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Treatment of Produced Water From Coal-Bed Methane Production Using Capacitive Deionization Final Report CRADA No. TSV-1380-97

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Disclaimer

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Treatment Of Produced Water From Coal-Bed Methane Production Using Capacitive Deionization

Project Accomplishments Summary
CRADA No. TSV-1380-97

Date: July 2, 1998 Revision: 2

A. **Parties**

The project was a relationship between the Lawrence Livermore National Laboratory (LLNL) and BPF, Inc.

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BPF, Inc.
1555 Valwood Parkway, Ste. 100
Carollton, TX 75006

B. **Background**

The production of Coal-Bed Methane (CBM) is always accompanied by the production of large amounts of water. The produced water is typically too high in dissolved solids and salinity to be suitable for surface disposal.

Several disposal options are available for CBM produced waters, including subsurface injection, thermal evaporation, hauling and off-site disposal, and reverse osmosis treatment/surface discharge. Subsurface injection into existing injection wells could have the lowest operating cost of the various alternatives; however, environmental regulations often prohibit subsurface injection or require the drilling of deeper and more costly injection wells. Evaporation and other techniques involving natural processes suffer from inconsistent treatment rates that vary with the seasons. Hauling and off-site disposal could cost up to $4.00/bbl, depending on state regulations, the time of year and distance to the disposal site. Surface discharge requires pretreatment to reduce the concentration of dissolved solids to dischargable levels.

At the time of the CRADA, only reverse osmosis (RO) had been implemented and demonstrated on a full-scale basis. RO was significantly more cost-effective than other existing a technologies, but an RO unit was usually part of a more complex treatment train due to the requirement of pretreatment systems and the high reject stream (typically 30% of the feed stream) that needed to be disposed of by injection.

Capacitive deionization (CDI) was developed by Lawrence Livermore National Laboratory (LLNL) as an alternative desalination technology. In laboratory demonstrations, CDI had shown to be up to a factor of 10 less energy intensive than RO, and produced a significantly smaller waste stream. Further, the robust structure of the system gave it potentially superior reliability over existing RO technology.

C. Description

This project evaluated the application of capacitive deionization technology to the desalination and removal of dissolved contaminants from CBM produced waters.

LLNL developed practical and cost effective manufacturing techniques for carbon aerogel, a material with high surface area, optimum pore size for use as a double-layer capacitor, and low electrical resistivity. LLNL also developed a process for the capacitive deionization of water using carbon aerogel electrodes.

BPF personnel have expertise in various aspects of oil and gas production, including production engineering activities, oilfield water treatment and corrosion control, regulatory and permitting requirements. BPF also has extensive laboratory facilities to provide a range of testing capabilities.

To determine the viability of this application several factors needed to be addressed, including the control of water-formed scales such as $CaCO_3$, $CaSO_4$, and $BaSO_4$, and the selectivity of the process for charged inorganic species.

Four tasks were assigned:

1. Characterization of CBM Produced Waters
2. Laboratory Trials
3. Closed-loop processing of actual produced water samples
4. Data analysis and report preparation

Characterization of CBM Produced Waters

BPF characterized CBM produced waters as to exact composition of the salts and organic species, especially the charged organic species.

BPF also analyzed several sources of CBM produced water for common ions, trace metals, sulfides, CO_2 content, total organic carbon content, and carboxylic acids. These analyses provided input data for the initial trials in Task 2.

Laboratory Trials
Based on the characterization data from Task 1, LLNL processed a variety of water samples.

a) samples with typical concentrations of $CaCl_2$, Na_2SO_4, $MgCl_2$ and $NaHCO_3$ to determine any rate differences among in adsorption/desorption among those salts
b) samples with a mixture of $CaCl_2$ and Na_2SO_4 to determine differences from single ion behavior
c) a typical produced-water composition
d) a mixture of sodium octanoate and sodium chloride and mixtures of sodium acetate and sodium chloride at pH 6.0 and at 0.5 pH units below the pK for each organic acid to determine effectiveness in removing the waters containing sodium chloride and typical amounts of iron (II) at pH values of 2, 4, 6, and 8 to determine whether fouling occurs. This process was repeated using low levels of peroxide to oxidize the iron prior to demineralization.

