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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

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Executive Summary

The use of freeze-crystallization is being 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 subfreezing temperatures seasonally occur. The objectives of this research are 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 1/1/94 to 3/31/94, project research concentrated on Subtasks 2.0 (Task 2 Project Reporting) and 2.1 (Laboratory-scale FTE Simulations). The objectives of Task 2 are to conduct laboratory- and bench-scale simulations for optimizing the design of the FTE process. Task 2 requires completion of six subtasks: Subtask 2.0 - Task 2 Project Reporting (initiated 3/1/93), Subtask 2.1 - Laboratory-scale FTE Simulations, Subtask 2.2 - Re-evaluation of Process Economics Based on Laboratory-scale Process Simulation Results, Subtask 2.3 - Bench-scale FTE Simulations, Subtask 2.4 - Economic Assessment of Bench-scale Simulations, and Subtask 2.5 - Technical Report of Task 2. The construction, shakedown, and operation of the laboratory-scale process simulations planned were planned for this quarter (Subtask 2.1). The operation of the simulations was delayed by:

- late equipment arrivals,
- malfunction of the simulator temperature control and data acquisition computer link, and
- failure of the simulator refrigeration unit's hot gas defrost cycle timer.

Late equipment arrivals resulted in approximately three weeks delay. Malfunction of the computer link was a result of incorrectly installed telephone wiring at RTC's facility and resulted in approximately six weeks delay. The failure of the hot gas defrost timer was a result of improper installation by the vendor, who repaired the unit at no cost to the contract and limited the delay to approximately three weeks. The construction of the laboratory-scale process simulator is near completion and simulator operation is anticipated to begin in April 1994. At the present time it is difficult to assess the long-term impact of this delay on the contract schedule. This delay is not expected to impact the contract budget.

Research efforts this quarter were:

- The "Task 1 Report" is in final form and plans are to have the report printed according to new GRI specification as soon as possible. RETEC has agreed to take care of the printing.
- An abstract was excepted and a paper subsequently submitted for presentation at the "1994 Rocky Mountain Symposium on Environmental Issues in Oil and Gas Operations" to be held July 11-13, at the Colorado School of Mines in Golden, CO.
- The laboratory-scale simulator construction was completed and several shakedown attempts resulted in identification of the problems previously mentioned.

- Samples of produced water from a natural gas producing well in Weld County, CO; an oil and gas producing well near Brighton, CO; and a coal bed methane well in the San Juan Basin are in-house. RTC wishes to express appreciation to Bill Hall of Silverado Oil for the sample from a natural gas producing well, Tom Shanor of Thorofare Resources for the sample from the oil and gas producing well, and Buddy Shaw of Amoco Production Company for the sample from the coal bed methane well.
- Subcontracting arrangements are near completion with Evergreen Analytical Laboratories in Wheatridge, CO for volatile organic analyses (VOA), semi-VOA, and radionuclide analyses of simulation samples; and, subcontracting arrangements are near completion with the University of North Dakota (UND) Energy and Environmental Research Center (EERC) in Grand Forks, ND for metals, dissolved solids, and total organic carbon analyses of simulation samples. Analyses of the produced water samples obtained are expected to begin in April.
- Negotiations are still in progress with Silverado and Thorofare Resources, Inc. to construct a 1,000 bbl/day FTE facility for commercial demonstration of the process.

Plans for the next quarter are to:

- conduct laboratory simulations and analyze samples,
- begin modification of the economic evaluation software, and
- continue negotiations with interested parties in an attempt to conduct a commercial demonstration of the process next year.

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 1/1/94 to 3/31/94, for evaluating the technical and economic feasibility of this water treatment process. The research, required for development of this process, has three distinct tasks:

Task 1: Literature Survey and Preliminary Economic Analysis

Task 2: Laboratory- and Bench-Scale Process Evaluation

Task 3: Field Demonstration of the Process

The current contract (US DOE contract No. **DE-AC22-92MT92009**) is for completion of research to be conducted in Tasks 1 and 2 only. If successful, funding for Task 3 will then be solicited.

