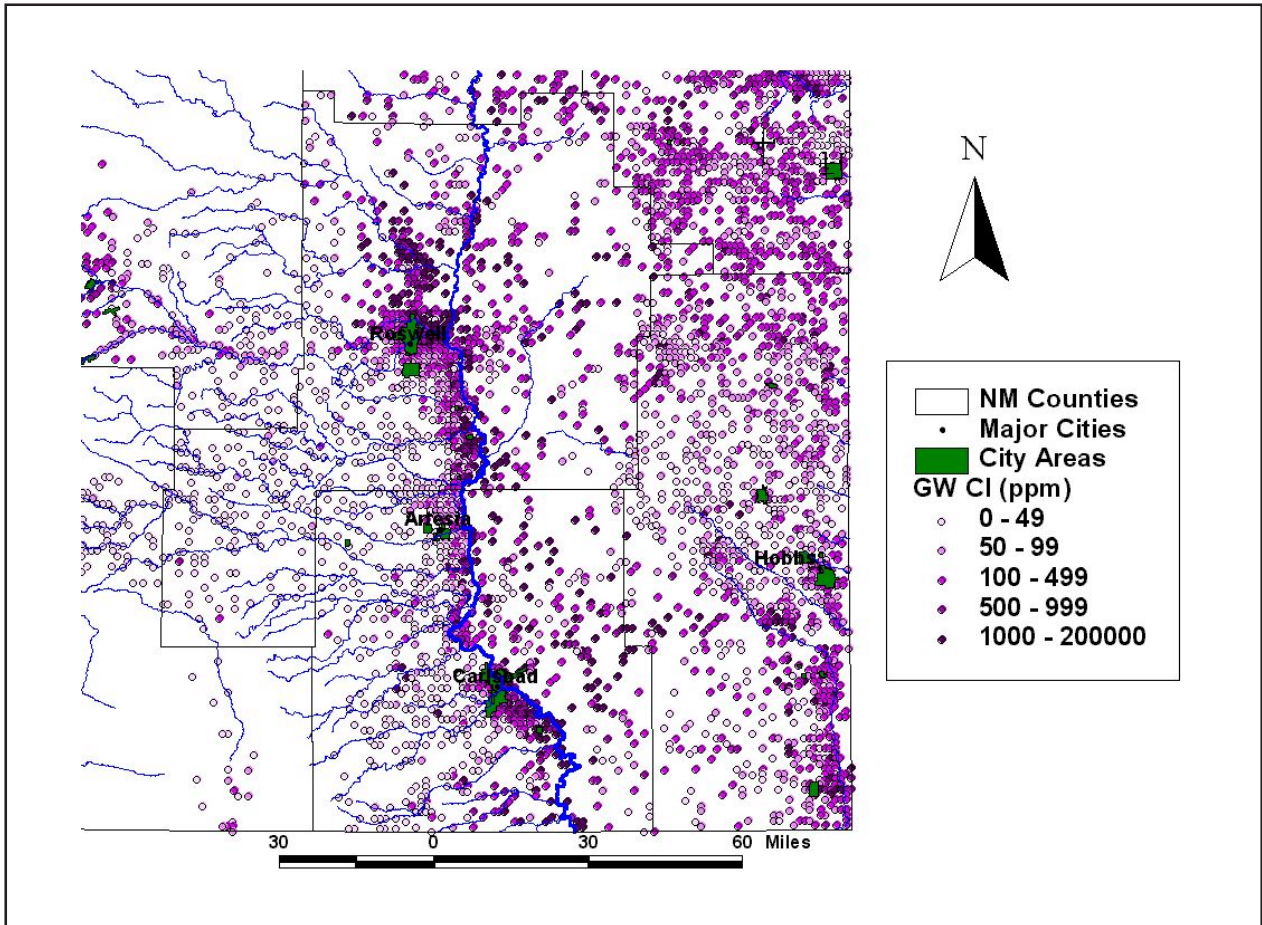


Figure 2. Chlorides distribution data in New Mexico.

pathways will be established for application of the best of these processes worldwide in the oil and gas industry.

