Oil & Natural Gas Technology

"Coalbed Methane Produced Water Treatment Using Gas Hydrate Formation at the Wellhead"

Submitted by:
BC Technologies, Ltd. LLC.
715 Grand Avenue
Laramie, WY 82070

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"Coalbed Methane Produced Water Treatment Using Gas Hydrate Formation at the Wellhead"

Final Scientific Report

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Principal Author:
John E. Boysen

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DISCLAIMER

ABSTRACT

Water associated with CBM production is a significant and costly process waste stream, and economic treatment and/or disposal of this water is often the key to successful and profitable CBM development. In the past decade, advances have been made in the treatment of CBM produced water. However, produced water generally must be transported in some fashion to a centralized treatment and/or disposal facility. The cost of transporting this water, whether through the development of a water distribution system or by truck, is often greater than the cost of treatment or disposal.

To address this economic issue, BC Technologies (BCT), in collaboration with Oak Ridge National Laboratory (ORNL) and International Petroleum Environmental Consortium (IPEC), proposed developing a mechanical unit that could be used to treat CBM produced water by forming gas hydrates at the wellhead. This process involves creating a gas hydrate, washing it and then disassociating hydrate into water and gas molecules. The application of this technology results in three process streams: purified water, brine, and gas. The purified water can be discharged or reused for a variety of beneficial purposes and the smaller brine can be disposed of using conventional strategies. The overall objectives of this research are to develop a new treatment method for produced water where it could be purified directly at the wellhead, to determine the effectiveness of hydrate formation for the treatment of produced water with proof of concept laboratory experiments, to design a prototype-scale injector and test it in the laboratory under realistic wellhead conditions, and to demonstrate the technology under field conditions. By treating the water on-site, producers could substantially reduce their surface handling costs and economically remove impurities to a quality that would support beneficial use.

Batch bench-scale experiments of the hydrate formation process and research conducted at ORNL confirmed the feasibility of the process. However, researchers at BCT were unable to develop equipment suitable for continuous operation and demonstration of the process in the field was not attempted.

The significant achievements of the research are:

- Bench-scale batch results using carbon dioxide indicate > 40% of the feed water to the hydrate formation reactor was converted to hydrate in a single pass.
- The batch results also indicate > 23% of the feed water to the hydrate formation reactor (> 50% of the hydrate formed) was converted to purified water of a quality suitable for discharge.
- Continuous discharge and collection of hydrates was achieved at atmospheric pressure.

Continuous hydrate formation and collection at atmospheric conditions was the most significant achievement and preliminary economics indicate that if the unit could be made operable, it is potentially economic. However, the inability to continuously separate the hydrate melt fraction left the concept not ready for field demonstration and the project was terminated after Phase two research.

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EXECUTIVE SUMMARY

A new, lower-cost treatment for CBNG produced water will reduce environmental compliance and disposal costs, and provide water for beneficial use in arid regions of the United States. U.S. oil production includes an average 10 barrels of water for each barrel of oil produced. Handling and disposal of this water is the single greatest environmental impediment to domestic oil production. Especially large volumes of produced water are generated in the Western States in association with oil and gas activities. High levels of total dissolved solids (TDS) make much of this water unsuitable for use, and it is economically infeasible to treat the water. However, a significant portion of the produced water, particularly water from CBNG development, has sufficiently low TDS levels to be used “as is” or to make treatment a feasible option.

There is tremendous need to turn wastewater from oil and gas operations into a useful product. Developing beneficial uses for produced water could reduce the costs of hydrocarbon development in the Western United States, thus increasing the Nation’s economically recoverable oil and gas resources. In addition, the produced water can be used to offset problems created by near-record drought conditions in recent years, develop wildlife habitat, and provide water for agriculture, industry, and other uses.

The project tasks are as follows:

Phase 1

Develop feasibility concept definition and proof of concept.

Perform background work, such as operator surveys, database searches, and literature review.

Conduct lab experiments using synthetic brines and gases.

Undertake lab testing of field brines and gases following the synthetic work.

Phase 2

Proceed with prototype development and testing.

Implement bench-scale, and, if successful, scale-up to larger prototype units.

Determine economic feasibility prior to proceeding to Phase 3.

Phase 3

Proceed with field demonstration and commercialization.

Implement field trial and technology transfer to other operators.

The following conclusions are drawn from the results of this research:

- Water can be treated at the wellhead to reduce surface handling costs.
- Reducing surface handling will also reduce environmental impacts such as fugitive dust created from truck traffic.
- Adverse impacts to sage grouse populations in southwestern WY will also be reduced with less truck traffic.
- Bench-scale batch results using carbon dioxide indicate > 40% of the feed water to the hydrate formation reactor was converted to hydrate in a single pass.
- These results also indicate > 23% of the feed water to the hydrate formation reactor (> 50% of the hydrate formed) was converted to purified water of a quality suitable for discharge.
- Continuous discharge and collection of hydrates was achieved at atmospheric pressure.
- The separation of melt fraction of the hydrates on a continuous basis proved very difficult and not suited for field demonstration at this time

- Preliminary economics indicate that if the unit could be made operable, it is potentially economic but at this time the concept is not ready for field demonstration.

While the batch bench-scale experiments indicated the process to be technically feasible, Phase 3 research was not attempted to the inability of developing a reliable continuous flow process

INTRODUCTION

Background

Finding sufficient natural gas reserves to meet future demands in the United States (U.S.) is a challenge facing energy producers today. Natural gas can be produced from a variety of sources. It can be generated in economic quantities from conventional natural gas wells, oil wells that produce natural gas in conjunction with oil, and methane production from coal seams. The long-term viability of the natural gas industry in the U.S. is depending increasingly on unconventional sources of natural gas such as coal bed methane (CBM) production. CBM production accounts for approximately 10% of the current U.S. natural gas production. 90% of this production is from basins in the Rocky Mountain region. In the future, the U.S. is expected to rely on CBM production from the Rocky Mountain basins to provide an even greater portion of the domestic natural gas supply. The estimated in-place natural gas in U.S. CBM basins is 646 trillion cubic feet (TCF) and less than 10% of this gas is estimated to be economically recoverable at present.

Produced water is the single largest residual generated during CBM production. In many cases, the management/disposal of produced water makes up a significant portion of the total gas production costs. The availability of cost-effective produced water management strategies plays a significant role in making vast potential CBM reserves within the U.S. economically viable. Field-ready produced water management options are needed to develop new and/or unconventional oil and gas resources.

Economic and efficient produced water management is complex. Produced waters contain mixtures of organic and inorganic compounds, including heavy metals. Many of these constituents interfere with treatment processes that are selective for other constituents. Further, the concentrations of organic and inorganic constituents vary widely with location and producing formation. In addition, regulations related to discharge and beneficial uses vary from state to state, basin-to-basin, and well location to well location.

Historically, acceptance by the oil and gas industry of advances in produced water management technology has been slow. The technical, regulatory, and economic viability of conventional deep well disposal under the Underground Injection Control program has made deep well injection the optimum water management solution in many areas of the U.S.. However, much of the new gas production from the continental U.S. is from coal seams centered in low-permeability basins. These basins often lack formations suitable for water disposal, and when a potential disposal zone is present, these formations are frequently deep and exhibit low-permeability, which significantly increases the cost of disposal well drilling, completion, and operation (due to the high pressures needed to inject into these formations). In these basins there is a great need for economic methods for produced water management.

In addition, many western CBM basins are in remote locations resulting in expensive water handling costs also being associated with produced water management. For example, in

CBM producing basins in southwestern Wyoming and northwestern Colorado currently under extensive development of both CBM and conventional natural gas, it is not uncommon for water transportation costs to range between $1.00 and $10.00 per bbl and disposal costs typically range between $1.00 and $2.50 per bbl. The two major CBM basins in this area are the Greater Green River Basin (GGRB) and the Piceance Basin (PB). Together these two basins contain an estimated 413 TCF of gas in-place with the GGRB containing 314 TCF and the PB containing 99 TCF. The two basins alone contain 64% of the estimated U.S. CBM gas in-place. The coal seams in these basins are deeper and of lower permeability than the San Juan and Powder River Basins which are currently commercially developed. Also, the quality of produced water from these seams is lower than the developed basins. For natural gas production from these CBM basins to be economic, technologies to reduce both water disposal costs and water handling costs are needed.

Further, in the arid climates typical of these two basins and much of the western U.S., the increasing population base and the prolonged drought conditions across the region, coupled with demands for fresh water (i.e. agricultural, industrial, recreational, and residential use), are steadily increasing demand for clean water. This has created a significant incentive to recycle produced water for a variety of beneficial uses. In addition, fugitive dust levels in these areas are high and a reduction in produced water hauling in these areas would have a significant positive impact on air quality.

Project Objectives

For the above reasons a research project was initiated with the following objectives:

- To develop a new treatment method for produced water where it could be purified at the wellhead.
- To determine the effectiveness of hydrate formation through laboratory experimentation.
- To design a prototype-scale injector and test it under realistic wellhead conditions.
- To demonstrate the technology under field conditions.

Desalination Concept

Natural gas hydrates contain concentrated gases such as methane or carbon dioxide and are a crystalline solid that consists of a gas molecule surrounded by a cage of water molecules. Figure 1 represents the natural gas hydrate molecule. The image is courtesy of Oak Ridge National Laboratory (ORNL).

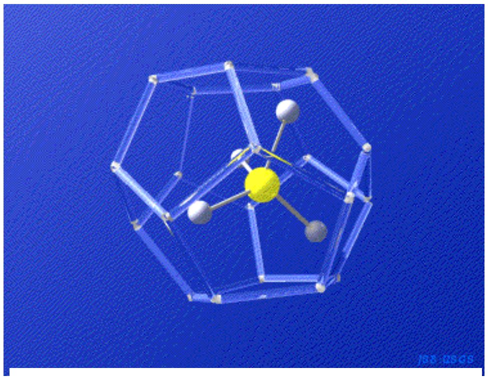

Figure 1. Natural Gas Hydrate Molecule

Hydrates are solid crystalline compounds composed of cages of hydrogen-bonded water molecules that trap gases such as CO_2 and CH_4. The formation of hydrate excludes solids, dissolved species and most organic species. When the hydrate is dissociated, gas, purified water and a stream with concentrated chemical constituents are produced.

Temperatures and pressures required for stable hydrate formation differ with the type of gas forming the hydrate. Stable hydrate formation using carbon dioxide requires relatively low temperatures (0 – 10^{o}C) and reasonably high pressures (10-13 MPa). The hydrate formation system U.S.es a self-contained co-flow (twin fluid) injection device for in-situ hydrate formation and operates at elevated pressures (10 – 13 MPa) and temperatures between 0 and 10°C. It is possible to reduce water treatment costs by converting a major portion of produced water from wells to gas hydrates at the wellhead. The gas hydrates can then be disassociated by pressure reduction to produced purified water and a stream with concentrated chemical constituents gas at the wellhead. The end result is a reduction in the volume of water requiring transportation and disposal and a significant reduction in related costs.

EXPERIMENTAL METHODS FOR CONTINUOUS HYDRATE FORMATION

The project phases and tasks are as follows:

Phase 1

- Develop feasibility concept definition and proof of concept.
- Perform background work, such as operator surveys, database searches, and literature review.
- Conduct lab experiments using synthetic brines and gases.
- Undertake lab testing of field brines and gases following the synthetic work.

