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

QUARTERLY TECHNICAL PROGRESS REPORT

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Prepared by:

Resource Technology Corporation
P.O. Box 1346
2931 Soldier Springs Road
Laramie, WY 82070

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Project Manager: John Boysen (307) 742-5651
Principle Investigator: John Boysen

Contracting Officer’s Representative: David Alleman (918)337-4455
United States Department of Energy
Bartlesville Project Office
P.O. Box 1398
220 North Virginia
Bartlesville, OK 74005

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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 1/1/96 to 3/31/96, project research concentrated on Subtasks 2.3 (Final Technical Report of the Simulation Results), 3.0 (Task 3 Project Reporting), 3.1 (Demonstration Sampling & Analysis), 3.2 (Demonstration Data Evaluation), and 3.3 (Final Project Report). The objectives of Task 3 are 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 technical and economic results of the field demonstration of the FTE process conducted in the San Juan Basin of New Mexico. Task 3 requires 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. Work on Subtasks 3.0, 3.1, 3.2, and 3.3 were conducted this quarter.

Research efforts this quarter were:

- to complete the draft of the "Task 1 and Task 2 Report",
- to complete sampling and analysis of the FTE demonstration process streams,
- to begin data evaluation of the demonstration based on the results of process stream analyses,
- to begin work on the final project report.

The Task 1 and Task 2 Reports were combined for publication and submitted on 1/20/96. The demonstration facility in the San Juan Basin of New Mexico was in operation during this period and sampling of the process streams has been completed. Initial process stream analyses have been favorable and analyses of the final samples collected are in progress. Operation of the demonstration plant was terminated in March 1996 due to difficulties at the Gas Research Institute (GRI). Originally, the demonstration plant was scheduled to run through the spring and summer to obtain evaporative data for evaluation. Agreement has been reached with the GRI to resume operation of the FTE demonstration plant in October 1996 and continue operation through the summer of 1997.

The Monthly reports for January, February, and March 1996 were submitted during the reporting period. The Quarterly Technical Progress Report for the time period of 10/1/95 to 12/31/95 was also submitted.

Plans for the next quarter are to:

- complete the process stream analyses,
- complete demonstration data evaluation, and
- complete work on the draft 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 1/1/96 to 3/31/95, 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. Tasks 1 and 2 are complete and the final report covering these tasks has been submitted. Funding for Task 3 has been solicited from other sources and a no cost contract extension of the period of performance to 8/6/96 was obtained from the Contracting Officer's Representative. A field demonstration of the FTE process is being conducted in-place of the bench-scale process simulations previously planned. Conducting the field demonstration at this time greatly reduces 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. 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 Subtask 2.3 and Task 3. Subtask 2.3 was completed in January of this reporting period. The objectives of Task 3 are 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 technical and economic results of the field demonstration of the FTE process conducted in the San Juan Basin of New Mexico. Task 3 requires 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 analyzed for organics, inorganics, and radionuclides. The results obtained were favorable. Final sampling of the demonstration plant process streams was completed on 3/18/96 and
final analyses for organics, inorganics, and radionuclides are in progress. Detailed analyses will be completed in the next reporting period.

Subtask 3.2 - Demonstration Data Evaluation - Preliminary data evaluation of the FTE demonstration plant in the San Juan Basin of New Mexico substantiates effective contaminant removal. Once detailed analyses are completed in the next reporting period, the demonstration data will be better quantified.

Subtask 3.3 - Final Project Report - Work has been initiated on the final project report. The results from the FTE demonstration plant in the San Juan Basin of New Mexico will be incorporated with the findings from the Task 1 and 2 Report.

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. 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 includes 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 has been 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 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. Sampling is complete and final analyses are in progress.
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 is being conducted. Task 3 research is being 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" supports 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 meets 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 2.3 - Final Technical Report of the Simulation Results and Revised Process Economics
The draft report of the simulation results and revised process economics was completed during the reporting period. No budget or schedule problems exist for this subtask.