As drinking water supplies diminish, produced water from oil and gas operations is increasingly being seen as a potential asset instead of an environmental liability. If cheap, high-volume desalination of oilfield brines and coalbed methane produced waters could provide water for industrial and agricultural use, an environmental liability would turn into a marketable asset. Equally important, the burden on freshwater aquifers could be relieved.

Coalbed methane production is especially problematic. Since water is usually not reinjected into CBM producing formations, unprecedented volumes of produced water, resulting from the rapid growth of CBM production in northwestern New Mexico, will be generated requiring treatment, surface discharge, or deep subsurface disposal. In basins where fresh water aquifers, springs, or wells are hydraulically connected to producing coal bed zones, CBM production could seriously deplete valuable groundwater resources. In other basins, where CBM produced water quality can range from 10,000 to 100,000 mg/l total dissolved solids, inappropriate water treatment and disposal could contaminate soil and surface and groundwater. CBM operators are facing increasing environmental problems and expense in disposing of produced water: these problems potentially could result in inhibiting the flow of natural gas production.

New Mexico, Texas, Oklahoma, and parts of the Rocky Mountain region, are all arid oil-producing areas. In the second arm of this project, southeast New Mexico is being used as a model to identify the cost/benefit ratios of oilfield brine reclamation; first on a pilot scale, then on a large scale.

Reclaiming oilfield brine for beneficial use could prove economical worldwide, if relevant performance factors can be worked out first at the pilot scale. For New Mexico, benefits could include lower oilfield operating costs and an exportable technology for regions where similar operations exist. A new industry would be brought to the state. Most importantly, drawdown of useable groundwater could drop significantly, conserving our shrinking water supplies.

Most reclamation methods for oilfield produced water require pretreatment of water to remove hydrocarbons, solids, and gases. These pretreated brines then undergo reverse osmosis, involving passage through a membrane (or other newer

desalination processes) to be converted for beneficial reuse.

Biofouling of membranes by organic material has historically been responsible for the largest number of failures in reverse osmosis desalination processes. Thus, effective pretreatment of oilfield-produced brines is necessary to prevent biofouling and scaling of reverse osmosis membranes.

New Mexico's industry experts and researchers from three of the state's research institutes will join in a bilateral approach in the north and south, in a) an integral approach to CBM produced water management focused on the San Juan and Raton Basins and b) in seeking out the best means of pretreating produced waters before these undergo desalination, with a pilot area in Lea County.

In the San Juan and Raton Basins project, the team's capabilities in water modeling and surface and subsurface contaminant and transport will be used to assess CBM produced water generation impacts on water in connected aquifers or surface water systems and surface and subsurface disposal options. Several different pretreatment techniques will be evaluated for removing the organic content of the CBM water, which can range to 100 ppm or higher. Newly developed water treatment techniques for anionic and cationic contaminants such as salts and metals may also be applied, depending on the contents of the CBM produced water.

In the Lea County project, several different methods for pretreating oilfield-produced brine will first be examined and evaluated by past field performance, further laboratory work, and/or actual field trials. The most promising pretreatment protocols will be tested in a producing oilfield under varying conditions of brine salinities and residual oil. Each pretreatment process will be evaluated for its economics, effectiveness, and environmental impact. When this work is completed, a pilot test, from pretreatment through desalination for two separate pretreatment processes, will be developed and performed.