Phase 2

- Proceed with prototype development and testing.
- Implement bench-scale, and, if successful, scale-up to larger prototype units.
- Determine economic feasibility prior to proceeding to Phase 3.

Phase 3

- Proceed with field demonstration and commercialization.
- Implement field trial and technology transfer to other operators.

Phase 1

Concept Definition and Proof of Concept

ORNL personnel were responsible for concept definition and proof of concept experiments. The first hydrate experiments were conducted in a small-scale pressure vessel to define the concept prove of concept. These experiments used a water solution with starting salinity of 3.5%, and were conducted by forming hydrate in a 450 ml stirred tank reactor filled with ~400 ml of salt water (see Figure 2). Hydrate was separated from the excluded saline water and then dissociated. The salinity of the thawed water was measured. In some experiments a nucleating agent (Snowmax ®) was introduced. These preliminary experiments showed that gas hydrates can reduce the salinity of water. In experiments with no nucleating agent, the salinity was lowered to approximately 0.9%. Experiments using nucleating agents yielded salinities of 0.5% and 0.2%. The successes of these experiments prompted the development of larger-scale experiments. (1)

In a previous ORNL research project, a co-flow injection system was demonstrated to rapidly and continuously produce hydrate deep in the Pacific Ocean from seawater with salinity levels of 3.5% using CO_2 as the hydrate forming gas. Based upon the results of this research, a new injector was developed to mix gas and water to rapidly form hydrate and a series of injections at high salinities were conducted in the 70 liter pressure vessel at ORNL. The ORNL co-flow injection technology was used to make gas hydrates from produced water and various selected gases.(1)

	Starting Salinity (ppt)	**Final Salinity (ppt)**
Expt. 1	35	**9**
*Expt. 2	35	**5**
*Expt. 3	35	**2**

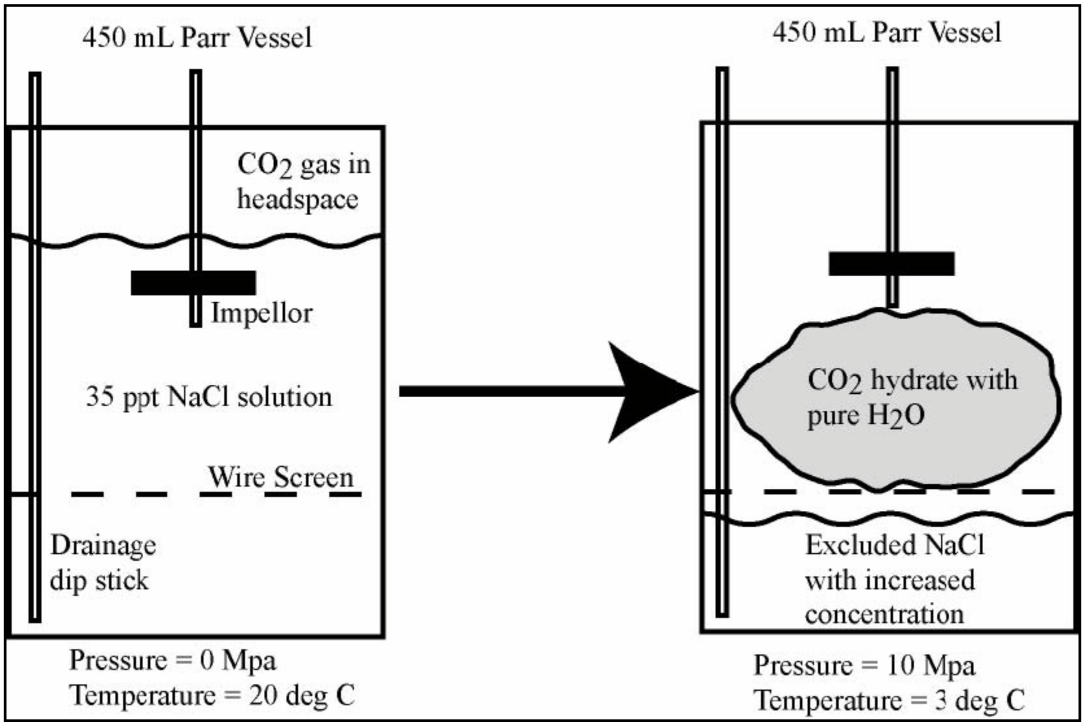

Figure 2. Preliminary Experimental Set-up and Results (1)

A continuous-jet hydrate reactor (CJHR) had already been developed to form hydrate on a continuous basis. The CJHR receives produced water and hydrate forming gas at one end and extrudes hydrate solid particles at the other end. Experiments are conducted using a 72-L pressure vessel that allows visual observation of the hydrate particles. The CJHR (Figure 3), which was developed to form hydrate on a continuous basis, was mounted inside the Seafloor Process Simulator (SPS) (Figure 4), a cylindrical Hastelloy C-22 vessel of 31.75-cm diameter, 91.44-cm length and 72-l volume. The vessel is equipped with sapphire windows and sampling ports and can be maintained at pressures of up to 20 MPa. (1)

The SPS allows operational pressures equivalent to those encountered at various ocean depths to be maintained during laboratory experiments. The entire reactor was submerged and at equilibrium with the vessel. This setup required the use of a submersible pump (Seabird SBE 5T) to circulate water from within the SPS, at a controlled flow rate, into the CJHR. Within the CJHR, the water was then mixed with liquid CO_2 injected from outside the SPS. This CO_2 was injected via a pulsating pump from a pressurized cylinder. During the operation, water was recycled. The SPS was configured with a pressure transducer and a thermocouple was submerged below the waterline within the SPS. LabView software was used to monitor and record internal pressure and temperature conditions. The SPS was filled with spiked water and nitrogen was used to pressurize the vessel. (1)

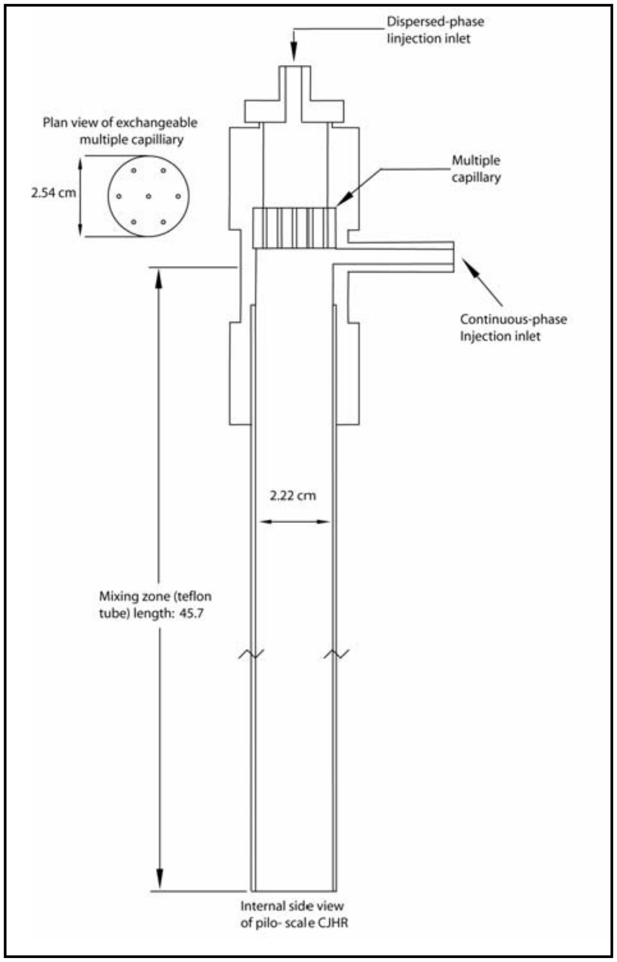

Figure 3. Schematic of the CJHR (1)

Figure 4 is an image of the SPS used at ORNL for proof of concept testing. The CJHR was used to form hydrate in all experiments. Experiments were conducted with under similar conditions. Pressures were maintained at within 0.3 MPa of 10.3 MPa for all experiments. Initial salinities of spike water were kept between 6000 TDS and 7000 TDS, and initial temperatures ranged between 1.5°C and 2.0°C. Continuous hydrate production was performed inside the pressurized vessel for up to 20 minutes, leading to the formation of several liters of hydrate.

After hydrate production stopped, unreacted water was drained from the vessel. The hydrate was allowed to dissociate. The salinity of the water released during hydrate dissociation was monitored. (1)

Hydrate treatment experiments were conducted with hydrate stored above and below water after formation and before dissolution. In experiments with hydrate stored under water, the CJHR was oriented so hydrate was extruded downward onto a submerged screen. Hydrate was formed for approximately 20 minutes. After pumps to the CJHR were stopped the water was drained and the hydrate was allowed to dissociate. (1)

Hydrate product was stored above water for two reasons: to decrease dissolution of hydrate through water contact, and to allow saline water to "drip" off of the hydrate after formation. In hydrate treatment experiments where hydrate was stored in gas, the CJHR was oriented so that hydrate was extruded upward onto a screen placed above the water within the 72-L high pressure vessel. Hydrate was formed for approximately 10 minutes. The water was drained and the hydrate was allowed to dissociate." (1)

Figure 4. ORNL Seafloor Process Simulator

Operator Surveys, Database Searches and Literature Review

Background work, such as operator surveys, database searches, and literature review were completed. The literature survey involved locating and reviewing applicable NEPA (National Environmental Policy Act) documents, such as Environmental Assessments and Environmental Impact Statements completed by producers with CBM leases in the GGRB. An extensive listing is provided in a internal report, which was used by the project team and was provided to DOE/NETL. The NEPA documents are available electronically on the Wyoming Bureau of Land Management website (http://www.wy.blm.gov" [external site]).

A review of the Wyoming Oil and Gas Conservation Commission (WOGCC) databases was completed to acquire well data on permitted CBM wells in the GGRB. In October-November 2005, data from the website (http://wogcc.state.wy.us./) were downloaded and entered into an Access database developed by BCT personnel. This database was checked and updated in December 2005, April 2006, and November 2006. Additional updates continued through the spring and summer of 2007 to add new wells and update production statistics. Tracking the well data in this fashion has provided considerable useful data on the level of permitting activity, operators, well locations, well depths, producing formations, production activity, and to a limited extent, water quality data for currently producing CBM wells in the basin.

Phase 2

Prototype Development and Testing

BCT personnel conducted prototype development and started bench-scale experiments in 2007. The primary issues to be addressed were how to operate the CJHR in a continuous or semi-batch mode and the design of the heat transfer systems required for hydrate formation and gas/treated water/brine separation during hydrate dissociation.

The CJHR was originally designed by ORNL to discharge hydrate into the deep ocean where substantial pressure exists. In effect, the CJHR discharges into a vessel operating at elevated pressure in the ORNL laboratory-scale experiments. Keeping the hydrate under pressure during dissociation causes operating difficulties related to gas/treated water/brine separation during hydrate dissociation and is difficult to envision in continuous or semi-batch mode operation. Further, the high pressures required by the process and relatively low hydrate density desired would require very expensive equipment to hold the hydrate under pressure during dissociation. However, the CJHR is compact and it was decided to determine if the CJHR could be operated under pressure to form hydrates that could be discharged into low pressure vessels for dissociation. To achieve this objective, an adjustable gas spring and a cone were added to the CJHR outlet to maintain the desired pressure inside the CJHR (Figure 5).

