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EVALUATION OF THE FREEZE-THAW/EVAPORATION PROCESS
FOR THE TREATMENT OF PRODUCED WATERS

QUARTERLY TECHNICAL PROGRESS REPORT

Contract No. DE-AC22-92MT92009-16

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Executive Summary

The use of freeze-crystallization is becoming increasingly acknowledged as a low-cost, energy-efficient method for purifying contaminated water. Freeze-crystallization has been shown to be effective in removing a wide variety of contaminants from water. Water purification by using natural conditions to promote freezing appears to be an extremely attractive process for the treatment of contaminated water in many areas where natural climatic conditions will seasonally promote freezing. The natural freezing process can be coupled with natural evaporative processes to treat oil and gas produced waters year-round in regions where sub-freezing temperatures seasonally occur. The objectives of this research were related to development of a commercially-economic natural freeze-thaw/evaporation (FTE) process for the treatment and purification of water produced in conjunction with oil and gas.

During the reporting period of 4/1/96 to 6/30/96, project research concentrated on Task 3. The objectives of Task 3 were to conduct detailed inorganic, organic, and radionuclide analyses of the process streams, evaluate the operation of the field demonstration based upon operating data collected and the results of sample analyses, and prepare a final report delineating the results of all project research conducted. Task 3 required completion of four subtasks: Subtask 3.0 - Task 3 Project Reporting, Subtask 3.1 - Demonstration Sampling & Analysis, Subtask 3.2 - Demonstration Data Evaluation, and Subtask 3.3 - Final Project Report. Work on Subtasks 3.0, 3.1, 3.2, and 3.3 were completed this quarter.

Research efforts this quarter were:

- to complete analyses of the FTE demonstration process streams,
- to complete data evaluation of the demonstration based on the results of process stream analyses and operating data, and
- to complete the final project report.

The Monthly reports for April, May, and June 1996 were submitted during the reporting period. The Quarterly Technical Progress Report for the time period of 1/1/96 to 3/31/96 was also submitted.

Plans for the next quarter are to:

- close out US DOE contract number DE-AC22-92MT92009

1.0 Introduction

1.1 Background

The cost of treating the water produced in association with oil and natural gas has prevented the completion of wells in economically marginal formations and has caused low-productivity wells to be prematurely shut-in. An economical method for treatment, disposal, and/or reuse of these waters on a commercial-scale would assist the oil and natural gas industries in continuing to provide reasonably priced fuels to the consumer by allowing for economic production from marginal, unconventional, and depleted reserves. A treatment process that could produce water of suitable quality for reuse would also be advantageous for municipal, industrial, and agricultural development in the arid western United States where there is significant oil and natural gas production.

The natural processes of freezing and evaporation can be coupled to effectively and inexpensively treat waters produced in association with natural gas. This document delineates research conducted, during the time period from 4/1/96 to 6/30/96, for evaluating the technical and economic feasibility of this water treatment process. The research required for development of this process was completed in three tasks:

- Task 1: Literature Survey and Preliminary Economic Analysis
- Task 2: Laboratory-Scale Process Evaluation
- Task 3: Evaluation of the Field Demonstration of the FTE Process in the San Juan Basin of New Mexico

1.2 Research for the Current Reporting Period

Research conducted during this time period was related to Task 3. The objectives of Task 3 were to conduct detailed inorganic, organic, and radionuclide analyses of the process streams, evaluate the operation of the field demonstration based upon operating data collected and the results of sample analyses, and prepare a final report delineating the results of all project research conducted. Task 3 required completion of three subtasks: Subtask 3.0 - Task 3 Project Reporting, Subtask 3.1 - Demonstration Sampling & Analysis, Subtask 3.2 - Demonstration Data Evaluation, and Subtask 3.3 - Final Project Report.

Subtask 3.0 - Task 3 Reporting - Required project reports were submitted.