Factors used in evaluating pretreatment protocols will include:

- Cost
- Hydrocarbon and solids removal percentage as a function of particle size
- Hydrocarbon recovery
- Collection of methane
- Hydrogen sulfide stripping and disposal

- Throughput potential
- Projected/actual down time to change filters and replenish chemicals, etc.
- Inhibition of scale buildup such as calcium carbonate and calcium sulfate
- Control of silica deposition, if appropriate
- Boron removal, if appropriate
- Disposal of by-product streams/solids
- Nature of by-product solids, such as naturally occurring materials (NORM)
- Success in various field trials

It is realized that not all processes as presented are self-contained enough to meet all these criteria. One or more components of a given process could be combined with components from other processes if the combination looks promising. The five pretreatment processes are called Processes 1, 2, 3, 4 and 5 respectively for simplicity. Three processes are not self-contained (Processes 3, 4 and 5). However, these processes appear promising enough to merit further consideration and augmentation if appropriate. Three of the pretreatments below (1, 2, and 4) have already been tested in the field for their effectiveness in addressing the issues of oilfield produced water or closely related issues and objectives. One pretreatment process emphasizes chemical process primarily and filters secondarily; one primarily emphasizes filters and secondarily focuses on chemical treatment; one utilizes bacteria; one is a new product, which must be examined more thoroughly; and the other two employ hydrocarbon extraction technology. The methods to be investigated include, but will not be limited to, those listed below.

Pretreatment Process 1 emphasizes chemical processes supplemented by filtration and has undergone some field trials with oilfield brine, including a trial in southeast New Mexico. The order of the stages was varied to optimize the protocol and, in this case, a minimization of residual hydrocarbons was achieved and simultaneously water with very low total dissolved solids was produced. With this protocol, the input brine stream passes through a settling tank into a micro air flotation system. After the settling tank, the brine enters an advanced oxidation system where it undergoes aeration, centrifuging, and oil-water separation. The input brine stream then passes through an additional advanced oxidation stage into a pair of filter banks. After the filter banks, the oilfield brine enters the reverse osmosis process. This approach lowers the

TDS of the oilfield brine in the New Mexico to well below expectations and merits additional evaluation. However, the TDS of the brines treated in the previous field trial were less than 25,000 TDS, which is considerably lower than the brines that are the focus of the proposed project, which are of major interest to area producers.

Pretreatment Process 2 has undergone field trials with oilfield brine in California. Parts of the pretreatment protocol have undergone field trials elsewhere. This system can be briefly described as a filter-based system utilizing cartridge filters, ultra filters, and nano filtration. The pH of the oilfield brine entering the initial brine feed tank is adjusted with sulfuric acid, and CO₂, with H₂S being “scrubbed.” The brine is then fed through prefilter cartridges to an ultra filter system (with recirculation). Antiscalent is added after this process. The brine stream is run through a nano filtration system prior to the reverse osmosis process. In this case, further CO₂ removal and boron removal are made in conjunction with the reverse osmosis system. An ion exchange system is available for even more boron removal, which may be necessary in some cases. Adjustments of the protocol can be (and have been) made to suit particular conditions of the input brine. This process appears to have some proven degree of flexibility. The cartridge filters, which are relatively inexpensive, bear much of the burden of the pretreatment. The team that used this approach has encountered many of the common and uncommon problems in pretreatment of oilfield brines and has experience in dealing successfully with the inevitable contingencies. An initial concern with the application of this process in high salinity oilfield produced water is the amount of acid that will be required to adjust pH of these highly buffered brines.

Pretreatment Process 3 differs from the other schemes in that it utilizes biological reactions to pretreat the brine. This novel approach is still under development and could ultimately include other steps to meet some of the criteria above. With this protocol, the input oilfield brine stream enters an anaerobic reactor where most of the organic material is removed along with the majority of the H₂S. Off-gas methane is collected. The brine next undergoes aerobic polishing for removal of the remaining organic material prior to entering the reverse osmosis process.

This process is under consideration because it is expected to result in a simple, inexpensive pretreatment process. This process may require additional laboratory and bench scale study and possibly augmentation. Specific questions that must be resolved include:

- Quantification of the extent of aerobic and anaerobic biodegradation, and
- Measurement of such process issues as culture acclimation under high salt conditions and sulfide stripping efficiencies.