3.1.2 Subtask 3.0 Task 3 Project Reporting
During the reporting period, monthly project reports required for the months of January, February, and March 1996 were completed and submitted to the US DOE Document Control Center at PETC. The Quarterly project report for the time period of 10/1/95 - 12/31/95 was also completed and submitted to the US DOE Document Control Center. No budget or schedule problems exist for this subtask.
3.1.3 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 analysed for organic, inorganics, and radionuclides. The results obtained were favorable. Final sampling was completed on 3/18/96 and detailed analyses will be completed in the next reporting period. No budget or schedule problems exist for this subtask.

3.1.4 Subtask 3.2 Demonstration Data Evaluation

Preliminary data evaluation of the FTE demonstration plant in the San Juan Basin of New Mexico have substantiated effective contaminant removal using the FTE process. Once detailed analyses are completed in the next reporting period, the demonstration data will be better quantified. No budget or schedule problems exist for this subtask.

3.1.5 Subtask 3.3 Final Project Report

Work has been initiated on the final project report. The results from the FTE demonstration plant in the San Juan Basin of New Mexico will be incorporated with the findings from the Task 1 and 2 Report. No budget or schedule problems exist for this subtask.

No other research was in progress during this reporting period.

3.2 Summary of Achievements

Project achievements for the time period of 1/1/96 to 3/31/96 are:

- Required monthly and quarterly reports were completed and submitted for the project.
- Operation of the FTE demonstration plant in the San Juan Basin of New Mexico was completed during the reporting period.
- Samples of demonstration process streams were taken on 2/1/96 and 3/18/96 for detailed organic, inorganic, and radionuclide analyses. Analytical results from February’s sampling have substantiated effective contaminant removal using the FTE process. Final analyses of March samples are currently in progress.
- The draft of the "Task 1 and Task 2 Report" was completed.

4.0 Planned Activities for the Next Quarter

During the upcoming quarter (April 1 - June 30, 1996), plans are to:

- complete analyses of demonstration process streams,
- complete demonstration data evaluation, and
- complete work on the draft final project report.

5.0 Summary

Task 1 (Literature Survey and Preliminary Economic Analyses) and Task 2 (Laboratory Scale Process Simulation) are complete. The draft "Task 1 and Task 2 Report" was submitted on 1/20/96. In the laboratory simulations (Task 2), a natural gas produced water, an oil and gas produced water, and a coal bed methane produced water were treated with varied climatic conditions. Results of these laboratory simulations and previous research 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). The feed water concentrations in simulations with 182 hours of freezing ranged from 2,640 to 10,900 ppm and the TDS concentrations in the evaporation pond prior to the onset of freezing conditions ranged from approximately 4,500 to 18,800 ppm. Treated waters generated from these simulations had TDS concentrations ranging from 200
to 430 ppm. The brines produced in these simulations indicated a 72 to 95% reduction in disposal volume is attainable using the FTE process. Results analysis indicated that the age of the ice pile (hours of freezing) was the key parameter affecting results.

Economic results indicate the FTE process can reduce water disposal costs by as much as 70% compared to conventional evaporation alone. The reduction depends upon the climate and feed water quality. Treatment costs are dependent upon the facility size, state and federal regulatory requirements for pit construction, facility operation, and water discharge/use.

Task 3 of this research is the evaluation of a field demonstration of the FTE process in the San Juan Basin of New Mexico. A 200 bbl/day facility was designed, constructed, and operated at an existing evaporation facility. The demonstration plant was in operation from December 1995 through March 1996. Subtask 3.1 (Sampling and Analyses of Field Demonstration Process Streams) is near completion. Initial samples from the demonstration process streams were taken on 2/1/96 and final samples were taken on 3/18/96. These samples were analyzed for organics, inorganics, and radionuclides. The detailed analysis of the final samples is in progress. Preliminary results illustrate effective contaminant removal in spite of the warmest winter in the San Juan Basin during the past 28 years.

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.

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