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

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Statement of Problem:

Coal Bed Methane (CBM) natural gas accounts for about 7 percent of the total natural gas production in the U.S. Spurred by increased energy needs, environmental emission advantages of natural gas, and technology advances in exploration and production, CBM production could easily double in the next 8-10 years, accounting for up to 15% of our total natural gas production. CBM production is expected to expand throughout the U.S. including the mountain west, midwest, northeast, and southeast. Today, approximately 10,000 CBM wells are operating in the U.S., but within 5-10 years as many as 100,000 additional wells could be in production.

Large volumes of water are often produced in conjunction with CBM natural gas. Wells often produce up to 400 barrels/day. CBM produced water quality ranges from nearly fresh water to 100,000 mg/l total dissolved solids. Reinjection of the CBM produced water either works against further CBM extraction, is economically unattractive, or both. Surface disposal in ponds is problematic where the water is not compatible with soils or where it may contaminate surficial aquifers. In basins where fresh water aquifers, springs, or wells are hydraulically connected to producing coal bed zones, CBM production could seriously deplete valuable ground water resources. CBM operators face increasing environmental problems and expense in disposing of produced water (from $1-$4+/ barrel in the San Juan Basin) that has the potential of severely restricting the flow of natural gas. The aggregate water volumes, and the disposal and attendant environmental problems they pose, are unprecedented. Operators relate that the problem of produced CBM water is very urgent on their agenda.

Unlike some older established oil fields, the San Juan and Raton Basins generally have relatively little infrastructure especially when compared to the Permian basin where complete gathering systems exist. Because these basins have relatively little infrastructure, treatment of produced water may have to be done on a well pad by well pad basis or gathering the produced CBM water from two or three adjacent well pads.

Comparison of New Technology With Existing Technology

Producers in the San Juan and Raton basins therefore continue to look for new, more robust, and cost-effective active or passive systems for treating CBM produced water that require less pre and post-treatment, are more compact and applicable to single or a small numbers of aggregated wells, and have lower energy and maintenance requirements. Three technologies are under investigation: capacitive deionization, ion exchange, and simple nano filtration.

An emerging treatment technology, capacitive deioization, has been identified which, in combination with a number of emerging pre-treatment options, for example, modified zoelite filtration, could become a suitable, economical, and robust treatment system for many CBM produced waters. Deionization has been used successfully for many years to purify water and is used for medical dialysis. The technology uses positively and negatively charged electrodes to attract charged ions in a liquid, such as dissolved salts, metals, and many organics to the electrodes. This concentrates the ions at the electrodes and reduces the ion concentrations in the liquid. Recent advances in manufacturing have enabled the development of large, high surface area, carbon electrodes significantly improving energy efficiency and potential for larger applications. Laboratory testing has been conducted at salinity levels near the mid-range of CBM produced water qualities. The results suggest that the technology requires less energy, is much less susceptible to organic fouling, and is more compact than equivalent RO systems. Combined with simple, low-cost pre-treatment technologies if needed, capacitive deionization could reduce the costs of CBM produced water treatment for irrigation and rangeland uses to 10-20% of the costs of RO treatment.

Another emerging treatment technology that could provide a compact, economical, robust treatment system for CBM produced water is an ion sorption method. This ion sorption system uses disposable or field regenerable media. The components of the process include: lime softening, Permutite (cation exchanger) and Hydrocalcite (an anion sponge). The cation ion exchange material Permutite is used for water softening in ion exchange resins. Permutite is amorphous aluminosilicate and is made from waterglass and alum. The Permutite exchange capacity exceeds that of clays. The anion exchange material Hydrocalcite is made as amorphous Mg/Al hydroxide. The anion exchanger sequesters anions and releases hydroxide as it crystallizes. Heating can regenerate it. This method has the potential of being more economical than the standard reverse osmosis method for desalination as well as being logistically appropriate for the limited infrastructure of these basins.

A third promising process under investigation is simply nano filtration preceded by a process to remove organic material. This simple process may be adequate to rehabilitate CBM produced waters for rangeland application. Nano filtration alone reduces the membrane pressures approximately twofold compared to reverse osmosis and is more economical.

Passive treatment systems may also have application for some CBM produced waters. For example, passing produced water through a calcium bed to improve Ca/Na ratios or using Ca-smectite/Ca-zoelite filtration could reclaim low to intermediate TDS-level produced waters by modifying the sodium adsorption ration (SAR) to a level compatible with

surface applications. These technologies will be evaluated with above technologies to identify the produced waters that can be treated passively to meet irrigation and rangeland rehabilitation uses.

Application and Benefits to Industry

The technologies above could provide desalination methods tailored for these regions. Their application could result in a necessary decrease in overall operating costs, as produced water disposal costs will be largely avoided. Management of CBM produced water in an economically and environmentally sound manner, along with efforts to provide an institutional/regulatory base for its beneficial use, will assure that producers can develop the nation's CBM resources.