1.2 Research for the Current Reporting Period

Research conducted during this time period was related to Task 2. The objectives of Task 2 are to conduct laboratory- and bench-scale simulations for optimizing the design of the FTE process. Task 2 requires completion of six subtasks: Subtask 2.0 - Task 2 Project Reporting (initiated 3/1/93), Subtask 2.1 - Laboratory-scale FTE Simulations, Subtask 2.2 - Re-evaluation of Process Economics Based on Laboratory-scale Process Simulation Results, Subtask 2.3 - Bench-scale FTE Simulations, Subtask 2.4 - Economic Assessment of Bench-scale Simulations, and Subtask 2.5 - Technical Report of Task 2.

During the reporting period, work conducted was related to Subtasks 2.0, and 2.1. Subtask 2.0 research efforts this quarter were related to monthly project reporting and acceptance of an abstract and subsequent submission of a paper for presentation at the "1994 Rocky Mountain Symposium on Environmental Issues in Oil and Gas Operations" to be held July 11-13, at the Colorado School of Mines in Golden, CO.. Subtask 2.1 efforts included the acquisition of all samples of produced waters required for the laboratory-scale simulations: 1) produced water from a natural gas producing well in Weld County, CO; 2) produced water an oil and gas producing well near Brighton, CO; and 3) produced water from a coal bed methane well in the San Juan Basin. RTC wishes to express appreciation to Bill Hall of Silverado Oil for the sample from a natural gas producing well, Tom Shanor of Thorofare Resources for the sample from the oil and gas producing well, and Buddy Shaw of Amoco Production Company for the sample from the coal bed methane well. Subcontracting arrangements are near completion with Evergreen Analytical Laboratories in Wheatridge, CO for volatile organic analyses (VOA), semi-VOA, and radionuclide analyses of simulation samples; and, subcontracting arrangements are near completion with the University of North Dakota (UND) Energy and Environmental Research Center (EERC) in Grand Forks, ND for metals, dissolved solids, and total organic carbon analyses of simulation samples. Analyses of the produced water samples obtained are expected to begin in April.

In addition, the laboratory-scale simulator construction was completed and several shakedown attempts resulted in identification of the following problems: 1) malfunction of the simulator temperature control and data acquisition computer link, and 2) failure of the simulator refrigeration unit's hot gas defrost cycle timer. The operation of the simulations was delayed by these problems. Late equipment arrivals resulted in approximately three weeks delay. Malfunction of the computer link was a result of incorrectly installed telephone wiring at RTC's facility and resulted in approximately six weeks delay. The failure of the hot gas defrost timer was a result of improper installation by the vendor, who repaired the unit at no cost to the contract and limited the delay to approximately three weeks. The construction of the laboratory-scale process simulator is near completion and simulator operation is anticipated to begin in April 1994. At the present time it is difficult to assess the long-term impact of this delay on the contract schedule. This delay is not expected to impact the contract budget.

Silverado Oil and Thorofare Resources, Inc. have both expressed strong interest in perusing commercial development of the process. Progress in negotiations to construct a 1,000 bbl/day FTE commercial demonstration facility in 1994 was not as great as expected this quarter. The current and significant drop in oil prices in the region has impacted progress.

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 will be conducted to evaluate the technical feasibility and commercial viability of the FTE process. Specific subtasks to be performed are:

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 1.2 - Characterization of Natural Gas 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.

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 of the environmental acceptability, regulatory requirements and costs of the FTE process to conventional methods.

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.

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.

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.

2.1.2 Task 2: Laboratory- and Bench-Scale Process Simulation

Task 2 is the laboratory and bench-scale evaluation of the FTE process. The following subtasks are 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 water tested to verify experimental results.

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.

