Gas Hydrate Storage of Natural Gas

Federal Assisted Program/Project Status Report

Final Report
July 13, 2006
(revision of June 21, 2006 submission)

Principal Investigators: Rudy Rogers, John Etheridge
Project Engineers: Larry Pearson, R. Arunkumar, Kristina Hogancamp
Control Specialist: Jay McCown

Mississippi State University
330 Swalm - Presidents Circle
Mississippi State, MS 39762

Report Issued: July 13, 2006

DOE Award Number: DE-FC26-01NT41297

ABSTRACT

Environmental and economic benefits could accrue from a safe, aboveground, natural-gas storage process allowing electric power plants to utilize natural gas for peak load demands; numerous other applications of a gas storage process exist. A laboratory study conducted in 1999 to determine the feasibility of a gas-hydrates storage process looked promising. The subsequent scale-up of the process was designed to preserve important features of the laboratory apparatus: (1) symmetry of hydrate accumulation, (2) favorable surface area to volume ratio, (3) heat exchanger surfaces serving as hydrate adsorption surfaces, (4) refrigeration system to remove heat liberated from bulk hydrate formation, (5) rapid hydrate formation in a non-stirred system, (6) hydrate self-packing, and (7) heat-exchanger/adsorption plates serving dual purposes to add or extract energy for hydrate formation or decomposition. The hydrate formation/storage/decomposition Proof-of-Concept (POC) pressure vessel and supporting equipment were designed, constructed, and tested.

This final report details the design of the scaled POC gas-hydrate storage process, some comments on its fabrication and installation, checkout of the equipment, procedures for conducting the experimental tests, and the test results.

The design, construction, and installation of the equipment were on budget target, as was the tests that were subsequently conducted. The budget proposed was met. The primary goal of storing 5000-scf of natural gas in the gas hydrates was exceeded in the final test, as 5289-scf of gas storage was achieved in 54.33 hours. After this 54.33-hour period, as pressure in the formation vessel declined, additional gas went into the hydrates until equilibrium pressure/temperature was reached, so that ultimately more than the 5289-scf storage was achieved.

The time required to store the 5000-scf (48.1 hours of operating time) was longer than designed. The lower gas hydrate formation rate is attributed to a lower heat transfer rate in the internal heat exchanger than was designed. It is believed that the fins on the heat-exchanger tubes did not make proper contact with the tubes transporting the chilled glycol, and pairs of fins were too close for interior areas of fins to serve as hydrate collection sites. A correction of the fabrication fault in the heat exchanger fin attachments could be easily made to provide faster formation rates.

The storage success with the POC process provides valuable information for making the process an economically viable process for safe, aboveground natural-gas storage.

TABLE OF CONTENTS

Page

LIST OF FIGURES

(Figures appear at document end.)

LIST OF TABLES

EXECUTIVE SUMMARY

The final full-scale test (Run #14) of the Proof-of-Concept hydrate gas storage process operated near 550 psig and 35°F. Two gas compositions were fed into the formation vessel to form gas hydrates. One composition was the 95.15/3.49/1.36 methane/ethane/nitrogen mixture used in the previous thirteen runs. The second composition was 92.09/4.15/3.76 of methane/ethane/ propane; it was the first POC use of a gas mixture containing propane that would form structure II hydrate. (Gas compositions used in prior runs formed Structure I.) Twelve compressed-gas cylinders of each composition comprised a feed bank that fed gas to a manifold. Gas from the manifold maintained a desired 550 psig on the downstream hydrate formation vessel. Five thousand standard cubic feet of natural gas were stored in gas hydrates over a 48.1 hours operating period of Run #14. After 54.33 hours of gas injection, 5289-scf of gas had been occluded in hydrates. The storage capacity exceeded project expectations, although the rate of formation was slower than designed.

After completion of the storage test, the 5300-scf of stored gases in Run #14 were vented and flared in a boiler/burner. Steam was generated and a fraction of that steam supplied the latent heat of further hydrate decomposition. The hydrate decomposition, burning, and steam generation were accomplished in approximately 8.8 hours, although the gas release and steam generation could have been over a shorter time frame. With the heat-exchanger design, there was no limitation to rate of hydrate decomposition. Decomposing gases from the hydrates flowed without disruption through the system as designed. The heat-exchanger/adsorption-plate arrangements proved to be an effective way to supply and to disperse the energy necessary for hydrate dissociation; the delivery of energy for the latent heat of dissociation could be controlled in the arrangement. The generation of steam from the flared gases was accomplished without problems and demonstrated that stored hydrate gases could be rapidly and efficiently liberated and utilized.

It is concluded that the following major elements of the hydrate storage process readily accomplished design goals of the Proof-of-Concept installation: (1) controlling rate of hydrate decomposition and exit flow of decomposed gases, (2) forming and self-packing symmetrically of gas hydrates on heat exchanger fins, (3) attaining and surpassing 5000-scf storage capacity, (4) functioning of heat exchanger system, refrigeration and boiler to add or remove heat evenly throughout the hydrate system.