Next, it was decided that control of the initial dissociation of the hydrate could be achieved and controlled by controlling the temperature in the first dissociation chamber. Brine and gas from hydrate dissociation can be easily separated and collected from the first chamber. The remaining solids (hydrates) can then be transferred to a final dissociation chamber where the hydrate is rapidly dissociated. The initial prototype is a batch system. A block flow diagram of the initial prototype is illustrated in Figure 6.

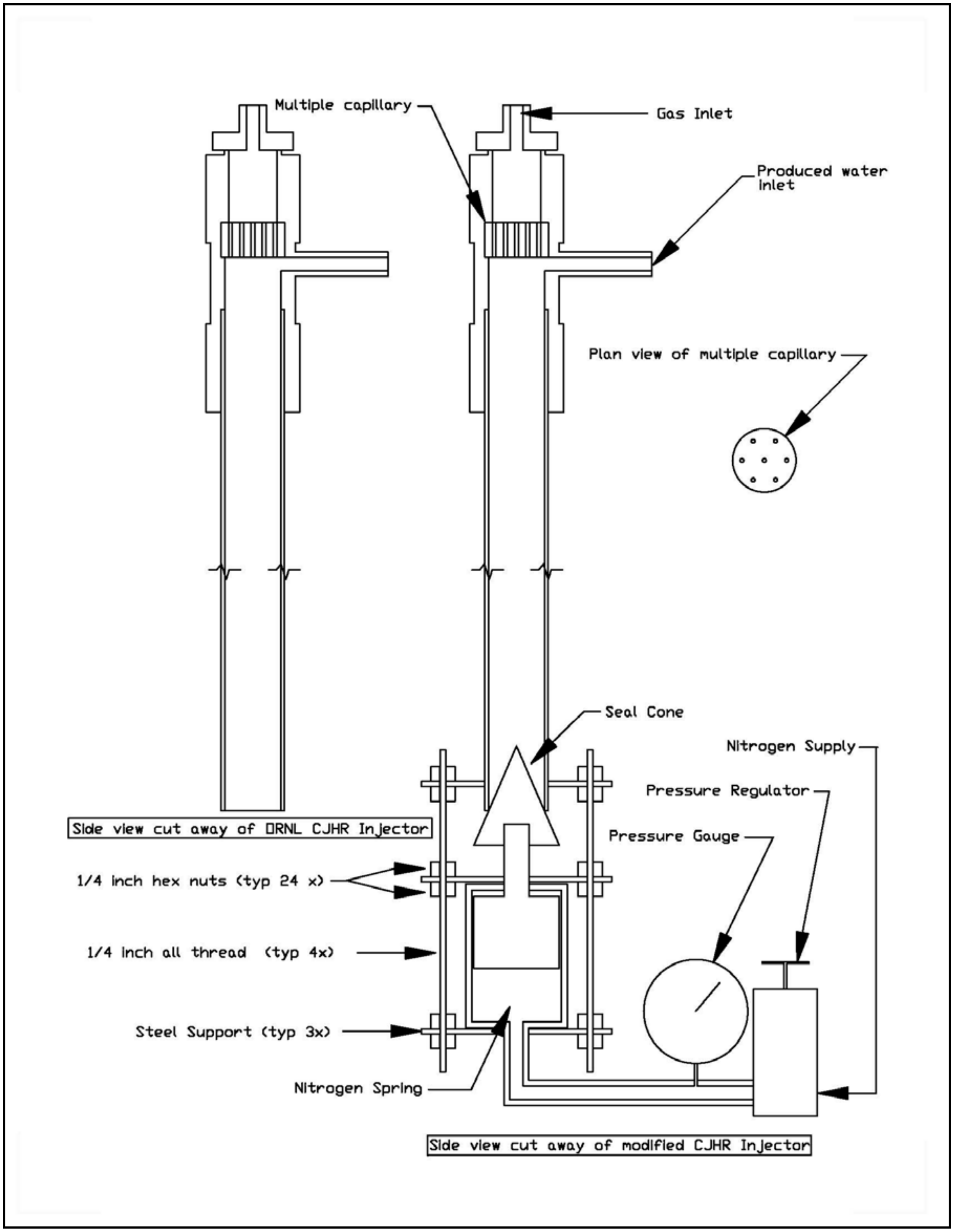

Figure 5. Modifications made to ORNL CJHR Injector for Hydrate Discharge at Atmospheric Pressure

Three heat exchange systems were designed for hydrate formation and gas/treated water/brine separation during hydrate dissociation. The first refrigeration system is the water chiller system. It utilizes a standard refrigerant compressor. The compressed refrigerant is cooled and condensed by ambient air. The condensed refrigerant is then evaporated in a shell and tube heat exchanger cooling the feed water (Figures 6). The second heat exchange system utilizes a standard "walk in cooler" refrigerant compressor with the compressed refrigerant air cooled. This refrigeration system is used to control the temperature in the hydrate collection chamber which operates at atmospheric pressure (Figure 6).

Construction of the bench-scale batch simulator was initiated in summer 2007 and tested in 2008. After a lengthy shakedown and modification period, production of carbon dioxide hydrate at atmospheric pressure was achieved. Hydrate formation and salinity reduction were tested first in a simple bench-scale unit constructed to evaluate the requirements for application of the concept. Seventy-five experiments were completed in the bench-scale unit. The experimental procedure used was as follows.

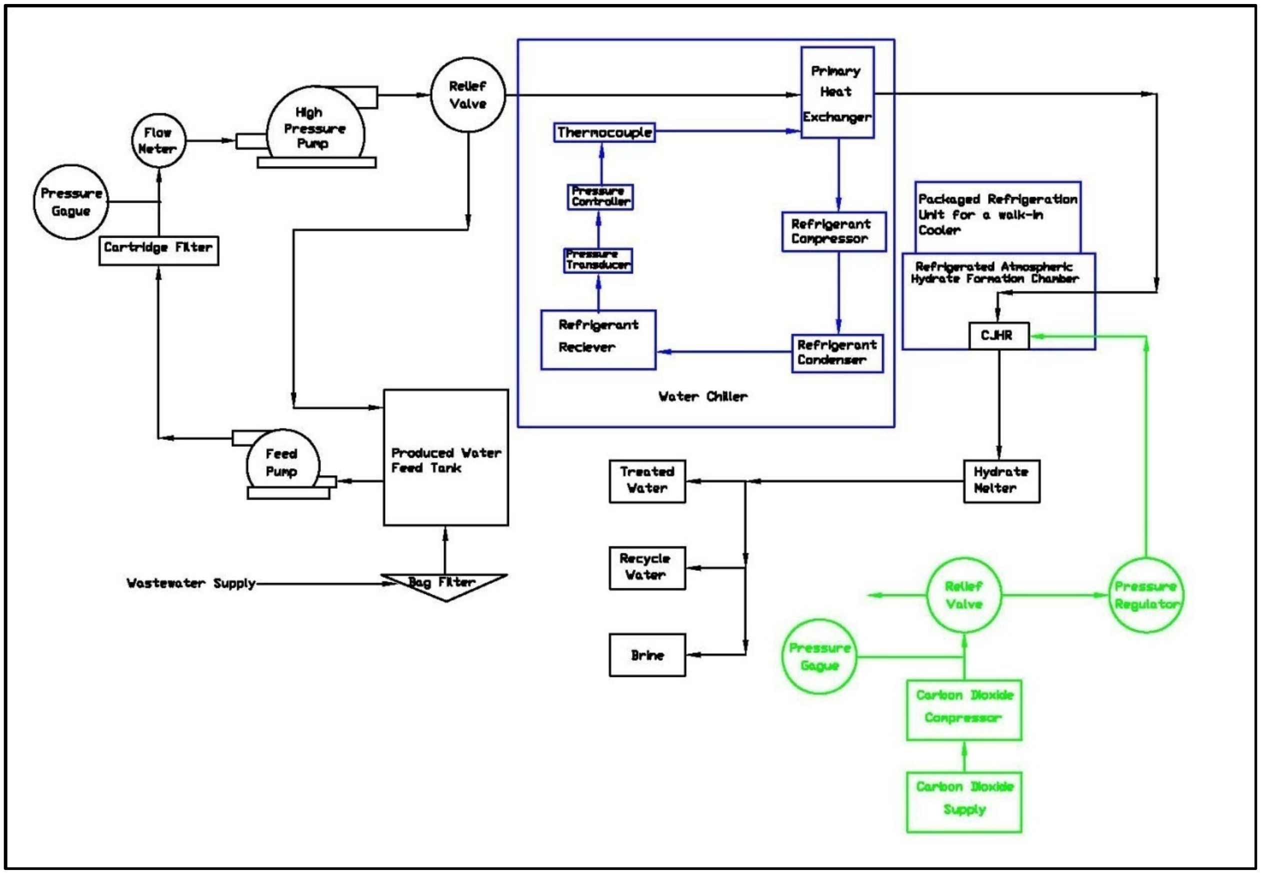

Figure 6. Block Flow Diagram of the Bench-scale Batch Hydrate Formation System

Experimental Procedure for Bench-scale Batch Hydrate Formation System

Set-up and Start-up:

- Make sure all water is pumped out of system and recorded properly from previous test.
- Measure water for feed tank and fill tank.
- Check and record electrical conductivity (EC) every three gallons.
- Turn on low pressure pump.
- Adjust water valves to ensure proper flow through system. System should be set up only for recycling water through both heat exchangers on chiller unit. No flow to injector.
- Check for flow.
- Measure EC of mixture after recycling 5 minutes.
- Close and secure all doors.
- Turn on Digital Temperature Scanner.
- Record starting water temperatures.
- Put on safety glasses and hearing protection.
- Turn on hydrate formation chamber refrigeration unit. (A/C unit)
- Turn on water chiller system.
- Set desired water temperature on the temperature controller.
- Turn on CJHR band heater. Set heater to 6 amps and 80°F.
- Wait for water to cool to temperature set point (typically 15-25 minutes).
- Ensure all valves on CO_2 manifold are correctly positioned.
- Open CO_2 bottle and record initial bottle pressure.
- The CO_2 booster compressor should read 34 psi on stage one. This is the pressure supplied through the regulator to the CO_2 compressor. Adjust if necessary.
- Turn on CO_2 booster compressor.
- Make sure the valve to CJHR is open and pressure is building.
- Turn on the high pressure pump. Open water valve to CJHR and slowly increase regulator pressure to desired level.
- Make sure that the injector opens and is spraying. It may take higher pressure levels to "crack" the injection port. Set pressure to desired level after initial "cracking".

Operation:

- Record temperatures and pressures on spreadsheet every 30 minutes.
- Record recycle water mass and ECs.
- Monitor water chiller refrigeration unit, hydrate formation chamber refrigeration unit, CO_2 booster compressor, and CJHR for proper function.
- Record adjustments, defrost cycles, and freeze-ups.
- Change CO_2 supply tanks as needed.