Subtask 2.3 - Bench-Scale FTE Simulations: 1) design and construct three bench-scale simulations to verify the process effectiveness under actual climatic conditions, 2) conduct the simulations for one year, 3) confirm laboratory-scale simulation results under atmospheric conditions in Laramie, WY, 4) demonstrate the effectiveness of the process, and 4) acquire data for process scale-up.

Subtask 2.4 - Re-evaluation of Process Economics Based Upon Bench-scale Simulation Results: 1) re-evaluate FTE process economics using the numerical model and the Subtask 2.3 simulation results, and 2) refine the process design, equipment selection, construction procedures, and plant operating procedures for field demonstration using an FTE process.

Subtask 2.5 - Final Technical Report of the Simulation Results, Revised Process Economics, and Final Demonstration Plant Design and Economic Requirements: 1) write a technical report summarizing the results of the FTE process simulations, providing a commercial-scale process economic projection and the finalized technical and economic requirements of an FTE process demonstration plant for the treatment of natural gas production waters. This report will also provide detailed requirements for completion of Task 3.

2.1.3 Task 3: Field Demonstration of the FTE Process

Task 3 will be a field demonstration of the FTE process conducted at an operating production site. Task 3 will be initiated if results of Task 2 show FTE to be a technically and economically viable process. The field demonstration

will confirm the process's commercial viability. It will incorporate all technical innovations and process improvements resulting from previous research efforts. The details relating to the work required to complete Task 3 will be determined in the research conducted in Tasks 1 and 2 of the current contract.

2.2 Project Objectives

The general objective of the research is 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 are to:

- develop an economic model for determining the commercial viability, economically significant parameters, and research issues of the FTE process,
- conduct laboratory- and bench-scale process simulations to optimize the design of the FTE process, and
- to conduct 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 2.0 Task 2 Project Reporting

As of the end of the reporting period, project reports required for the months of January, February, and March 1994 were complete and submitted to the US DOE Document Control Center at PETC and to Remediation Technologies, Inc. In addition, an abstract was accepted and a paper subsequently submitted for presentation at the "1994 Rocky Mountain Symposium on Environmental Issues in Oil and Gas Operations" to be held July 11-13, at the Colorado School of Mines in Golden, CO. No budget or schedule problems exist for this subtask.

3.1.2 Subtask 2.1 Laboratory-scale FTE Simulations

During the reporting period, Subtask 2.1 efforts included:

- The acquisition of all samples of produced waters required for the laboratory-scale simulations: 1) produced water from a natural gas producing well in Weld County, CO; 2) produced water an oil and gas producing well near Brighton, CO; and 3) produced water from a coal bed methane well in the San Juan Basin.
- Negotiation of subcontracting arrangements with Evergreen Analytical Laboratories in Wheatridge, CO for volatile organic analyses (VOA), semi-VOA, and radionuclide analyses of simulation samples; and, subcontracting arrangements with the University of North Dakota (UND) Energy and Environmental Research Center (EERC) in Grand Forks, ND for metals, dissolved solids, and total organic carbon analyses of simulation samples.
- The laboratory-scale simulator construction was completed and several shakedown attempts resulted in identification of the following problems: 1) malfunction of the simulator temperature control and data acquisition computer link, and 2) failure of the simulator refrigeration unit's hot gas defrost cycle timer. The operation of the simulations was delayed by these problems. Late equipment arrivals resulted in approximately three weeks delay. Malfunction of the computer link was a result of incorrectly installed telephone wiring at RTC's facility and resulted in approximately six weeks delay. The failure of the hot gas defrost timer was a result of improper installation by the vendor, who repaired the unit at no cost to the contract and limited the delay to approximately three weeks.

At the present time it is difficult to assess the long-term impact of this delay on the contract schedule. However, the delay is not expected to impact the contract budget.

No other subtasks were scheduled for this reporting period. However, negotiations are still in progress with Silverado and Thorofare Resources, Inc. to construct a 1,000 bbl/day FTE facility for commercial demonstration of the process.