Subtask 3.1 - Demonstration Sampling & Analysis - Samples from the demonstration process streams were taken on 2/1/96 and 3/18/96 and analyzed for organics, inorganics, and radionuclides. Solids were also analyzed by XRD. Detailed analyses were completed in this reporting period and the results obtained were favorable.

Subtask 3.2 - Demonstration Data Evaluation - Data evaluation of the FTE demonstration plant in the San Juan Basin of New Mexico substantiated effective contaminant removal.

Subtask 3.3 - Final Project Report - The final project report was completed during this reporting period. The results from the FTE demonstration plant in the San Juan Basin of New Mexico (Task 3) were incorporated with the results from all project research conducted. All research tasks are completed.

2.0 Project Description

2.1 Project Research Tasks and Subtasks

Following is a brief description of the project tasks and subtasks. The research required to complete each task/subtask is also summarized:

2.1.1 Task 1: Literature Survey and Preliminary Economic Analyses

A literature survey and preliminary economic feasibility and sensitivity analyses was conducted to evaluate the technical feasibility and commercial viability of the FTE process. Specific subtasks performed were:

Subtask 1.1 - Literature Survey of FTE Research: 1) identify economically important FTE process parameters, 2) summarize the response of organics, metals and salts in contaminated waters to the FTE process, and 3) estimate potential interactions between constituents that may impact the process. Subtask 1.1 objectives have been achieved with one exception: a literature survey to provide data depicting the behavior of organics and heavy metals in a natural freezing water purification process. Natural freezing process data found in the literature was related to salts only. However, data in the literature related to artificial freezing processes confirm organic and heavy metals compounds can be successfully and efficiently removed from contaminated water by freezing processes.

Subtask 1.2 - Characterization of NG Production Waters and Conventional Treatment Costs: 1) review of literature and data bases to characterize typical waters that are generated in association with production from natural gas reservoirs, oil and gas reservoirs, and methane drainage from coal seams, 2) survey meteorological data to establish an expected range of atmospheric conditions at selected production sites where the FTE process is applicable (survey will include daily wind velocity and temperature cycles), and 3) survey local producers to determine their current treatment/ disposal methods, costs, and willingness to participate in a field demonstration of the process. All objectives of Subtask 1.2 have been achieved.

Subtask 1.3 - Evaluation of Process and Environmental Constraints: 1) estimate FTE discharges and evaluate regulatory requirements for field and commercial-scale demonstration, 2) assess process discharges, regulatory requirements, and costs of conventional methods of disposal/treatment of production waters, and 3) compare the environmental acceptability, regulatory requirements and costs of the FTE process to conventional methods. All objectives of Subtask 1.3 have been achieved.

Subtask 1.4 - Conceptual Process Design: 1) design a preliminary FTE process based on the results of work elements 1.1 through 1.3 to address environmental, regulatory and process issues for various types of produce waters. All objectives of Subtask 1.4 have been achieved.

Subtask 1.5 - Preliminary Economic Feasibility and Sensitivity Analyses: 1) develop a numerical discounted cash flow /rate of return economic model for the preliminary FTE process design resulting from Subtask 1.4; 2) evaluate the economics of a probable, base case operating scenario which assumes reasonable fixed values for: a) facility size and location, b) concentrations of salts, organics and heavy metals in the production water, c) atmospheric conditions, d) capital equipment costs, e) annual operating expenses, f) debt to equity ratio, g) bond interest, and h) return on investment after taxes; and 3) determine the economic sensitivity of the FTE process by evaluating the projected water treatment costs for a minimum of 33 differing operating scenarios. All

objectives of Subtask 1.5 have been achieved.

Subtask 1.6 - Task 1 Summary Report: 1) provide a comprehensive analysis of the results of Tasks 1.1 through 1.5 and 2) determine if the FTE process is technically feasible, economically viable and economically stable. All objectives of Subtask 1.6 have been achieved.