Shutdown:

- Record final temperatures and pressures.
- Slowly reduce pressure to high pressure water pump.
- Close water valve to CJHR.
- Turn off CO_2 booster compressor, high pressure water pump, hydrate formation chamber refrigeration unit and CO_2 recycle pump.
- Turn off both heat exchangers on water chiller unit.
- Recycle water and wait for unit to decompress.
- Turn off band heater.
- Spin hydrate formation chamber rotation motor.
- Record recycle water amount and EC.
- Pump out remaining feed water. Record amount and EC.
- Disassemble unit to dry.
- Collect any hydrate still in chamber.
- Melt hydrates and record weight and EC of melt fractions.

After completion of the experiments using the bench-scale batch simulator effects were conducted to construct a continuous flow prototype system (CFPS). The batch simulations of hydrate production and dissociation provided data to estimate brine and treated water yields and qualities. This information was used to complete the designs of the gas collection and recompression systems, the continuous flow hydrate formation chamber and continuous flow hydrate melt separator for the CFPS.

The gas collection and recycle system was modified by adding a low pressure recycle CO_2 compressor to provide gas to the CO_2 booster compressor from the hydrate formation system. The hydrate formation chamber was mounted with seal bearings, an electric motor and belt drive to rotate the hydrate formation chamber. As the formation chamber rotates, a knife that was also installed scrapes the hydrates from the walls of the chamber allowing them to drop into the feed system for the screw conveyor installed for separating the hydrate melt fractions. A 2-inch diameter feed screw was installed for this function. The screw could be operated at adjustable angles and speeds. Also, an electric heater with fan was also installed on the screw to increase the speed of melting if need. The screw also had three ports for collecting the different melt fractions.

Thirty-seven experiments were attempted using the screw conveyor for hydrate melt separation. All were unsuccessful. A feed hopper with a twin screw conveyor was added to the system to assist the movement of the hydrates through the conveyor for melt separation. The conveyor operation was tested at angles ranging from -10 to 45 degrees. In all cases the conveyor separation was not effective. However, the rotating hydrate formation chamber and CO_2 recycle systems operated effectively. It was decided to replace the screw conveyor for melt separation.

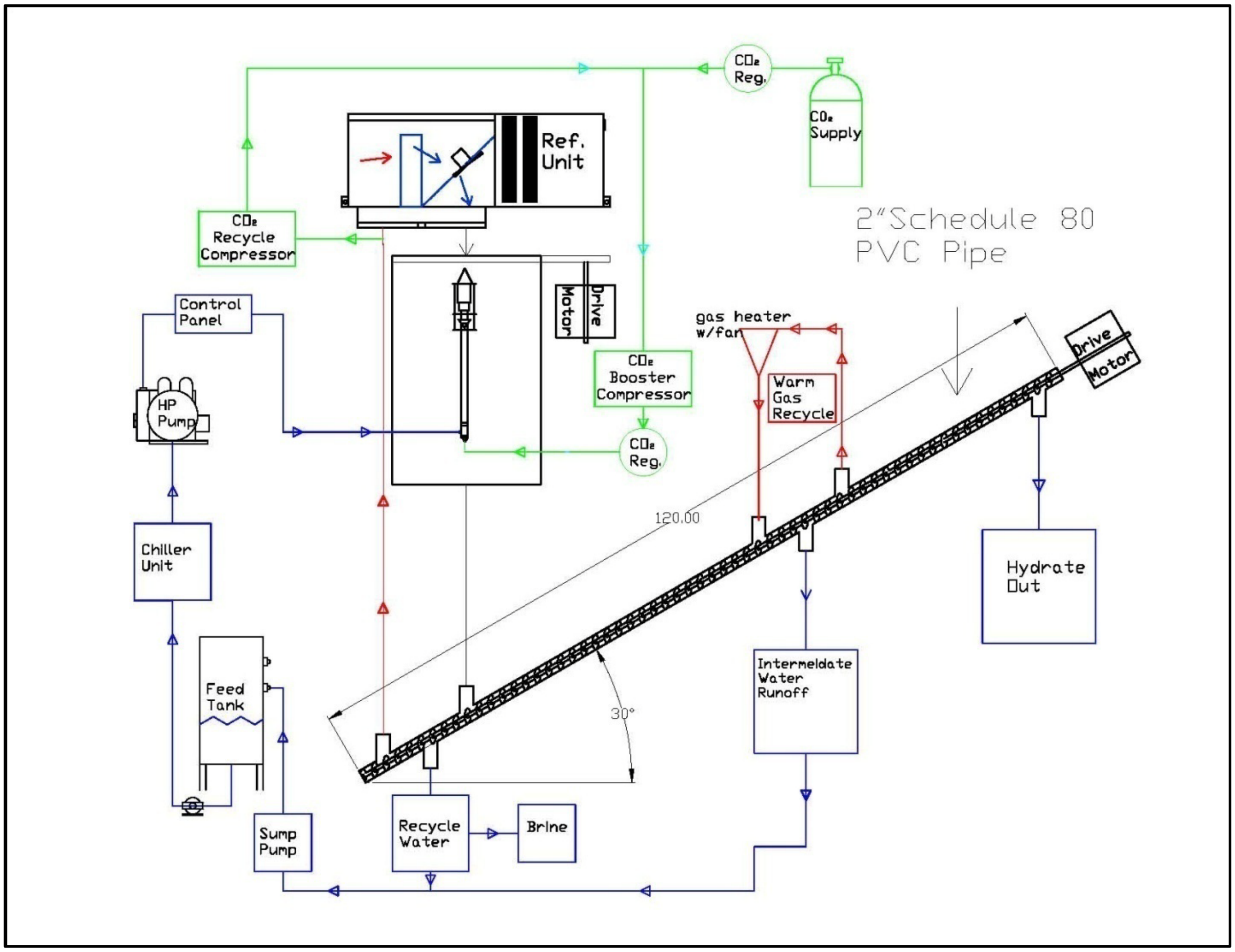

Figure 7. Block Flow Diagram of the Initial Continuous-flow Prototype System

A four compartment rotating hydrate melter (FCRHM) was added to the unit to improve the performance of the CFPS (Figures 8 and 9). In addition, the return air flow duct to the refrigeration unit cooling the atmospheric hydrate formation chamber was increased in size to increase the cool gas flow rate through the chamber.

The construction of the FCRHM is illustrated in Figure 9. The FCRHM is cart mounted for ease of maintenance. A heavy duty turntable is mounted to the cart and a high density polyethylene (HDPE) frame was constructed and mounted to the turntable. The HDPE frame was design to hold the four hydrate collection chambers each having a volume of five gallons.

During operation of the CFPS, hydrates drop from the hydrate formation chamber into one of the collection chambers. The chambers are rotated on a timed sequence so that one hydrate chamber is filling (position 1), one chamber is in initial melt flowing brine (position 2), the next chamber is in intermediate melt flowing water that will be recycled (position 3) and the fourth chamber is in final melt producing treated water (position 4). Positions 3 and 4 are equipped electric air heater with fans to control the melt rate in these chambers.