The application of these technologies could result in the utilization of produced water for beneficial use, relieving increasing pressure on dwindling surface water and groundwater resources. Produced water from CBM operations are increasingly being seen as an asset rather than an environmental liability. New advances in water treatment technology would reclaim needed waters for enhanced agricultural and industrial use. This is especially true in arid areas in the west and in CBM producing regions where fresh surface and groundwater water supplies are becoming limited.

Tasks and Contributions of the Research Team

Task 1: Develop a team of national laboratory, university, producer, and resource management and environmental personnel to support and provide industry direction for this effort. (Sandia, PRRC, Industry Partners, Resource Managers)

Task 2 Determine hydrologic and chemical characteristics of the San Juan and Raton Basins with respect to CBM produced water quality ranges and constituent ranges. Identify with resource management agencies the treated water quality needed for agricultural, rangeland habitat improvement, and livestock watering beneficial uses in the San Juan and Raton Basins. (PRRC, Industry Partners, Sandia, NMSU Ag. Research Center, BLM)

Task 3: Using San Juan and Raton Basin CBM produced water (~2,000 mg/l, ~10,000 mg/l, ~24,000 mg/l TDS) evaluate the ability of combinations of pre-treatment technologies: capacitive deionization, ion sorption, passive techniques, and perhaps reverse osmosis (on a smaller scale) to meet identified, rangeland rehabilitation and livestock water standards in bench scale testing. Assess overall operational performance and costs of appropriate combinations for a range of produced waters. Bench scale system evaluations will be used as a baseline for technology cost and performance comparisons. (Sandia, NM Ag Research Center, Resource Managers, and Industry Partners)

Task 4: Based on the bench scale results in Task 3, coordinate and conduct a pilot operation on location at an industry partner site. This will include cooperation with the NM State University Agricultural Research Center at Farmington, and the BLM on use of the treated water for rangeland rehabilitation and will also include application and permit approvals needed. (Sandia, PRRC, Industry Partners, NM State Ag. Research Center, BLM)

Task 5: Extend future work to other CBM Basins.

Deliverables

Sandia requests $240K in FY04 and $290K in FY05.

FY03, First quarter FY04 Report on San Juan and Raton Basin produced water characteristics. Report baseline range rehabilitation work. Report on initial work on applying ion exchange technology to CBM produced water and initial results of investigating nano filtration for reducing the TDS of produced water. (To be delivered second quarter, FY 04).

FY04 Reports on: 1) additional lab and bench studies. Report on San Juan and Raton Basin pre-treatment and treatment technology cost and performance evaluations. Include comparisons to RO technology cost and performance. Identify lessons learned on system advantages and disadvantages and possible expected system applications.

FY05 Reports on: 1) rangeland rehabilitation results with treated water, 2) Pilot-scale study, 3) laboratory and bench scale data from other basins, and 4) expected full-scale cost and performance aspects vs. water quality and beneficial use.

Sandia received $240K in FY03**Why DOE Should Support this Project:**

Reclamation/disposal of CBM water is a national problem that impacts our ability to meet the growing demands for natural gas from domestic resources. Though industry is attempting to evaluate the applicability of commercial treatment technologies for CBM produced water treatment applications, they are limited in their ability or expertise to evaluate emerging innovative technologies. DOE is the agency with the federal role and capabilities to help accelerate the evaluation and implementation of new technologies to increase our energy supplies. Water shortages are severe throughout many states with CBM production. Reclaimed CBM water is one of the few sources of "new" water.

Critical Decision Points:

1. **June, FY04 –** Determine deionization and pretreatment technology applicability for CBM produced water treatment based on bench-scale performance and select optimum system combinations for pilot testing.
2. **March, FY05 –** Determine performance of pilot system and evaluate performance of treated water for rangeland rehabilitation. Assess overall system operational costs and applicability to a range of CBM produced waters.

Results:

Task 1: A team of producers (XTO energy, Dugan, Williams, Burlington, Bayless Production, ConocoPhillips, Terra, and others), service companies (BEST, Tri Energy, Aztec Well Service, and others), universities (NM Tech, NMSU) and resource manager personnel (BLM & OCD, NM) and Sandia has been formed (6/03). Task 2: Samples (inorganic and organic) have been taken and analyzed from both the San Juan and Raton basins. Laboratory facilities have been further

improved and upgraded to try both pretreatments, to remove organic material, to try different desalination treatments on the CBM produced water and to try possible post treatments. "Baseline" work in rangeland improvement has been done, i. e. watering appropriate grass seedlings with produced water (4 - 10/03). Task 3: A brief description of the initial desalination of CBM water using new treatment technologies (ion sorption (11/03) and nano filtration (7/03)) is also included. The advisory group, Task 1, decided that the three TDS groups (below) would be examined (12/03).