2.1.2 Task 2: Laboratory-Scale Process Simulation

Task 2 was the laboratory-scale evaluation of the FTE process. The following subtasks were required for completion of Task 2:

Subtask 2.1 - Laboratory-scale Process Simulations: 1) design and construct a laboratory-scale simulator to test the FTE process; 2) conduct an initial series of nine process simulations to optimize the FTE process design by evaluating the effectiveness of the three different freezing design options: wetted column freezing, conventional water sprays, and atomizing sprays and three different evaporation techniques: conventional evaporation ponds, solar evaporation ponds, and solar distillation ponds; 3) conduct an additional series of eight process simulations, using the optimum process design for treating three different produced waters under three differing sets of atmospheric conditions, to determine the effectiveness of the FTE process in removing organic, metal, and salt constituents from mixtures; 4) conduct a duplicate simulation for each of the produced waters tested to verify experimental results. This subtask has been completed and laboratory-scale simulation results confirm the feasibility and commercial potential of the process.

Subtask 2.2 - Re-evaluation of Process Economics Based Upon Laboratory-scale Simulation Results: 1) re-evaluate FTE process economics using the numerical model developed in Subtask 1.5 based upon Subtask 2.1 simulations results. All objectives of Subtask 2.2 have been achieved.

Subtask 2.3 - Final Technical Report of the Simulation Results, Revised Process Economics, and Final Demonstration Plant Design and Economic Requirements: 1) summarize the results of all FTE process research including process and economic model results and laboratory-scale FTE process simulation results; 2) develop accurate commercial-scale process economic projections; and 3) provide detailed equipment and economic requirements for the completion of the related project entitled "Demonstration of the FTE Process for the Treatment of Produced Waters in the San Juan Basin of New Mexico." All objectives of Subtask 2.3 have been achieved.

2.1.3 Task 3: Evaluation of the Field Demonstration of the FTE Process in the San Juan Basin of New Mexico

Task 3 of this research included evaluation of a demonstration of the FTE process conducted at an operating production site in the San Juan Basin of New Mexico. Task 3 research was conducted in conjunction with a separate project entitled "Demonstration of the FTE Process in the San Juan Basin of New Mexico." The field demonstration confirmed the process's commercial potential. The details relating to the work required to complete the field demonstration of the process are discussed in the following section. The technical report generated in Subtask 2.3 provides the detailed requirements for completion of Task 3. Specific subtasks required for completion of Task 3 are described below:

Subtask 3.1 - Sampling and Analyses of Field Demonstration Process Streams: 1) collect samples and conduct detailed inorganic, organic, and radionuclide analyses of the produced water in the demonstration holding pond prior to initiation of sub-freezing temperatures and 2) collect samples and conduct

detailed inorganic, organic, and radionuclide analyses of the ice pile created, treated water produced, brine produced, and the demonstration holding pond during the freezing operation of the demonstration plant.

Subtask 3.2 - Evaluation of Field Demonstration Operating Data: 1) evaluate the operation of the field demonstration based upon operating data collected and the results of sample analyses.

Subtask 3.3 - Preparation of the Final Report: 1) prepare a final report delineating the technical and economic results of the field demonstration of the FTE process conducted in the San Juan Basin of New Mexico.

2.1.4 Modification of Contract Tasks and Subtasks

Limited laboratory data already acquired and results of previous research, conducted by others, strongly confirm the technical feasibility of the process. In addition, the results of Task 1 and Subtasks 2.1 and 2.2 of this research strongly suggest economic viability of the process. For these reasons an evaluation of a field demonstration of the process was conducted. Task 3 research was conducted in conjunction with a separate project entitled "Demonstration of the FTE Process for the Treatment of Produced Waters in the San Juan Basin of New Mexico." This project entitled "Evaluation of the FTE Process for the Treatment of Produced Waters" supported the demonstration project by evaluating the technical and economic operation of the FTE operation. The field demonstration of the process better met the project objective of developing and demonstrating a cost-effective economically viable commercial technology utilizing the FTE process to treat water produced in conjunction with oil and natural gas. The field demonstration met the two key process development needs required for commercial application of the process: 1) demonstration of the technical and economic viability of the process and 2) obtaining regulatory acceptance of this novel process. Funding for the field demonstration was obtained and a no-cost contract extension of the period of performance to 8/96 was approved by the Contracting Officer's Representative.

