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TECHNOLOGY STATUS ASSESSMENT
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1 Current State of Technology

1.1 Summary of Existing Industry/Sector

New technologies and advances in existing technologies are needed to minimize environmental impacts associated with hydrocarbon production from our nation's conventional and unconventional resources. Unconventional resources currently account for 30% of U.S. gas production, and the importance of unconventional gas is expected to increase in the next 25 years (NPC, 2007). Production of both conventional and unconventional oil and gas generates large volumes of water. Handling of these large volumes of produced water and the associated costs have limited the development of both conventional and unconventional reservoirs (e.g. Anderson *et al*., 2003). Because development of oil and gas resources is becoming increasingly constrained due to environmental concerns and regulations, new methods are needed for the efficient handling of produced water using environmentally acceptable and economically viable technology.

1.2 Technologies/Tools Being Used

The most common mode of handling produced water is reinjection into designated geological formations (API, 2000). Cost can be high, and geological formations suitable for injection must be available. Although the cost may be affordable for larger exploration and production facilities, the expense of reinjecting produced water is commonly a significant economic burden for smaller or older facilities. Injection is becoming increasingly regulated, and requirements regarding quality and quantity of injected fluids are becoming more stringent

Thermal processes, including distillation, can be effective in reducing water volumes requiring reinjection, but cost can be high because of the large amount of energy required (Fenton, 1983; Semiat, 2000). The solar-desalination still uses the sun's radiation to evaporate saline water and produce a vapor. In the solar pond desalination method, water evaporates to form a highly concentrated salt solution that typically occurs at the bottom of the pond with an overlying layer of lower salinity, diluted water. Application of the solar pond technique to desalination is limited because of technical difficulties and low efficiency (Semiat, 2000). However, recent studies (e.g., Gilron *et al*., 2003; Arnal *et al*., 2005) have demonstrated that the use of wet porous materials on the surface of evaporation ponds can increase evaporation rates and promote crystallization of solids that may have commercial value. The freeze/thaw method of desalination, which involves production of salt-free ice, holds some promise in colder climates where natural freezing can be coupled with evaporative processes (Boysen *et al*., 1996, 2002).

The reverse osmosis (RO) membrane technique is the most promising and fastest-growing desalination method and is the most commonly used process for reducing ionic concentration in seawater. Quality of water after treatment by RO depends on membrane rejection properties, degree of water recovery, and proper system design (Semiat, 2000; Humphries and Wood, 2004). Membranes are sensitive to changes in pH, temperature, small concentrations of oxidized substances such as chlorine oxides, a wide range of organic materials, and the presence of algae and bacteria. The permeate from RO may require additional treatment before discharge or reuse because certain compounds, particularly small molecules such as hydrogen sulfide, ammonia, silica, boric acid, and small organic molecules, commonly penetrate through the RO membrane. The use of hybrid systems, which combine RO with another desalination method such as thermal process, can increase the useful life of RO membranes and reduce operating cost (e.g. Awerbuch *et al*., 1989; Hamed, 2005; Slesarenko, 2005).

Electrodialysis and electrodialysis reversal have been applied to the treatment of soluble salts in produced waters (Hayes, 2004; Hayes and Arthur, 2004). According to Hayes (2004) electrodialysis has advantages over RO, including the possibility to reduce brine volume by a factor of 10:1 or more (compared with 3:1 with reverse osmosis) and membrane life of 8-10 years (compared with 1-2 years for RO). For removal of organics, which are common in many produced waters, other methods such as induced gas flotation or biological treatment must be used prior to removal of ions by electrodialysis (Hayes, 2004).

Nanofiltration membranes can be used to reduce ionic concentration of produced waters (e.g., Xu and Drewes, 2006; Xu *et al*., 2008; Cakmakce *et al*., 2008), but, like other types of membranes, are subject to fouling by organic compounds (Mondal and Wickramasinghe, 2008).

Ions in produced waters can be sorbed by minerals having high cation exchange capacity, such as zeolites and smectites. Therefore, sorption is a potential treatment approach, and studies are ongoing to evaluate its potential in treating produced waters (Zhao *et al*., 2008).

1.3 Benefits and Inadequacies of Current Technology

Although targeted constituents in produced waters vary among oil and gas reservoirs, metals, organics, and biocides are among the more difficult to treat and tend to limit the utility of these waters for reuse or other purposes. Mercury, arsenic, and selenium present a difficult challenge for many types of current treatment options, and concentrations of these constituents in some produced waters can be high. Use of membrane technologies, such as RO and electrodialysis, for treating oil and gas produced waters has been limited by the presence of organics in these waters, which can cause rapid and severe deterioration of membranes.