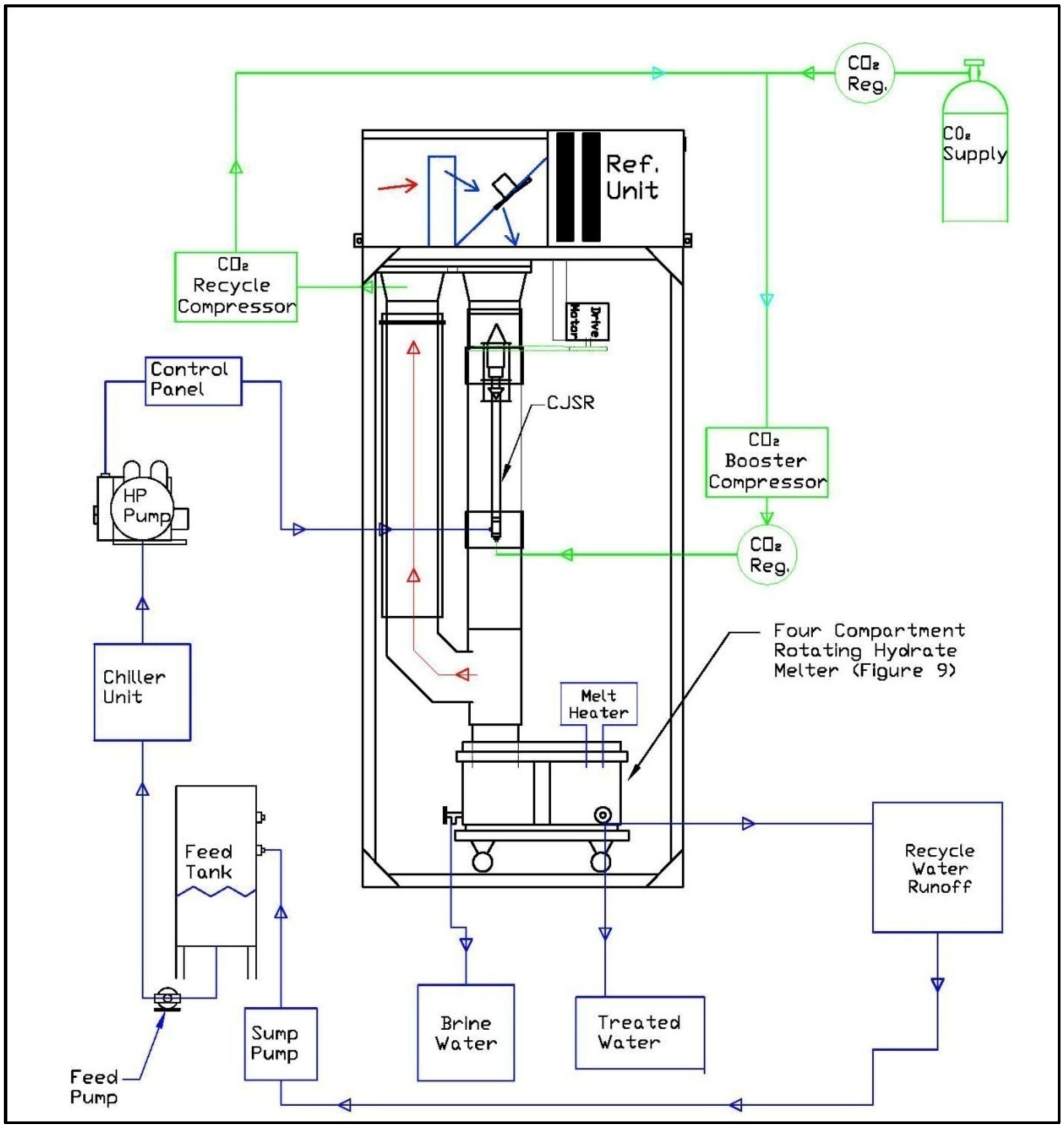

Figure 8. Flow Schematic of the Final Continuous-flow Prototype System

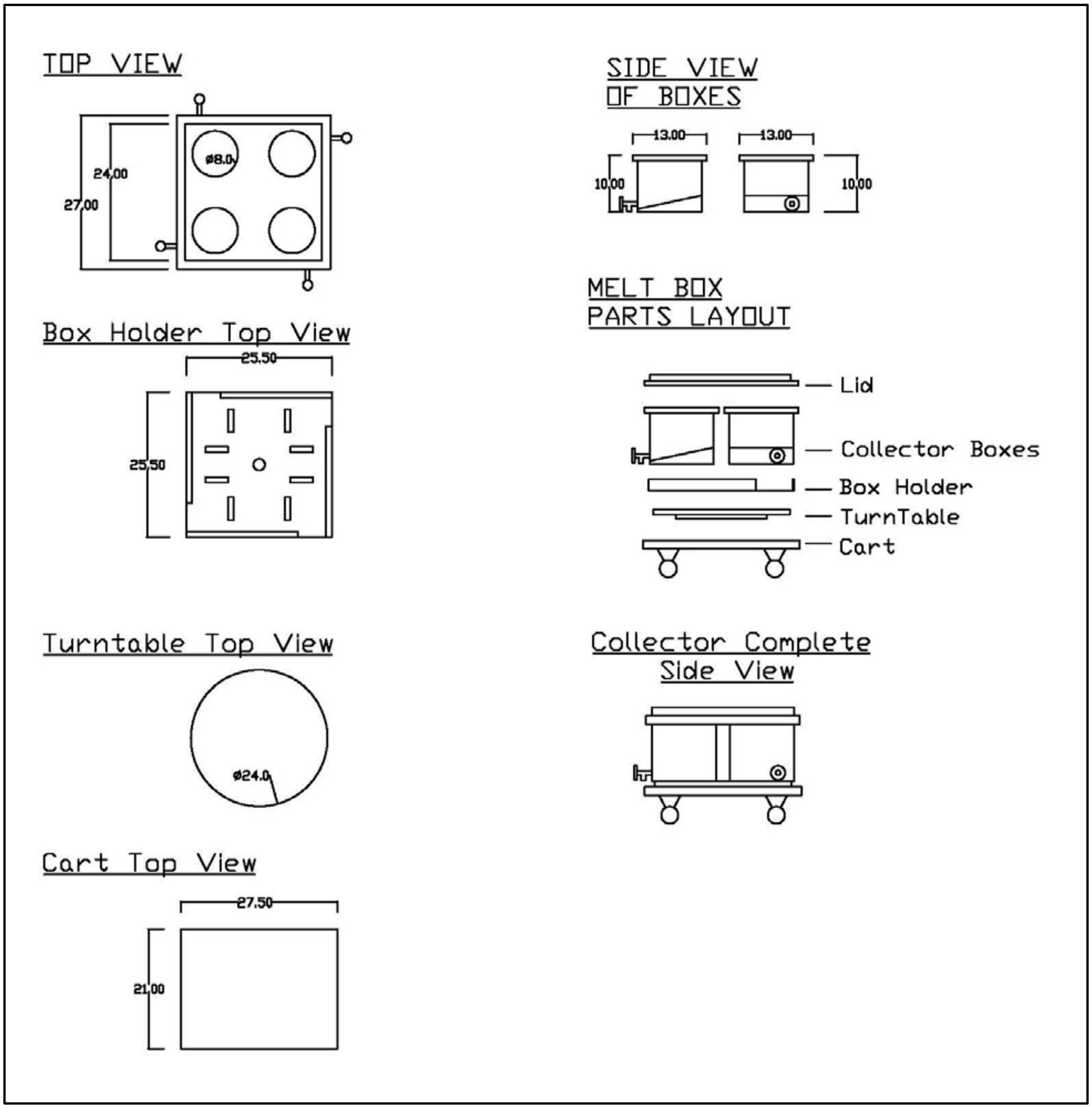

Figure 9. Construction Details of the Four Compartment Rotating Hydrate Melter

Upon completion of the modifications to the CFPS twenty experiments were completed in the unit. Following is the experimental procedure for these experiments.

Experimental Procedure for the Final Continuous-flow Prototype System

Set up and Start up:

- Make sure all water is pumped out of the system and recorded properly from the previous test.
- Clean bearings on spin chamber and properly lubricate as needed.
- Check gaskets for normal wear. Replace if necessary.
- Assemble spinning chamber and 8" tee, then place into position. Tighten bolts onto the frame.
- Slide melt boxes into position and lock wheels in place.
- Slide recycle tank into position and open valve on desired melt box.
- Place the insulation around the 8" tee and elbow.
- Measure water for feed tank and fill.
- Check and record EC every three gallons.
- Turn on low pressure pump.
- Adjust water valves to ensure proper flow through system. System should be set up only for recycling water through both heat exchangers on the chiller unit. No flow to injector.
- Check for flow.
- Measure EC of mixture after recycling 5 minutes.
- Turn on digital temperature scanner.
- Record starting water temperatures.
- Put on safety glasses and hearing protection.
- Turn on hydrate formation chamber refrigeration unit. (A/C unit)
- Turn on water chiller system.
- Set desired water temperature on the temperature controller.
- Turn on CJHR band heater. Set heater to 6 amps and 80°f.
- Wait for water to cool to temperature set point (typically 5-10 min).
- Turn on hydrate formation chamber rotation motor - set to 5 amp.
- Ensure all valves on CO_2 manifold are correctly positioned.
- Open CO_2 bottle and record initial bottle pressure.
- The CO_2 booster compressor should read 34 psi on stage one. This is the pressure supplied through the regulator to the CO_2 compressor. Adjust if necessary.
- Turn on CO_2 booster compressor.
- Make sure the valve to CJHR is open and pressure is building.
- Open water valve to CJHR and slowly increase the water pressure to desired level.

- Make sure that the injector opens and is spraying. It may take higher pressure levels to "crack" the injection port. Set pressure to desired level after initial "cracking".

Operation:

- Turn on CO_2 recycle pump.
- Open/close valves as required.
- Record temperatures and pressures on spreadsheet every 30 min.
- Record recycle water mass and EC's.
- Monitor water chiller refrigeration unit, hydrate formation chamber refrigeration unit, CO_2 booster compressor, and CJHR for proper function.
- Record adjustments, defrost cycles, and freeze-ups.
- Change CO_2 supply tanks as needed.
- Rotate melt boxes as needed.
- Connect melt hose.
- Melt hydrates - record grams and EC.

Shutdown:

- Record final temperatures and pressures.
- Slowly reduce pressure to high pressure water pump.
- Close water valve to CJHR.
- Turn off CO_2 booster compressor, high pressure water pump, hydrate formation chamber refrigeration unit and CO_2 recycle pump
- Turn off both heat exchangers on water chiller unit.
- Recycle water and wait for unit to decompress.
- Turn off band heater.
- Spin hydrate formation chamber rotation motor.
- Record recycle water amount and EC.
- Pump out remaining feed water. Record amount and EC.
- Disassemble unit to dry.
- Collect any hydrate still in chamber.
- Melt hydrates and record weight and EC of melt fractions.

The modifications to the CFPS improved the performance of the system. The rate of hydrate formation increased considerably. Separation of the melt improved considerably over the screw conveyor separator. However the separation required to generated significant water for discharge was not achieved and it is obvious that the CFPS is not economic or suited for field demonstration. For this reason, Phase #3 of the process was not conducted.

RESULTS AND DISCUSSIONS

Phase 1

ORNL was funded to conduct Phase 1 of this research under a separate contract from the United States Department of Energy (USDOE). A report providing detailed results of the research can be found in the literature (1). In their research, they proved the technical feasibility of the concept, developed a CJHR suitable for making hydrates from produced water in a batch system and provided temperature and pressure operating ranges for CO_2 hydrate formation from produced water.

Phase 2

Using the injector provided by ORNL, the ORNL system was scaled up to handle larger volumes of water produced. Hydrate formation and salinity reduction under atmospheric conditions were tested in the bench-scale batch hydrate formation system. A bench-scale (1-2 bbl/day) demonstration of the process was used to verify the scale-up (25-50 bbl/day are typical CBM flow conditions). Summaries of experimental results and conditions of the bench-scale batch hydrate formation system are provided in Appendix A. With respect to the mass yield summaries in the appendix, the experimental products are defined by their composite EC as follows:

- Brine EC > 2 * Feed EC
- 2 * Feed EC > Recycle EC > 3
- 3 > treated water EC

The combined results of three selected experiments that were in sequence without disassembly are used to illustrate the general behavior of the hydrate process. The EC of the hydrate melt for these experiments verses the percent of melt is illustrated in Figure 10. The asymptotic shape of the curve is typical of the hydrate melt in general. The figure illustrates reasonably similar melt curves for these three experiments that were operated under similar conditions. The feed in these experiments was produced water from a treatment facility in south-central Wyoming with an EC of 24.5 mS/cm. The combined mass yield expressed as a percentage of the total feed for the selected experiments is illustrated in Figure 11. The data in the figure illustrate that for these three experiments in a single pass to treated water, 26.1% of the total feed water converted with a EC of approximately 3 mS/cm, 70.1 % of the feed would need to be recycled further having an EC of 23.6 mS/cm and experimental losses were reasonable at 3.8% of the feed. These results are near the average results for all 75 batch-simulations. The average, maximum and minimum values for mass yield data from the 75 batch experiments are provided in Table 1:

- average treated water yield = 19.6% of feed
- average recycle water yield = 59.7% of feed
- average brine yield = 2.4% of feed
- average losses = 18.3% of feed.

These data illustrate that experimental losses were a significant problem. These losses were generally related to equipment failure.

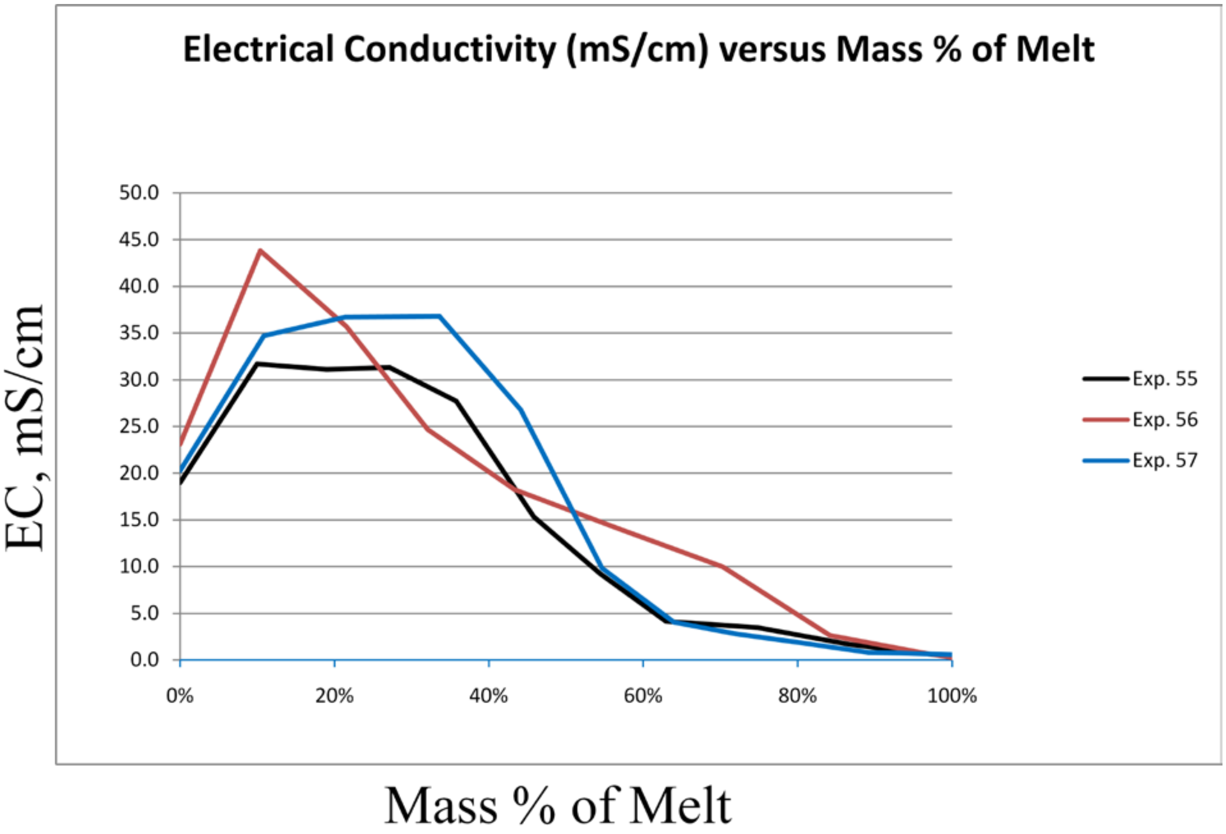

Figure 10. EC of Hydrate Melt Versus Mass of Melt for Bench-scale Batch Hydrate Formation Experiments #55, #56 and #57.

