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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 sub-freezing 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 7/1/95 to 9/30/95, project research concentrated on Subtasks 2.0 (Task 2 Project Reporting) and 2.3 (Final Technical Report of the Simulation Results, Revised Process Economics, and Final Demonstration Plant Design and Economic Requirements). The objectives of Task 2 are to conduct laboratory-scale simulations for optimizing the design of the FTE process. Task 2 requires completion of three subtasks: Subtask 2.0 - Task 2 Project Reporting, Subtask 2.1 - Laboratory-scale FTE Simulations, Subtask 2.2 - Re-evaluation of Process Economics Based on Laboratory-scale Process Simulation Results, and Subtask 2.3 - Final Technical Report of the Simulation Results, Revised Process Economics, and Final Demonstration Plant Design and Economic Requirements. Subtasks 2.0 and 2.3 were planned to continue and Task 3 was scheduled to begin this quarter.

Research efforts this quarter were:

- to complete the required annual reports,
- to continue work to finalize the draft of the "Task 1 and Task 2 Report" (RETEC has requested that the Task 1 and Task 2 reports be combined for publication), and
- to obtain site information and design a 200 bbl/day FTE demonstration plant to operate in the San Juan Basin of New Mexico.

Subtask 2.2 was completed during the previous quarter. The revised process economics resulting from Subtasks 2.1 and 2.2 are more favorable than the initial economics resulting from Task 1 efforts. The results of the laboratory-scale FTE process simulations conducted in Subtask 2.1 were more favorable than the assumed process performance in Task 1. The key process performance parameters determined from Subtask 2.1 results that improved the process economics were:

- the contaminant concentration of the treated water produced was lower in the laboratory-scale simulations than the value assumed in Task 1 calculations,
- the contaminant concentration of the brine produced was generally higher in the laboratory-scale simulations than the value assumed in Task 1 calculations, and
- the evaporation efficiency, expressed as % of PAN evaporation, for the produced water holding pond was higher in the laboratory-scale simulations than the value assumed in Task 1 calculations.

The required annual reports were completed and submitted during the reporting period. Reports submitted included the Summary Annual Report, the Annual Revision of the Management Plan, the Milestone Plan and Milestone Log, and the Cost Plan for the next fiscal year. Monthly reports for July, August, and September 1995 were also submitted. The Quarterly Technical Progress Report for the time period of 4/1/95 to 6/30/95 was submitted.

Funding to conduct a field demonstration of the FTE process in the San Juan Basin of New Mexico has been obtained. John Boysen and John Harju of the

University of North Dakota Energy and Environmental Research Center (UND EERC) met with personnel from Amoco's Southwestern Business Unit August 28 - September 1, 1995 to begin work on the demonstration. A 200 bbl/day demonstration plant was designed for the site and construction will begin in October.

The draft of the "Task 1 and Task 2 Report" delineating all project research completed thus far is continuing at the end of the reporting period.

Plans for the next quarter are to:

- complete the final editing of the "Task 1 and Task 2 Report,"
- construct the demonstration plant in the San Juan Basin of New Mexico and begin operation,
- begin sampling and analysis of demonstration process streams,
- begin demonstration data evaluation, and
- start work on the final project report.

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 7/1/95 to 9/30/95, for evaluating the technical and economic feasibility of this water treatment process. The research required for development of this process can be completed in three tasks:

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

These three tasks as described above represent a change from previous plans which contained three tasks: 1) Literature Survey and Preliminary Economic Analysis, 2) Laboratory-and Bench-Scale Process Evaluation, and 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 the original Tasks 1 and 2; and if successful, funding for Task 3 will be solicited from other sources. Task 1 research has been completed. Results of Task 1 and the laboratory-scale process simulations completed in Subtask 2.1 strongly confirm the technical and economic viability of the process. Based upon these results, conversations with personnel of the Gas Research Institute (GRI), and conversations with independent oil and gas producers in the Rocky Mountain Region, a field demonstration of the FTE process will be conducted in-place of the bench-scale process simulations previously planned. Conducting the field demonstration at this time will greatly reduce the amount of time required for commercial-scale application of the process by: 1) demonstrating the technical and economic feasibility of the process and 2) demonstrating the environmental acceptability of the process. Demonstration of the technical and economic feasibility of the process is needed to obtain investment capital for commercialization and demonstration of the environmental acceptability of the process is needed to obtain the required permits for a commercial facility. A no-cost contract extension of the period of performance to 8/96 has been obtained and the demonstration plant is scheduled to begin operation during the next quarter. The FTE process can be proven ready for commercialization within the next twelve months. The modification to the original research plan is consistent with the project objectives and is cost-effective.

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-scale simulations for optimizing the design of the FTE process. Task 2 requires completion of three subtasks: Subtask 2.0 - Task 2 Project Reporting, Subtask 2.1 - Laboratory-scale FTE Simulations, Subtask 2.2 - Re-evaluation of Process Economics Based on Laboratory-scale Process Simulation Results, and Subtask 2.3 - Final Technical Report of the Simulation Results, Revised Process Economics, and Final Demonstration Plant Design and Economic Requirements.

Subtask 2.0 - Task 2 Reporting - Required project reports were submitted.

Subtask 2.3 - Task 1 and Task 2 Report - Work on the report of the simulation results, revised process economics, and final demonstration plant design and economic requirements continued during the reporting period. The demonstration plant design was completed during the reporting period for a 200 bbl/day facility in the San Juan Basin of New Mexico. Work on construction of the demonstration plant will begin in October 1995.

No other subtasks were scheduled for this reporting period.

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 1.1 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 is the laboratory-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 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.

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."