Closed-loop processing of actual produced water samples
LLNL processed actual water samples to verify conclusions from Tasks 1 and 2, and to gather data on the long term performance of the CDI system on CBM produced water. This assured that the CDI unit would function effectively under actual field conditions.

Data analysis and report preparation
The data from Tasks 1-3 were used to establish operating parameters and scenarios for CDI treatment of CBM-produced water. LLNL and BPF presented the data and results from all tasks in a final report.

D. **Expected Economic Impact**
Application of CDI to the treatment of produced waters from coal-bed methane production was of particular interest to private industry and to various federal government agencies (namely EPA) because of the great volumes of water involved and the disposal problems using existing technology. An economical solution to the treatment/disposal problem would benefit the U.S. economy by promoting the production of coal-bed methane as a source of natural gas.

The ultimate goal of this project, and any follow-on work to be conducted, is to transfer CDI technology to the industrial partner for commercialization in the coal-bed methane production industry. This project greatly benefited the partner to develop CDI as an economical alternative to existing treatment methods for produced waters and other contaminated waste waters.

E. **Benefits to DOE**

This project benefited DOE by evaluating the feasibility of CDI as a process for cleanup of aqueous solutions of inorganic contaminants. We believed that if such feasibility was shown, CDI would become a useful tool for cleanup of waste streams at DOE facilities, including the Cr(VI) and other contaminants in ground water at the LLNL site itself.

The project also directly supports DOE Fossil Energy objectives to reduce the operating costs of oil and gas production.

We expected that the compositions of waters involved in this project were similar to other hazardous waste waters; developing a plan and method for treating these waters would facilitate the development of means for treatment of wastes at DOE sites.

This project was consistent with the DOE's mission of Technology Transfer and provided benefits and positive impact on both DOE and the partners. This program did not negatively impact any current DOE program.

F. **Industry Area**

Waste Disposal

G. **Project Status**

This project was completed in May 1997.

H. **LLNL Point of Contact for Project Information**

LLNL was represented by Tri D. Tran (Principal Investigator); L-322; 925/422-0915; 925/423-4897 (fax) of the Chemistry & Material Sciences Directorate.

I. **Company Size and Point(s) of Contact**

BPF, Inc. was represented by Dr. Charles C. Patton, Director of Technology, 972/247-5928 ext. 21; 972/241-4474 (fax). Company 1995 sales were approximately $1M, and the company employs 7 people. The President, Dr. Thomas O. Bush, can be contacted for further feedback.

J. **Project Examples**

A series of 30 experiments were done on 20 surrogate and actual field samples over a 2-week period. A semi-automatic capacitive deionization unit was dedicated to this project. This unit contains 100 cells with 200 10 cm x 20 cm electrodes. The unit was charged to 1.2 V for ion removal and discharged to 0V for regeneration. Preliminary analysis indicated that complete deionization can be accomplished when the samples were deionized successively. Samples were stored and shipped to BPF for chemical analysis. Initial results and a draft were being prepared by BPF engineers. Publication of the results and further collaboration are being discussed.

K. **Subject Inventions**

This small value contractual mechanism did not anticipate any generation of Intellectual Property (IP) including subject inventions. To the best of our knowledge no IP was created.

☐ Yes ☑ No _____

If yes, list all IP created under this agreement.

L. **Release of Information**

I certify that all information contained in this report is accurate and releasable to the best of my knowledge.

Karena McKinley, Director
Industrial Partnerships
and Commercialization

2/3/00
Date

Release of Information

I have reviewed the attached Project Accomplishment Summary prepared by Lawrence Livermore National Laboratory and agree that the information about our CRADA may be released for external distribution.

Thomas O. Bush, President
BPF, Inc.

1/24/00
Date