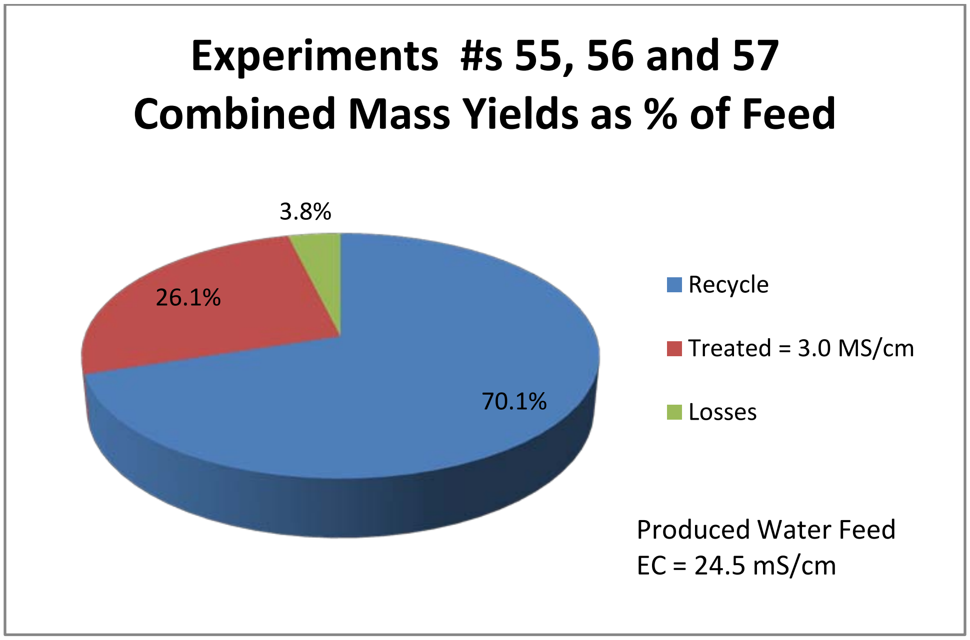

Figure 11. Combined Mass Yield from Bench-scale Batch Hydrate Formation Experiments #55, #56 and #57.

Table 1. Experimental Product Yields the Bench-scale Hydrate Formation System Evaluation

	Treated Water % of Feed	Recycled Water % of Feed	Brine % of Feed	Losses % of Feed
Average Value	19.6%	59.7%	2.4%	18.3%
Minimum Value	0.0%	13.4%	0.0%	-21.6%
Maximum Value	51.6%	95.1%	13.3%	60.9%

From all 75 experiments with complete data sets

	Treated Water % of Feed	Recycled Water % of Feed	Brine % of Feed	Losses % of Feed
Average Value	26.8%	66.9%	2.7%	3.6%
Minimum Value	7.4%	39.6%	0.0%	-4.8%
Maximum Value	51.6%	87.7%	13.3%	9.9%

From 15 experiments with complete data sets and Losses <10%

The second set of data in the table represents the average, minimum and maximum yield values when the experiment had losses less than plus or minus 10%. These data look very similar to those illustrated in Figure 10.

Figures 12 through 19 illustrate the construction and operation of the batch reactor system:

- Figure 12 shows the front view of the unloaded batch reactor system. The system has it cover panels removed in this picture.
- Figure 13 shows the rear view of the unloaded batch reactor system. The system has it cover panels removed in this picture.
- Figure 14 shows the atmospheric hydrate formation chamber.
- Figure 15 shows the modified CJHR.
- Figures 16 through 21 show the hydrate formation and growth in the atmospheric collection chamber.
- Figure 22 shows the produced water feed to the reactor and the treated water produced

from the reactor.

- Figure 23 shows a sample of the hydrate produced from the batch reactor system.

Figure12. Batch Reactor System (Front View)

Figure 13. Batch Reactor System (Rear View)

Figure 14. Atmospheric Hydrate Formation Chamber **Figure 15.** Modified CJHR Injector

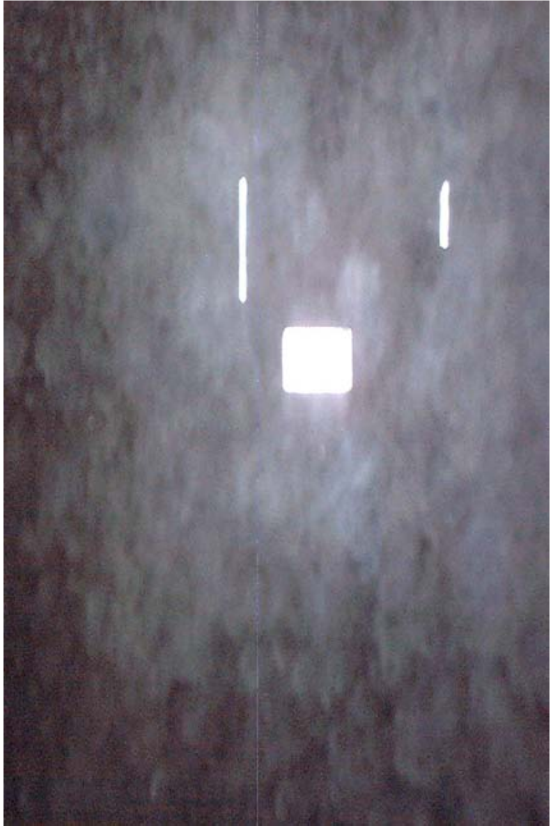

Figure16. Hydrates begin to Form **Figure 17**. Hydrates Collecting on Splash Shield

Figure 18. Hydrate Close-up

Figure 19. Hydrate Growth on Chamber Walls

Figure 20. Hydrate Formation Chamber

Figure 21. Modified CJHR at Shutdown

Produced Water
Feed – Right

Hydrate Reactor
Treated Water - Left

Figure 22. Produced Water Feed to and Treated Water from the Batch Hydrate Reactor System

Sample of CO_2
Hydrate Made
Using Produced
Water

Figure 23. Hydrate Produced in the Bench-scale Batch Hydrate Reactor System

As previously stated, the initial CFHS which used a screw conveyor did not operate successfully. In only three experiments were the operators able to operate the unit long-enough to get a full set of experimental data. These data are also provided in Appendix A. A review of the data from these experiments indicate all of the experiments producing melt meeting the treated standards had losses in excess of plus or minus 10%.

Thirteen experiments were completed using the final CFHS. Three of these experiments yielded treated water and were within the acceptable the loss criteria of plus or minus 10%. Data from these experiments are also provided in Appendix A. Figures 23 through 26 are provided to show the CFHS and hydrate produced. The CFHS was prolific in hydrate production but though the continuous melt separation was reasonable successful it was difficult to get a significant separation in an EC of 3 mS/cm

Process economics were not examined in depth due to the inability to consistently operate the system in a long-term stable fashion. Table A-2 provides a breakout of the equipment and fabrication and assembly costs for the final prototype. The total cost is $48,843 for a unit that should have been capable of 25 bbl/day. If this capital investment is amortized over 10 years to yield a 15% discounted cash flow rate of return, the annual cost of capital is $9456. Fuel costs are estimated at $3066 based upon horse power and amperage of the equipment. Operating labor costs are estimated at one hour per day per unit at $60/hr including benefits, overheads and vehicle expenses and maintenance. The annual costs for labor total $21,900/unit. Also, annual maintenance costs are estimated at 5% of total capital or $2,442. The total operating and capital amortization costs are $36,864. The unit should have been capable 25 bbl/day or 8,213 bbl/yr assuming a 90% load factor. The resulting water treatment cost would have been $4.50/bbl if we could have made the unit operable.

CONCLUSIONS

The following conclusions are drawn from the results of this research:

- Water can be treated at the wellhead to reduce surface handling costs.
- Reducing surface handling will also reduce environmental impacts such as fugitive dust created from truck traffic.
- Adverse impacts to sage grouse populations in southwestern WY will also be reduced with less truck traffic.
- Bench-scale results using carbon dioxide indicate > 40% of the feed water to the hydrate formation reactor was converted to hydrate in a single pass.
- These results also indicate > 23% of the feed water to the hydrate formation reactor (> 50% of the hydrate formed) was converted to purified water of a quality suitable for discharge.
- Continuous discharge and collection of hydrates was achieved at atmospheric pressure.
- The separation of melt fraction of the hydrates on a continuous basis proved very difficult and not suited for field demonstration at this time
- Preliminary economics indicate that if the unit could be made operable, it is potentially economic but at this time the concept is not ready for field demonstration.