2.2 Project Objectives

The general objective of the research was to develop and demonstrate a cost-effective economically viable commercial technology that utilizes the natural FTE process to treat water produced in conjunction with oil and natural gas. The specific objectives of the research were to:

- develop an economic model for determining the commercial viability, economically significant parameters, and research issues of the FTE process,
- conduct laboratory-scale process simulations to optimize the design of the FTE process, and
- to evaluate on-location treatment of water from a producing well to demonstrate the technical and economic viability of the FTE process.

3.0 Project Status

3.1 Work Performed during the Reporting Period

3.1.1 Subtask 3.0 Task 3 Project Reporting

During the reporting period, monthly project reports required for the months of April, May, and June 1996 were completed and submitted to the US DOE Document Control Center at PETC. The Quarterly project report for the time period of 1/1/96 - 3/31/96 was also completed and submitted to the US DOE Document Control Center. No budget or schedule problems exist for this subtask.

3.1.2 Subtask 3.1 Sampling and Analyses of Field Demonstration Process Streams

Initial samples from the demonstration process streams were taken on 2/1/96 and analyzed for organic, inorganics, and radionuclides. The results obtained were favorable. Final sampling was completed on 3/18/96 and detailed analyses were completed in this reporting period. In addition, analyses of solids from the demonstration plant holding pond were completed. No budget or schedule problems exist for this subtask.

3.1.3 Subtask 3.2 Demonstration Data Evaluation

Data evaluation of the FTE demonstration plant in the San Juan Basin of New Mexico is complete and has substantiated effective contaminant removal using the FTE process. No budget or schedule problems exist for this subtask.

3.1.4 Subtask 3.3 Final Project Report

The draft final project report is complete and contains the results of all three tasks. No budget or schedule problems exist for this subtask.

3.2 Summary of Achievements

Project achievements for the time period of 4/1/96 to 6/30/96 are:

- Required monthly and quarterly reports were completed and submitted for the project.
- Sample analyses for detailed organic, inorganic, and radionuclide analyses were completed.
- Evaluation of the operation of the field demonstration based upon operating data collected and the results of sample analyses was completed.
- The draft of the final project report was completed.

4.0 Planned Activities for the Next Quarter

During the upcoming quarter (July 1 - September 30, 1996), plans are to:

- close out US DOE contract number DE-AC22-92MT92009

5.0 Summary

All tasks of the research program are complete. Results confirm that the FTE process is effective in removing a wide variety of constituents from produced water, such as salts, organics, and heavy metals (including NORM). Further, the FTE process is capable of economically providing significant quantities of water of a quality suitable for beneficial use from oil and gas produced waters. An FTE field demonstration plant was in operation from December 9, 1995 through March 7, 1996 in the San Juan Basin of northwestern New Mexico. Results from the evaluation of the FTE field demonstration indicate significant and simultaneous removal of salts, metals, and organics from produced water. The total dissolved solids concentrations of the FTE demonstration streams were 11,600 mg/l (feed), 56,900 mg/l (brine), and 940 mg/l (ice). In addition, process yields demonstrate disposal volume reductions on the order of 80% and confirm the potential for economical production of water suitable for various beneficial uses.

Results of all research conducted indicate that the FTE process has significant commercial economic potential and is an environmentally acceptable option to produced water disposal by deep well injection. An additional benefit of the process is that the treated water produced during the winter months can be used for municipal, agricultural, and industrial development in arid regions. Therefore, research related to the development of the process should continue in order to investigate the numerous potential applications of the process.

6.0 Report Distribution

The quarterly progress report distribution specified by the current contract is three copies of quarterly reports to:

Document Control Center
United States Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, MS 921-118
Pittsburgh, PA 15236 - 0940

7.0 References

None

8.0 Publications

None