Pretreatment Process 4 utilizes a proprietary absorbent that can reduce inlet hydrocarbon solutions with a hydrocarbon concentration as high as the 10,000 ppm range to a concentration of 5 ppm. This product has been field tested for cleanup of oily water. It is made of a polymeric material backbone and is advertised as chemically neutral, non-toxic, and reusable. Its advertised features also include but are not limited to:

- 100% hydrocarbon recovery in unaltered state by oil recovery system
- Reusable
- No waste sludge generated
- Can handle shock loads of oil in the thousands of ppm
- Low energy consumption
- Additional chemicals (for oil removal) not needed
- Advertised applications include seawater protecting an actual seawater desalination plant

This product has produced exceptional field results; thus, it is felt that a direct application to pretreating oilfield brines should be considered along with the other pretreatment processes. There is also a possibility of combining this product with other processes.

Pretreatment Process 5 uses a macroporous polymer extraction (MPPE) technology, which has been used for removing hydrocarbons from offshore produced waters. In the MPPE process, water containing hydrocarbons is passed through a column containing porous polymer beads with pore sizes of 0.1 to 10 microns that contain a specific extraction liquid. The immobilized extraction liquid removes hydrocarbon components (dispersed aliphatic compounds and polycyclic aromatic compounds) from the water. In situ generation of the extraction liquid is accomplished

periodically by stripping the hydrocarbons with low pressure steam. After the hydrocarbons are removed by the extraction liquid, the purified water can be reclaimed for beneficial use. Literature results cite the use of this process for the treatment of water produced with natural gas and condensate. These results merit the evaluation of this process in combination with other processes, especially in applications where the presence of aromatics (such as benzene, toluene, and xylene) and polycyclic aromatic hydrocarbons are of concern in the treated effluent.

The large potential market for membranes needed to reclaim CBM and oilfield produced brines is attracting the attention of the membrane industry. These projects will culminate in developing solid institutional and economic bases for the beneficial uses of desalinated brine. This study is a joint effort between SNL and PRRC/NM Tech. More information can be obtained from Mike Hightower at (mmhight@sandia.gov, 505-844-5499).

Brine treatment innovations

Some visions cannot be quickly realized. Long-term research is the key with a painstaking evaluation of possibilities, testing of theories, and end results that can be translated into practical solutions. The question of how to develop a cost-effective, portable desalination unit that can be easily applied in the oilfield has been occupying scientists for years, and promises to intrigue them for some time to come.

Reverse osmosis is a process of water purification during which the salt water, under pressure, sweeps along one side of a semi-permeable membrane (fabricated from expensive synthetic materials), causing fresh water to diffuse through the membrane, leaving behind a concentrated solution. Conventional reverse osmosis has been used since the 1950s on a large scale, but at this time, it is too capital-intensive to be used at the wellhead. The need for chemical pretreatment of the water contributes further to this high operating cost. To make reverse osmosis cost-effective for the oilfield, it is necessary to find a way to economically remove solids from produced water and make it suitable for surface disposal, fresh water aquifer recharge, drinking water, irrigation, or release to streams. Further needed is a system to precipitate the dissolved salts in produced waters from solution, without added chemicals, so that the salts can easily be removed from the system.

Conventional reverse osmosis desalination applied to the produced water from the oilfield is problematic, for the following reasons:

- Various agents in the produce water may damage the membrane or affect the reverse osmosis process. Pretreatment of the water is frequently needed, but pretreatment adds significantly to the cost.
- Conventional water treatment methods are seldom applied economically to waters more saturated than seawater. Produced water, as we have seen, can be up to six times more saturated than seawater.
- Reverse osmosis desalination of seawater often requires pressures from 800 psi to 1200 psi. Conventional reverse osmosis treatment with more concentrated brines would require much greater pressures, potentially greater than the membrane could withstand.
- The resulting waste stream from conventional reverse osmosis methods can be between 50 and 80% of the total volume treated. These waste brines are still expensive to dispose.