Sampling Detail, Task 2--Samples were collected in both the San Juan and Raton Basins (figure, bottom left). Individual wells were sampled in the San Juan and Raton Basins, especially in regions lacking infrastructure. Also some areas in the San Juan Basin have centralized disposal, "SWD" sites. A SWD is a well that is constructed to properly and safely dispose of produced water, often in a saline aquifer formation deeper than the zone from which the water was produced (usually Mesaverde Group, Dakota-Morrison Formations, or Entrada Sandstone). A SWD can "average" multiple wells.

The sampling revealed four major "domains" or water types in these basins. The Raton Basin yields the freshest water ~ 2,000 TDS. The San Juan Basin is divided into three domains, (figure, bottom center); (1) the "northern fairway area" in south west Colorado where water is fresh and abundant being nearest to recharge areas, also ~2000 TDS, (2) the "high productivity fairway" just south of the Colorado border, yields prolific gas wells that produce a majority of the water from the basin in New Mexico ~10,000 TDS. Fairway producers tend to be large independent operators. (3) The "non-fairway" wells, just south and west of high productivity fairway, are often marginal gas producers and yield the highest salinity water, ~24,000 TDS. Non-fairway producers tend to be small independent operators. Some fairway production is in environmentally sensitive public land areas. Some non-fairway production is in populated areas.

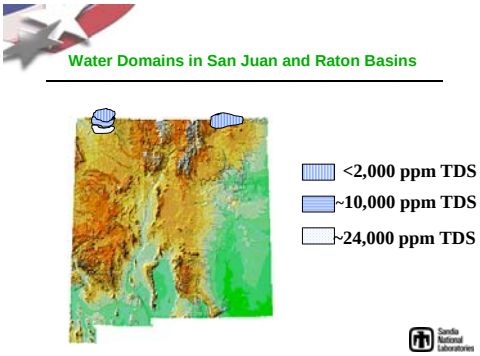
Rangeland Improvement Detail, Task 2--The New Mexico State University Agricultural Experiment station and the Bureau of Land Management temporarily agreed to allow produced water on rangeland for the planting of grasses. This allows the establishment of a baseline of untreated produced water to be used at 5000, 10,000 and 15,000 TDS. This temporary. Continued application of the untreated water could compromise the soil, not only the TDS but also the optimization of the sodium to potassium absorption ratio.

The basics of rangeland improvement include plowed soil, a brine storage tank, a pump and a sprinkler system. Tillage was done with a spring tooth harrow or disc before planting of plots on a well site. The actual application of CBM produced water to seedlings applying to seedling is shown (figure, bottom right). Some applications of ~TDS produced CBM water has been applied to grasses. In one case, approximately 1200 barrels of produced water, approximately 5000 mg/L TDS at 180°F were applied to 0.25 acres. This equals approximately 2.5 in of water applied per irrigation or a total of approximately 7.5 in on a per acre basis. Irrigations were made on August 12, 20, and September 16, 2003. It would take approximately 5 to 6 hours to apply 400 barrels of water. Many different grasses were planted on August 6, 2003. The growth of grasses from applying this ~5000 TDS water are promising. We will follow with additional irrigations to establish best irrigation practices and continue to improve grassland with minimal salt build up.

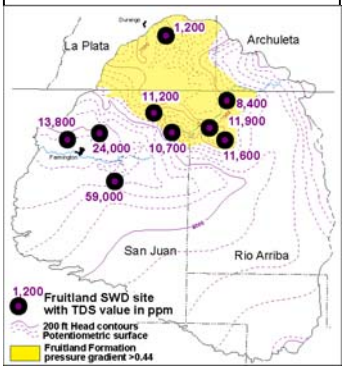
New Technology Detail, Task 3--An initial laboratory/ bench scale laboratory application of the ion exchange method run was accomplished on San Juan CBM produced water containing ~11,000 TDS, pH 8.4. After lime softening the TDS was reduced to ~ 8,000 ppm and the ph was increased to 12.4. After the cation exchange column, the TDS was reduced to ~2,600 ppm and the pH was decreased to 2.9. After the anion exchange column, the TDS was reduced to ~600 ppm and the pH was increased to 5.0.

Nano filtration reduced the TDS of produced water from ~11,000 to ~7000. Nano filtration is effective on divalent ions. Preliminary pilot scale applications have shown good results on waters in the 8000 TDS range. A new nano filtration pilot scale operation, with new electrical controls and a new pump will undergo a 90-day testing in February.

Contacts continue to be made with those that can supply capacitive deionization equipment. Arrangements will be made to desalinate samples of CBM water from the basins above with the capacitive deionization equipment..



Sampling Locations, San Juan Basin, NM & CO



Produced Water Applied to Seedlings on Rangeland