Most current technologies for treating produced waters are costly, especially considering the large volumes of water produced and energy requirements, and are often unable to achieve the new, rigorous water-quality standards. A major limitation of many of these technologies is that their operating cost rises dramatically as the price of energy increases.

2 Development Strategies

2.1 Why New Technology and Research are Required

New, low cost, and readily implemented approaches are needed for management of water associated with development of conventional and unconventional oil and gas reserves. Drilling of wells is limited in some areas by lack of cost-effective methods for treating or disposing of the produced water. Discharge into surface waters is controlled by strict regulations, including those of the Clean Water Act (CWA) and the National Pollutant Discharge Elimination System (NPDES). Regulations regarding the discharge and reuse of produced waters are becoming increasingly stringent while volumes of water associated with oil and gas development in the U.S. are increasing. Costs associated with managing these waters are expected to rise, not only in terms of treatment or disposal, but also in terms of potential liability. Finding new approaches to assessing and mitigating risks posed by produced waters is essential for continued operation of many fields and development of new plays.

2.2 Problems to be Addressed in this Research Project

Technologies are needed that effectively and efficiently reduce the concentrations of multiple constituents, including metals, organics, and biocides, in produced waters to levels that allow reuse or discharge. A goal of our project is to develop the technology of using constructed wetland systems as a low cost method of treating produced water for beneficial reuse or discharge. A primary objective of this novel approach for sustainable treatment of produced waters is to transfer targeted constituents such as metals from the aqueous phase to the solid or sediment phase and to biodegrade organics.

3 Future

3.1 What Barriers shall the Research Overcome

We will investigate the use and design of constructed wetland treatment systems to decrease targeted constituents in produced waters to achieve reuse criteria or discharge limitations established by the NPDES and CWA. These treatment systems will be designed to support transfers and transformations of the targeted constituents in produced waters. It will be important to accumulate and sequester potentially toxic inorganic elements (e.g. copper, zinc, mercury, selenium, and arsenic) in nonbioavailable forms within hydrosoil of the constructed wetland treatment system. Organics must be retained and biodegraded. To achieve reduction of targeted constituents, design of the systems will be based in sound biogeochemical theory and modeling, as well as in published literature. Design parameters will be incorporated that take into account factors such as footprint, life expectancy, and closure plan.

Remediation of water can relieve disposal expenses and provide renovated water of sufficient quality for a variety of reuse purposes (e.g. Crook and Tsang, 1994; Doran *et al*., 1997; Doran *et al*., 1998; Tao *et al*., 1998). The use of constructed wetlands for treatment of produced water for reuse is potentially a lower cost opportunity to remediate specific constituents of concern (Gillespie *et al*., 2000; Murray-Gulde *et al*., 2003; Rodgers and Castle, 2008). Cost benefits of using constructed wetland treatment systems rather than conventional treatment approaches have been demonstrated in previous studies (e.g. Myers *et al.*, 2001; Mooney and Murray-Gulde, 2008).

3.2 Impact on Produced Water Management and the Domestic Oil and Natural Gas Supply

Development of new technology for managing waters generated in association with domestic oil and gas production is expected to reduce the cost and increase the efficiency of producing these resources while minimizing environmental impact. This is a critical issue for the sustainability of oil and gas drilling and for expansion in emerging areas.

In addition to greatly reducing environmental risks associated with current practices, produced waters renovated by constructed wetland treatment systems have the potential to be reused for a variety of purposes, such as irrigation, livestock watering, municipal water use, domestic use, discharge to receiving aquatic systems for other use downstream, and support of critical aquatic life and wildlife. This can allow continued operation of existing wells and lead to increased drilling and production.

3.3 Deliverables (Tools, Methods, Instrumentation, Products, etc.)

Scientific studies will be conducted to address ecological, environmental, and regulatory concerns that limit options for managing produced water, including surface discharge. We will investigate the use and design of constructed wetland treatment systems to decrease targeted constituents in produced waters to achieve reuse criteria or discharge limitations established by the NPDES and CWA. Pilot-scale and field demonstration studies will provide crucial information and important benefits.

The comprehensive approach to our investigation including both measurement of constituents that limit reuse/discharge and analysis of toxicity will help to identify the requisite reactions and conditions for biogeochemical treatment processes that can be incorporated in the constructed wetland systems. We will take advantage of these reactions and the ability to poise constructed wetland treatment systems for sustained performance. We will measure performance in terms of chemical criteria, water reuse criteria, and risk mitigation.

The results of this investigation will provide treatment performance data and design parameters applicable to constructing wetland treatment systems specifically for produced waters.

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