The principal needs in a reverse osmosis system that can be used at the wellhead are for a suitable low-cost, easily available membrane, and for an inexpensive, environmentally friendly system of solute disposal. Such a system is the target of research being undertaken jointly at PRRC and the University of Missouri-Rolla. This project aims to take current reverse osmosis techniques beyond the state-of-the-art. More information can be obtained from Robert Lee at (lee@prrc.nmt.edu, 505-835-5408).

Bentonite clay—readily available, cheap, and extensively used commercially—has been identified as a material potentially suitable for RO membranes. Clay membrane efficiency can be controlled by compaction, increasing with increasing compaction or decreasing porosity. Thus, membranes could be constructed that would allow separation of solutes from very highly saturated water without requiring unreasonable fluid pressures. The project currently underway has been working on the fabrication of clay membranes compressed enough to allow such separation, but sturdy enough to withstand the process. Progress is being made with the fabrication of membranes in various configurations and degrees of compression. In addition, data on actual water chemistry from oilfields in New Mexico have been

collected in order to target the fabrication of these membranes to specific problems.

The dissolved organics present in produced water may damage polymer membranes used in the conventional reverse osmosis process. It is believed that clay membranes should overcome this drawback. In this project, a clay membrane made of bentonite is compacted inside a specially made cross-flow experimental cell with an integral piston. Both synthetic NaCl solution and produced water are used to test the clay membrane and determine various membrane properties from the bench experiments. For produced water, the rejection rates of the ions decrease when TDS (Total Dissolved Solids) increases (Fig. 3).

It is our opinion that if a reverse osmosis waste reduction system is to be widely applicable to treatment of produced waters, the system must be able to precipitate highly soluble dissolved minerals, such as sodium chloride, as well as other less soluble dissolved minerals. Figure 4 shows the NaCl crystal distribution across the surface of the clay membrane under a microprobe scan. Efforts to increase the quantity and speed of this crystallization process are ongoing.

It is not anticipated that research results will culminate in the desired outcome—a prototype RO unit for use in the oilfield—for some time to come. This valuable research is advancing steadily with the support of statewide producers, but development of an effective prototype will require careful planning and bench testing. When such a system is realized, its applications may well extend beyond the oilfield.

Acknowledgements

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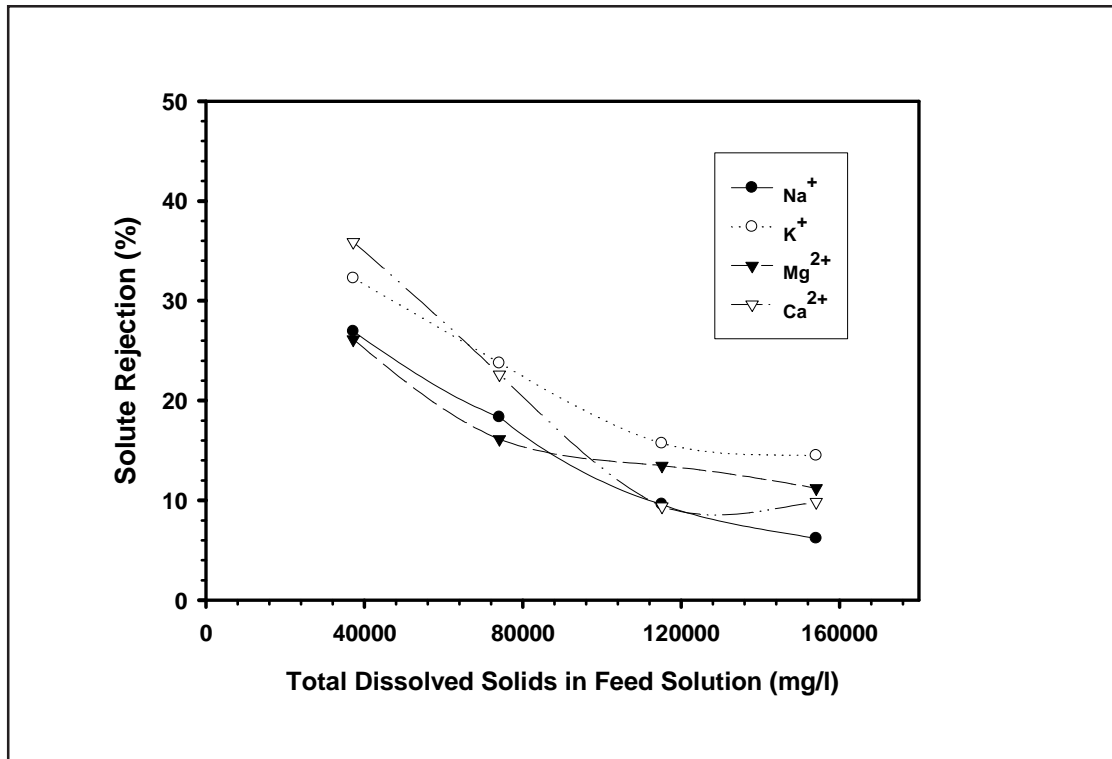