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 will include 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 will be conducted in conjunction with a separate project entitled "Demonstration of the FTE Process in the San Juan Basin of New Mexico." The field demonstration will confirm 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 will provide 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 will be conducted. Task 3 research will be 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" will support the demonstration project by evaluating the technical and economic operation of the FTE operation. The field demonstration of the process would better meet 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 will meet 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 has been 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 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-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 2.0 Task 2 Project Reporting

During the reporting period, monthly project reports required for the months of July, August, and September 1995 were completed and submitted to the US DOE Document Control Center at PETC and to RETEC. The Quarterly project report for the time period of 4/1/95 - 6/30/95 was also completed and submitted to the US DOE Document Control Center at PETC and to RETEC. The required annual reports were completed and submitted during the reporting period. Reports submitted included the Summary Annual Report, the Annual Revision of the Management Plan, the Milestone Plan and Milestone Log, and the Cost Plan for the next fiscal year. No budget or schedule problems exist for this subtask.

3.1.2 Subtask 2.3 - Final Technical Report of the Simulation Results, Revised Process Economics, and Final Demonstration Plant Design and Economic Requirements

Work on the report of the simulation results, revised process economics, and final demonstration plant design and economic requirements continued during the reporting period. The demonstration plant design was completed during the reporting period for a 200 bbl/day facility in the San Juan Basin of New Mexico. Work on construction of the demonstration plant will begin in October 1995. This subtask will be completed during the next quarter. No budget or schedule problems exist for this subtask.

Meetings were held during the reporting period with personnel from Amoco's Southwestern Business Unit to finalize plans for the field demonstration. John Boysen and John Harju of UND EERC attended these meetings in Farmington, NM from August 28 to September 1, 1995. The field demonstration plant was designed for the site to treat 200 bbl/day. Construction of the demonstration plant will occur during the next quarter. Sampling of process streams and data analysis will begin following the plant construction.

No other research was in progress during this reporting period.

3.2 Summary of Achievements

Project achievements for the time period of 7/1/95 to 9/30/95 are:

- Required monthly, quarterly, and annual reports were completed and submitted for the project.
- Meetings were held during the quarter to finalize field demonstration plant design requirements. The demonstration plant was designed to treat 200 bbl/day in the San Juan Basin of New Mexico. Construction of the demonstration plant will begin in October 1995.
- The draft of the "Task 1 and Task 2 Report" delineating all project research completed thus far is continuing at the end of the reporting period. (RETEC has requested that the Task 1 and Task 2 reports be combined for publication).

4.0 Planned Activities for the Next Quarter

During the upcoming quarter (October 1 - December 31, 1995), plans are to:

- complete the final editing of the "Task 1 and Task 2 Report",
- construct the demonstration plant in the San Juan Basin of New Mexico and begin operation,
- begin sampling and analysis of demonstration process streams,
- begin demonstration data evaluation, and
- begin work on the final project report.

5.0 Summary

Task 1, and Subtasks 2.1 and 2.2 have been completed. A literature survey, environmental regulatory assessment, survey of current disposal practices and economics, and numerical process and economic modeling have been completed (Task 1). Twenty one laboratory-scale process simulations have been also been completed (Subtask 2.1). Previous research and laboratory simulation results both confirm the process' potential to produce a useable quality treated water by significant and simultaneous removal of salts, organics, and heavy metals (including NORM). Results of twenty-one simulations completed all show significant concentration reductions of these species in the treated water. In the simulations, a natural gas produced water, an oil and gas produced water, and a coal bed methane produced water were treated with varied climatic conditions. Treated waters generated from simulations in which only 182 hours of sub-freezing conditions existed had TDS concentrations ranging from 200 to 430 ppm. The feed water TDS concentrations in these simulations ranged from 2640 to 10900 and the estimated TDS concentration in the evaporation pond prior to freezing ranged from approximately 4500 to 18,800 ppm. Detailed analyses of all of the treated waters produced in Simulation Series #5 indicate virtually all detectable inorganic, organic, and radionuclide components were significantly reduced compared to either the produced water feed or the water in the evaporation pond when the freezing treatment was initiated. The masses of brine produced in these simulations ranged from 5 to 28% of the feed input indicating a 72 to 95% reduction in disposal volume is achievable using the FTE process. The

simulations were designed to simulate climatic conditions of various regions but results analysis indicates the age of the ice pile (hours of freezing) was the key parameter affecting results. Since the simulations ran a year of climatic conditions in twenty four days, we expect a field demonstration to yield more favorable results. Even in a relatively mild climate such as the Farmington, New Mexico region, 1100 hours with sub-freezing temperatures typically occur annually. The maximum hours with sub-freezing temperatures in the simulations was 182 hours.

Economic results indicate the FTE process could reduce water disposal costs by 5 to 70% compared to conventional evaporation alone. The reduction depends upon the climate and feed water quality. Water disposal costs for an FTE facility in the San Juan that is fed with more than 500 bbl/day of 12,000 ppm TDS water range from \$0.05 to \$0.50/bbl. Treatment costs are dependent upon the facility size, state and federal regulatory requirements for pit construction, facility operation, and water discharge/use.

Results of all research completed continue to indicate the process has significant commercial economic potential and is an environmentally acceptable option to produced water disposal by deep well injection.

A no-cost contract extension of the period of performance to 8/96 has been obtained to continue this research through the next fiscal year to support a demonstration project in the San Juan Basin of New Mexico. Task 3 of this research will evaluate the field demonstration. Funding to conduct the field demonstration of the FTE process has been obtained. A 200 bbl/day facility was designed to operate in the San Juan Basin of New Mexico. Construction of the demonstration plant will begin in October 1995.

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