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LIST OF ACRONYMS AND ABREVIATIONS

CBM	Coal Bed Methane
CFPS	Continuous. Flow Prototype System
CJHR	Continuous Jet Hydrate Reactor
EC	Electric Conductivity
FCRHM	Four Compartment Rotating Hydrate Melter
GGRB	Greater Green River Basin
HDPE	High Density Poly-Ethylene
NEPA	National Environmental Policy Act
ORNL	Oak Ridge National Laboratory
PB	Piceance Basin
SPS	Seafloor Process Simulator
U.S.	United States
U.S. D.O.E.	United States Department of Energy
WOGCC	Wyoming Oil and Gas Conservation Commission

APPENDIX A

EXPERIMENTAL RESULTS AND CONDITIONS OF THE HYDRATE FORMATION SYSTEM EVALUATIONS

Table A1 Experimental Conditions of the Bench-scale Hydrate Formation System Evaluation

Exp. #	Feed EC mS/cm	Salt Added (g)	Water Temp (°F)	Box Temp. (°F)	Water Pressure (psi)	CO_2 Pressure (psi)	Chiller Flow Rate (gpm)	HP Flow Rate (gpm)	Injector Orientation	Treated Water % of Feed	Recycle Water % of Feed	Brine % of Feed	Losses % of Feed	Reactor Type
1	12.7	???	???	???	???	???	???	???	???	26.0%	67.5%	6.6%	0.0%	Batch
2	13.3	???	???	???	???	???	???	???	???	22.6%	73.9%	0.0%	3.6%	Batch
3	15.5	100	34	18	1050	34	0.7	N/A	Up	29.3%	60.8%	0.0%	9.9%	Batch
4	14.7	100	34	19	1000	34	0.7	N/A	Up	31.6%	50.8%	3.4%	14.2%	Batch
5	8.7	100.23	34	23	1050	34/2000	0.7	0.18	Up	17.0%	51.6%	10.3%	21.2%	Batch
7	8.2	100	34	25	1000	34/2000	0.7	0.19	Up	39.9%	57.7%	7.2%	-4.8%	Batch
8	9.07	100	34	21	1000-1150	34/2000	0.7	0.16	Up	16.9%	69.4%	5.1%	8.6%	Batch
9	12.62	???	???	???	???	???	???	???	???	5.6%	82.3%	0.0%	12.1%	Batch
10	8.3	100.04	34	19	950-1150	34/2000	0.7	.16-.19	Up	44.8%	39.6%	13.3%	2.3%	Batch
11	14.33	100.03	34	19	1000-1150	34/2000	0.7	0.14	Up	7.8%	65.5%	0.0%	26.7%	Batch
12	12.7	100	34	21	1000-1150	34/2000	0.7	0.16	Up	27.6%	52.8%	0.0%	19.6%	Batch
13	13.5	100	41	31.5	1600	40/2000	1.4	0.27	Down	7.6%	71.9%	0.0%	20.4%	Batch
14	???	100.17	34	30-24	1350-1750	34-40/2000	1.7	0.8-0.4	Down	28.9%	64.5%	0.0%	6.6%	Batch
15	10.13	100.03	34	30-28	1000-1600	34-40/2500	1.7	N/A	Down	21.9%	66.1%	0.0%	12.0%	Batch
16	11.72	100.05	34	30-24	1000-1600	0	1.7	N/A	Down	5.0%	46.2%	0.0%	48.7%	Batch
17	10.94	100.28	34	30-25	1500	0	1.7	N/A	Down	22.7%	59.4%	0.0%	17.9%	Batch
18	10.94	100.2	32	25-28.6	1500	0	1.6	0.5-0.6	Up	17.0%	82.3%	0.0%	0.7%	Batch
19	11.4	100.01	32	23	1500	0	N/A	N/A	Up	10.3%	87.7%	0.0%	2.0%	Batch
20	11.31	100.63	32	25	1300	0	1.5	N/A	Up	51.6%	51.5%	0.0%	-3.1%	Batch
21	11.37	100	32	23	1300	0	1.4	N/A	Up	33.2%	13.4%	13.3%	40.2%	Batch
22	N/A	100	32	23	1250	0	1.4	N/A		14.3%	81.3%	0.0%	4.4%	Batch
23	14.95	100	32	27	1400	0	1.5	N/A		29.3%	85.0%	0.0%	-14.3%	Batch
24	10.63	100	32	21	1400	0	1.5	N/A		30.8%	59.0%	0.0%	10.2%	Batch
25	12.95	100.04	32	21	1350	0	1.5	N/A		22.8%	59.5%	0.0%	17.7%	Batch
26	12.67	100.13	32	19-26	1375	0	1.4	N/A	Up	16.4%	51.6%	0.0%	32.0%	Batch
27	11.58	100.09	32-36	19-24	1400	0	1.5	N/A	Up	34.9%	55.7%	0.0%	9.4%	Batch
28	12.05	100.04	32-36	25	1600	0	1.5	N/A	Up	9.3%	60.9%	0.0%	29.8%	Batch
29	11.61	100.17	32-36	26	1600	0	1.5	N/A	Up	16.7%	56.8%	0.0%	26.5%	Batch
30	13.96	100.03	32-36	N/A	1600	0	1.4	N/A	Up	15.2%	59.6%	0.0%	25.2%	Batch
31	12.53	100.02	32-36	19	1300	0	1.2	N/A	Up	21.8%	65.5%	0.0%	12.7%	Batch
32	11.72	100.02	32-36	20	1250-1500	0	1.25	N/A	Up	13.5%	59.8%	0.0%	26.7%	Batch
33	19.63	100.12	32-36	15-20	1500	0	1.4	N/A	Up	14.9%	58.4%	0.0%	26.7%	Batch
34	12.25	100.06	32-36	15-20	1600	0	1.3	N/A	Up	10.8%	71.3%	0.0%	17.9%	Batch
35	13.88	100.00	32-36	15-20	?	0	1.3	N/A	Up	23.9%	53.8%	4.8%	17.5%	Batch
36	12.78	100	32-36	15-20	1500	0	1.46	N/A	Up	29.0%	45.8%	5.0%	20.1%	Batch
37	9.06	100.19	32-36	15-20	1400	0	1.25	N/A	Up	16.9%	67.2%	4.6%	11.2%	Batch
39	12.53	100.65	32-36	15-20	1400	0	1.2	0.15		13.6%	51.8%	6.1%	28.5%	Batch
40	10.51	100.51	32-36	15-20	N/A	0	1.26	N/A		28.5%	45.5%	10.2%	15.8%	Batch
41	10.9	100.05	32-36	15-20	N/A	0	1.2	N/A		14.1%	78.4%	5.5%	2.1%	Batch
42	11.2	100.14	34	15	1325	0	1.25	0.14	Up	44.8%	30.6%	6.7%	17.9%	Batch
43	11.32	100.02	36	15.9	1250-1500	0	1.28	0.1	Up	27.9%	45.0%	4.0%	23.0%	Batch
44	9.57	100.01	37	17	1325	0	N/A	0.06	Up	12.1%	49.7%	4.4%	33.8%	Batch
45	7.84	100.15	38	17.3	1350	0	N/A	0.07	Up	36.0%	35.3%	8.1%	20.7%	Batch
46	8.93	100.24	33	17	1375	0	1	0.07	Up	37.3%	41.1%	3.6%	18.0%	Batch
47	7.47	100.15	33	17	1350	0	0.8	0.06	Up	44.3%	46.4%	3.6%	5.7%	Batch
48	8.43	100.02	36	15	1350	0	1.3	0.04	Up	30.2%	24.1%	9.3%	36.4%	Batch
49	9.23	100.01	36	21	1375	0	0.9	0.06	Up	23.0%	57.4%	0.0%	19.6%	Batch
50	10.54	?	?	?	1350	0	?	?	Up	4.6%	34.5%	0.0%	60.9%	Batch
51	10.06	100.07	32	30	1350-1400	1500-1700	0.75	0.06	Up	34.9%	43.0%	7.9%	14.2%	Batch
52	15.37	100.08	32	32	1475	1700	0.75	0.06	Up	29.9%	44.7%	0.0%	25.4%	Batch
53	12.32	100.09	34	18	1400	1500-1700	0.7	0.055	Up	19.6%	56.8%	0.0%	23.5%	Batch
54	11.45	100.22	33	23	1400-1500	1500-1700	0.65	0.06	Up	30.3%	41.3%	0.0%	28.4%	Batch
55	24.4	PW	37	27.5	1400	1700	0.45	0.05	Up	26.5%	95.1%	0.0%	-21.6%	Batch
56	24.65	PW	33	21	1400-1500	1700	1.3	0.06	Up	13.9%	44.0%	0.0%	42.1%	Batch
57	24.55	PW	34	22	1400-1500	1700	1.3	0.06	Up	26.6%	82.1%	0.0%	-8.7%	Batch
58	26.3	PW	40	19	1400-1500	1700	1.3	0.03	Up	4.8%	70.5%	0.0%	24.7%	Batch
59	25.1	PW	34	19	1400-1500	1700	1.4	0.025	Up	10.2%	70.2%	0.0%	19.6%	Batch
60	24.7	PW	34	26.5	1400-1500	1700	1.35	0.025	Up	4.8%	84.3%	0.0%	10.9%	Batch
61	23.94	PW	34	22	1500+	1700	1.45	0.03	Up	20.4%	59.3%	0.0%	20.3%	Batch

Table A1 Experimental Conditions of the Bench-scale Hydrate Formation System Evaluation

62	24.2	PW	41	30	1525-1550	1700	1.55	0.02	Up	14.8%	73.7%	0.0%	11.4%	Batch
63	25.1	PW	36	19.6	1500-1650	1700	1.4	0.03	Up	22.2%	51.8%	0.0%	26.0%	Batch
64	25.86	PW	39	21	1500	1700	1.4	0.03	Up	15.0%	80.6%	0.0%	4.4%	Batch
65	56.35	PW	34	21	1500-1650	1700-1800	1.45	0.027	Up	0.0%	86.5%	0.0%	13.5%	Batch
66	47.8	PW	34	27	1300	1700-1800	N/A	N/A	Up	0.6%	71.9%	0.0%	27.4%	Batch
67	57.6	PW	33	15	1400	1700-1800	0.8	N/A	Up	5.2%	71.0%	0.0%	23.8%	Batch
68	57.57	PW	34	22	1500	1700-1800	1	N/A	Up	1.8%	65.6%	0.0%	32.6%	Batch
69	47.9	PW	34	28	1500	1500	NA	NA	UP	0.0%	71.8%	0.0%	28.2%	Batch
70	25	PW	34	22	1550	???	1.25	0.02	Up	7.7%	39.9%	9.4%	43.0%	Batch
71	28	PW	34	24	1500-1550	N/A	1.4	0.025	Up	4.2%	48.1%	4.7%	43.0%	Batch
72	24.935	PW	34	???	1450	1800	1.35	0.025	Up	6.2%	83.2%	0.0%	10.6%	Batch
73	25.28	PW	34	???	1450	???	1.1		Up	7.4%	86.4%	0.0%	6.2%	Batch
74	18.8	PW	32-38	17-35	1450-1550	1500-1550	1.1	1.1	down	16.1%	48.9%	8.9%	26.1%	Batch
75	20.8	PW	34	25	1400	1500-1550	1.1	0.9	down	7.2%	58.2%	4.9%	29.6%	Batch
76	24.9	PW	33-39	19-29	900-1350	1500-1550	1	1	down	21.2%	57.9%	0.0%	20.8%	Batch
77	21.3	PW	32-38	24	1350-1550	1500-1550	1.1	1.1	down	15.0%	41.7%	9.6%	33.7%	Batch
78	16.03	PW	34-37	19-26	1250	2000	1.1	1.1	down	7.8%	48.5%	6.5%	37.2%	CFPS - Screw
79	7.1	PW	34-37	19-26	1250	2000	1.1	1.1	down	33.4%	52.0%	0.0%	14.6%	CFPS - Screw
80	44.9	PW	34-37	19-26	1500	2000	1.1	1.1	down	0.0%	97.9%	0.0%	2.1%	CFPS - Screw
81	38.4	PW	35*44	15-33	1500-1550	1500-1550	0.9	0.9	down	18.9%	79.4%	3.0%	-1.4%	CFPS - Rotating
82	37.5	PW	32-38	17-35	1450-1550	1500-1550	1.1	1.1	down	1.4%	80.9%	0.0%	17.7%	CFPS - Rotating
83	15.44	PW	33-39	19-29	900-1350	1500-1550	1	1	down	6.4%	70.4%	0.0%	23.2%	CFPS - Rotating
84	17.71	PW	32-38	17-35	1450-1550	1500-1550	1.1	1.1	down	0.0%	109.3%	0.0%	-9.3%	CFPS - Rotating
85	15.64	PW	32-38	17-35	1450-1550	1500-1550	1.1	1.1	down	20.2%	73.7%	2.8%	3.3%	CFPS - Rotating
86	14.1	PW	35*44	15-33	1500-1550	1500-1550	0.9	0.9	down	6.1%	61.0%	3.2%	29.8%	CFPS - Rotating
87	13.93	PW	41-52	16-29	1400	1500-1550	0.8	0.8	down	0.0%	93.2%	0.0%	6.8%	CFPS - Rotating
88	17	PW	41-34	16-29	1400-1525	1500-1550	1.1	0.8	down	1.8%	77.8%	1.5%	18.8%	CFPS - Rotating
89	20.08	PW	34-45	16-37	1400-1550	1500-1550	0.7	0.7	down	0.0%	94.9%	0.0%	5.1%	CFPS - Rotating
90	16.19	PW	35-39	16-21	1400-1550	1500-1550	0.9	0.8	down	0.0%	71.0%	0.0%	29.0%	CFPS - Rotating
91	18.73	PW	34-38	16-28	1400-1550	1500-1550	0.8	0.8	down	6.6%	102.1%	0.0%	-8.7%	CFPS - Rotating
92	20.54	PW	35-44	15-33	1450-1500	1500-1550	0.8	0.8	down	0.0%	79.7%	0.0%	20.3%	CFPS - Rotating
93	20.34	PW	36-73	17-33	1400-1550	1500-1550	0.9	0.9	down	0.0%	78.9%	0.0%	21.1%	CFPS - Rotating