Figure 3. Solute rejection of cat ion as a function of TDS (membrane compacted to 36.1 Mpa) for produced water.

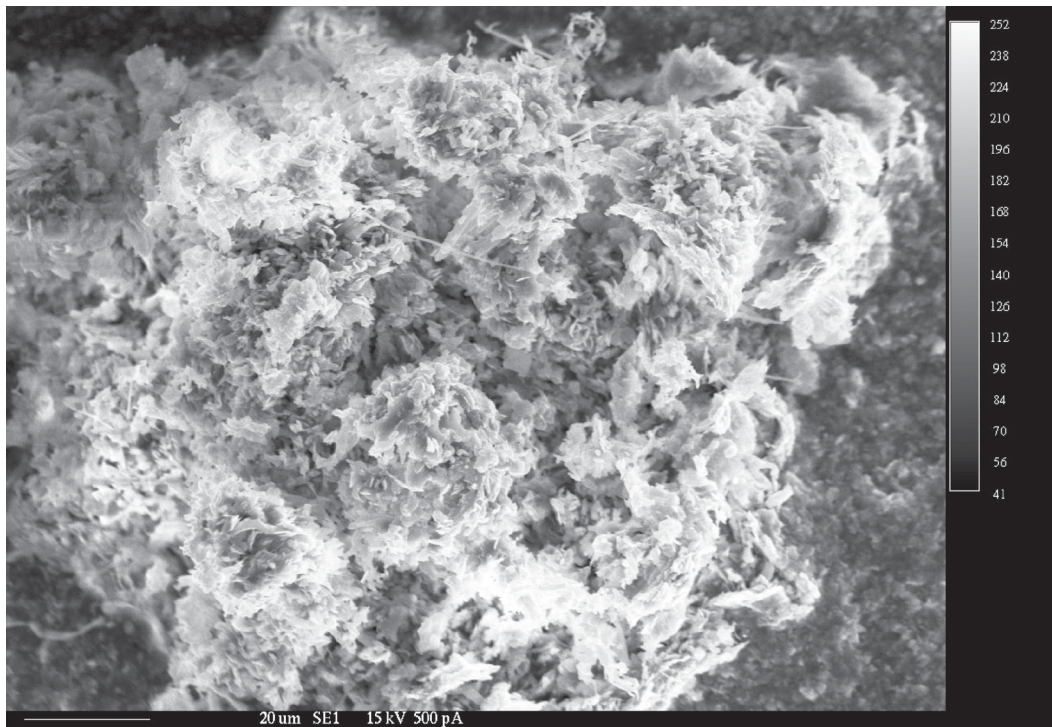


Figure 4. Microprobe scan showing distribution of NaCl crystals.