3.2 Summary of Achievements

Project achievements for the time period of 1/1/94 to 3/31/94 are:

- The "Task 1 Report" is in final form and plans are to have the report printed according to new GRI specification as soon as possible. RETEC has agreed to take care of the printing.
- An abstract was accepted and a paper subsequently submitted for presentation at the "1994 Rocky Mountain Symposium on Environmental Issues in Oil and Gas Operations" to be held July 11-13, at the Colorado School of Mines in Golden, CO.
- The laboratory-scale simulator construction was completed and several shakedown attempts resulted in identification of two problems which delayed the simulator operation.
- Samples of produced water from a natural gas producing well in Weld County, CO; an oil and gas producing well near Brighton, CO; and a coal bed methane well in the San Juan Basin are in-house.
- Subcontracting arrangements are near completion with Evergreen Analytical Laboratories in Wheatridge, CO for volatile organic analyses (VOA), semi-VOA, and radionuclide analyses of simulation samples; and, subcontracting arrangements are near completion with the University of North Dakota (UND) Energy and Environmental Research Center (EERC) in Grand Forks, ND for metals, dissolved solids, and total organic carbon analyses of simulation samples. Analyses of the produced water samples obtained are expected to begin in April.
- Negotiations are still in progress with Silverado and Thorofare Resources, Inc. to construct a 1,000 bbl/day FTE facility for commercial demonstration of the process.

4.0 Planned Activities for the Next Quarter

During the upcoming quarter (April 1 - June 30, 1994), plans are to:

- conduct laboratory simulations and analyze samples (Subtask 2.1),
- begin modification of the economic evaluation software (Subtask 2.2), and
- continue negotiations with interested parties in an attempt to conduct a commercial demonstration of the process next year (Task 3).

The requirements for and work planned for Subtasks 2.1 2.2 are:

4.1 Subtask 2.1 Laboratory-scale Freeze-Thaw/Evaporation Simulations

The objectives of Subtask 2.1 are to: 1) design and construct a laboratory-scale simulator and simulation procedure for the freeze-thaw evaporation process; 2) optimize the FTE process design by conducting process simulations to evaluate the effectiveness of three differing freeze-thaw design options, two differing evaporation pond design options, and one solar distillation pond design option; 3) determine experimentally the impact of production water quality on the effectiveness of the FTE process; and 4) determine experimentally the impact of atmospheric conditions on the effectiveness of the FTE process. During the next quarter all efforts related to Subtask 2.1 will be directed towards the attainment of objectives 2 and 3.

4.2 Subtask 2.2 Re-evaluation of Process Economics Based Upon Laboratory-scale Simulation Results

The objective of Subtask 2.2 is to re-evaluate FTE process economics using the numerical model developed in Subtask 1.5 based upon Subtask 2.1 simulations results. As data are obtained from laboratory simulations, model modifications will be conducted during the next quarter

5.0 Summary

Task 1 is complete. Results of Task 1 research indicate the process has significant commercial economic potential and is an environmentally acceptable option to produced water disposal by deep well injection. Contacts have been and will continue to be made with oil and gas producers in the area. The objectives of these contacts are to obtain representative produced waters for testing and to discuss possible future involvement in the process demonstration. At the present time Thorofare Resources, Inc., Silverado Oil, and Southwest Water Disposal have expressed interest in demonstration of the process. Negotiations will continue with Silverado Oil and Thorofare Resources, Inc. to construct a 1,000 bbl/day FTE facility for commercial demonstration of the process in 1994.

The current project status is behind schedule but with no budget problems. The long-term impact of the schedule problem resulting from Subtask 2.1 efforts is not expected to delay contract completion at this time. Completion of Subtasks 2.1 and 2.2 will be delayed.

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

There were no project related publications during the reporting period. However, an abstract was accepted and a paper subsequently submitted for presentation at the "1994 Rocky Mountain Symposium on Environmental Issues in Oil and Gas Operations" to be held July 11-13, at the Colorado School of Mines in Golden, CO.

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