Table A1 Experimental Conditions of the Bench-scale Hydrate Formation System Evaluation

Exp. #	Date	Feed Ec	Salt Added (g)	Water Temp (°F)	Box Temp. (°F)
43	12/4/2008	11.32	100.02	36	15.9
44	12/5/2008	9.57	100.01	37	17
45	12/5/2008	7.84	100.15	38	17.3
46	12/9/2008	8.93	100.24	33	17
47	12/9/2008	7.47	100.15	33	17
48	12/11/2008	8.43	100.02	36	15
49	12/11/2008	9.23	100.01	36	21
50	12/12/2008	10.54	?	?	?
51	12/17/2008	10.06	100.07	32	30
52	1/6/2009	15.37	100.08	32	32
53	1/7/2009	12.32	100.09	34	18
54	1/7/2009	11.45	100.22	33	23
56	1/8/2009	24.65	PW	33	21
57	1/8/2009	24.55	PW	34	22
58	1/9/2009	26.3	PW	40	19
59	1/12/2009	25.1	PW	34	19
60	1/13/2009	24.7	PW	34	26.5
61	1/14/2009	23.94	PW	34	22
62	1/15/2009	24.2	PW	41	30
63	1/16/2009	25.1	PW	36	19.6
64	1/16/2009	25.86	PW	39	21
65	1/21/2009	56.35	PW	34	21
66	1/22/2009	47.8	PW	34	27
67	1/23/2009	57.6	PW	33	15
68	1/26/2009	57.57	PW	34	22
69	1/27/2009	47.9	PW	34	28
70	1/28/2009	25	PW	34	22
71	2/9/2009	28	PW	34	24
72	2/11/2009	24.935	PW	34	???
73	2/12/2009	25.28	PW	34	???

Table A1 Experimental Conditions of the Bench-scale Hydrate Formation System Evaluation (continued)

Exp. #	Water Pressure (psi)	CO_2 Pressure (psi)	Chiller Flow Rate (gpm)	HP Flow Rate (gpm)	Injector Orientation
1	???	???	???	???	???
2	???	???	???	???	???
3	1050	34	0.7	N/A	Up
4	1000	34	0.7	N/A	Up
5	1050	34/2000	0.7	0.18	Up
7	1000	34/2000	0.7	0.19	Up
8	1000-1150	34/2000	0.7	0.16	Up
9					
10	950-1150	34/2000	0.7	.16-.19	Up
11	1000-1150	34/2000	0.7	0.14	Up
12	1000-1150	34/2000	0.7	0.16	Up
13	1600	40/2000	1.4	0.27	Down
14	1350-1750	34-40/2000	1.7	0.8-0.4	Down
15	1000-1600	34-40/2500	1.7	N/A	Down
16	1000-1600	0	1.7	N/A	Down
17	1500	0	1.7	N/A	Down
18	1500	0	1.6	0.5-0.6	Up
19	1500	0	N/A	N/A	Up
21	1300	0	1.4	N/A	Up
22	1250	0	1.4	N/A	
23	1400	0	1.5	N/A	
24	1400	0	1.5	N/A	
25	1350	0	1.5	N/A	
26	1375	0	1.4	N/A	Up
27	1400	0	1.5	N/A	Up
28	1600	0	1.5	N/A	Up
29	1600	0	1.5	N/A	Up
30	1600	0	1.4	N/A	Up
31	1300	0	1.2	N/A	Up
32	1250-1500	0	1.25	N/A	Up
33	1500	0	1.4	N/A	Up
34	1600	0	1.3	N/A	Up
35	?	0	1.3	N/A	Up
36	1500	0	1.46	N/A	Up
37	1400	0	1.25	N/A	Up
39	1400	0	1.2	0.15	
40	N/A	0	1.26	N/A	

Exp. #	**Water Pressure (psi)**	**CO_2 Pressure (psi)**	**Chiller Flow Rate (gpm)**	**HP Flow Rate (gpm)**	**Injector Orientation**
41	N/A	0	1.2	N/A	
42	1325	0	1.25	0.14	Up
43	1250-1500	0	1.28	0.1	Up
44	1325	0	N/A	0.06	Up
45	1350	0	N/A	0.07	Up
46	1375	0	1	0.07	Up
47	1350	0	0.8	0.06	Up
48	1350	0	1.3	0.04	Up
49	1375	0	0.9	0.06	Up
50	1350	0	?	?	Up
51	1350-1400	1500-1700	0.75	0.06	Up
52	1475	1700	0.75	0.06	Up
53	1400	1500-1700	0.7	0.055	Up
54	1400-1500	1500-1700	0.65	0.06	Up
56	1400-1500	1700	1.3	0.06	Up
57	1400-1500	1700	1.3	0.06	Up
58	1400-1500	1700	1.3	0.03	Up
59	1400-1500	1700	1.4	0.025	Up
60	1400-1500	1700	1.35	0.025	Up
61	1500+	1700	1.45	0.03	Up
62	1525-1550	1700	1.55	0.02	Up
63	1500-1650	1700	1.4	0.03	Up
64	1500	1700	1.4	0.03	Up
65	1500-1650	1700-1800	1.45	0.027	Up
66	1300	1700-1800	N/A	N/A	Up
67	1400	1700-1800	0.8	N/A	Up
68	1500	1700-1800	1	N/A	Up
69	1500	1500	NA	NA	UP
70	1550	???	1.25	0.02	Up
71	1500-1550	N/A	1.4	0.025	Up
72	1450	1800	1.35	0.025	Up
73	1450	???	1.1		Up

Table A2 Experimental Yield Summary Expressed as % of Feed from the Bench-scale Hydrate Formation System Evaluation

Exp. #	**Treated Water**	**Recycled Water**	**Brine**	**Losses**
1	26.0%	67.5%	6.6%	0.0%
2	22.6%	73.9%	0.0%	3.6%
3	29.3%	60.8%	0.0%	9.9%
4	31.6%	50.8%	3.4%	14.2%
5	12.8%	51.6%	10.3%	21.2%
7	39.9%	4.1%	4.8%	-4.8%
8	16.9%	69.4%	5.1%	8.6%
9	5.6%	82.3%	0.0%	12.1%
10	44.8%	39.6%	13.3%	2.3%
11	7.8%	65.5%	0.0%	26.7%
12	27.6%	52.8%	0.0%	19.6%
13	7.6%	71.9%	0.0%	20.4%
14	28.9%	64.5%	0.0%	6.6%
15	21.9%	66.1%	0.0%	12.0%
16	5.0%	46.2%	0.0%	48.7%
17	22.7%	59.4%	0.0%	17.9%
18	17.0%	82.3%	0.0%	0.7%
19	10.3%	87.7%	0.0%	2.0%
21	33.2%	13.4%	13.3%	40.2%
22	14.3%	81.3%	0.0%	4.4%
23	29.3%	85.0%	0.0%	-14.3%
24	30.8%	59.0%	0.0%	10.2%
25	22.8%	59.5%	0.0%	17.7%
26	16.4%	51.6%	0.0%	32.0%
27	34.9%	55.7%	0.0%	9.4%
28	9.3%	60.9%	0.0%	29.8%
29	16.7%	56.8%	0.0%	26.5%
30	15.2%	59.6%	0.0%	25.2%
31	21.8%	65.5%	0.0%	12.7%
32	13.5%	59.8%	0.0%	26.7%
33	14.9%	25.3%	0.0%	26.7%
34	10.8%	71.3%	0.0%	17.9%
35	23.9%	53.8%	4.8%	17.5%
36	29.0%	45.8%	5.0%	20.1%
37	16.9%	67.2%	4.6%	11.2%
39	13.6%	51.8%	6.1%	28.5%
40	28.5%	45.5%	10.2%	15.8%
41	14.1%	78.4%	5.5%	2.1%

Exp. #	**Treated Water**	**Recycled Water**	**Brine**	**Losses**
42	44.8%	30.6%	6.7%	17.9%
43	27.9%	45.0%	4.0%	23.0%
44	12.1%	49.7%	4.4%	33.8%
45	36.0%	35.3%	8.1%	20.7%
46	37.3%	41.1%	3.6%	18.0%
47	44.3%	46.4%	3.6%	5.7%
48	30.2%	24.1%	9.3%	36.4%
49	23.0%	57.4%	0.0%	19.6%
50	4.6%	34.5%	0.0%	60.9%
51	34.9%	43.0%	7.9%	14.2%
52	29.9%	44.7%	0.0%	25.4%
53	19.6%	56.8%	0.0%	23.5%
54	30.3%	41.3%	0.0%	28.4%
56	13.9%	44.0%	0.0%	42.1%
57	26.6%	82.1%	0.0%	-8.7%
58	4.8%	70.5%	0.0%	24.7%
59	10.2%	70.2%	0.0%	19.6%
60	4.8%	84.3%	0.0%	10.9%
61	20.4%	59.3%	0.0%	20.3%
62	14.8%	73.7%	0.0%	11.4%
63	22.2%	51.8%	0.0%	26.0%
64	15.0%	80.6%	0.0%	4.4%
65	0.0%	86.5%	0.0%	13.5%
66	0.6%	71.9%	0.0%	27.4%
67	5.2%	71.0%	0.0%	23.8%
68	1.8%	65.6%	0.0%	32.6%
69	0.0%	71.8%	0.0%	28.2%
70	7.7%	39.9%	9.4%	43.0%
71	4.2%	48.1%	4.7%	43.0%
72	6.2%	83.2%	0.0%	10.6%
73	7.4%	86.4%	0.0%	6.2%

Average	19.3%	58.5%	2.2%	18.7%
Maximum	44.8%	87.7%	13.3%	60.9%
Minimum	0.0%	4.1%	0.0%	-14.3%

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

One West Third Street, Suite 1400
Tulsa, OK 74103-3519

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South
Suite 201
Fairbanks, AK 99709

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