Failures in achieving design goals were limited to the lower than desired hydrate formation rate and realizing a functioning camera to view interior action in the formation tank.

The process as demonstrated verified technical capability to serve stationary natural gas storage needs on a small scale. This R&D formation vessel cost must be reduced to make the process economically attractive for stationary storage, but means are detailed to do this.

It is recommended that the surfactant process could be competitive in gas transport by altering the POC design to parallel high-pressure, small-diameter semi-continuous reactors feeding into a 1-atm storage vessel. Technical capability exists to accomplish the semi-continuous design and 1-atm stable storage.

I. INTRODUCTION

A 1997- 1999 DOE grant to study the feasibility of storing natural gas in gas hydrates gave encouraging results in the laboratory. A breakthrough resulted from using the surfactant sodium dodecylsulfate (SDS) in water solution at concentrations above a critical threshold concentration of surfactant, whereupon much faster hydrate formation rates were realized without stirring and the hydrates self-packed as they formed. This action portends cost reductions in a potential hydrate storage process.

The SDS surfactant solubilized natural gas and acted as nucleation sites for hydrate formation. Hydrate crystals formed subsurface around individual surfactant molecules, associations of molecules, or micelles. Surfactant attached to the developing hydrate crystals instigated mass transfer adsorption on cold metal surfaces at the water-gas interface. Hydrates subsequently built radially and symmetrically from the walls of the cold metal until the cell was filled with hydrates in a short time. As hydrates formed, surfactant was excluded from the hydrate structure and concentrated in the interstitial water of the hydrate particles; gas diffused through the porous particles to continue reacting with the interstitial water until most of the water had reacted. A storage capacity of 155-vol/vol of gas was measured in the laboratory apparatus.

By taking advantage of important aspects of the surfactant-hydrate catalysis phenomena demonstrated in the laboratory, a process was designed to form and store 5000-scf of a 90% methane, 6% ethane, and 4% propane hydrocarbon mixture taken as a typical natural gas. The process was also designed to be applicable to storing methane or any other hydrocarbon natural gas mixtures.

The process is designed for minimum labor to form, store, and dissociate the hydrates. First, the process is a non-stirred system because the action of the surfactant moves the hydrates from the surface of the water to adsorption plates at the interface, thus keeping the water surface clear of any solid film. The process is designed for simplicity: (1) No filtering or manual collection of hydrate particles is necessary. (2) Adsorption plates serve as heat exchangers to either add or take away heat depending on the cycle to form or decompose hydrates. (3) Water-surfactant solution is reused. (4) There are no moving parts. That is, the gas is admitted to the cell by a constant pressure regulator as hydrates form. (5) Formation, storage, and decomposition are performed in the same tank.

The Proof-of-Concept process to store 5000-scf of natural gas was designed around the hydrate formation/storage tank. It is necessarily the most expensive piece of equipment because it must accommodate an operating pressure of 550 psig.

Although the gas-hydrate process was developed with a primary goal of establishing an alternative means to store natural gas for peak-load use at electrical power plants, the process may have numerous applications for natural gas storage in remote regions, small-scale utilizations, retrieval of stranded gas, or even storage/transportation of natural gas in competition with LNG. The many and varied uses for a hydrate natural-gas storage process was evident in the multiple inquiries into the project.

II. OBJECTIVE

The objective of the project was to scale up a promising process to store natural gas in gas hydrates. The primary target was suitable in-place storage at electrical power plants, but the process is amenable for quite a few other gas storage and possibly gas transportation needs.

The goal of the work was to take important findings of the preceding laboratory feasibility study, incorporate them into a design for a Proof-of-Concept (POC) scale process. The POC design, construction, and demonstration would confirm the potential of the hydrate storage procedure, act as an intermediate step for further expansion of the process by industry, and give better definition of the hydrate process economics.

The POC hydrate storage process aimed at storing 5000-scf of natural gas in gas hydrates. The process would utilize sodium dodecylsulfate anionic surfactant to promote rapid hydrate formation and to cause the hydrates to adsorb as they formed and self-pack on metal surfaces at the gas-water interface. Such a procedure would then require a simplified operating procedure of maintaining 550-psi on the formation vessel during formation until hydrates packed the formation vessel to capacity. The procedure eliminates expensive procedures of processing the hydrate slurries, especially by reducing labor requirements. The design allows controlling gas hydrate decomposition by the hydrate’s forming on the heat exchanger surfaces.

During the final stages of the grant, a goal was to seek industry interest and support to carry the process to the next level of scale and deployment.

III. PROCEDURE

A. REVIEW OF LABORATORY FEASIBILITY STUDY

Design of the POC process was based on attributes of the small-scale (3900 ml) vessel and on observations of hydrate formation in the laboratory feasibility study.

The laboratory feasibility study (Contract DE-AC26-97FT33203) of the storage of natural gas in hydrates determined that the process is enhanced by the use of at least 242-ppm sodium dodecylsulfate surfactant in water solution. The surfactant helps solubilize hydrocarbon gas and acts as nuclei for hydrate crystallization. Hydrocarbon gas capacity, pressure and time relationships for the laboratory process are such that about 155- 157 (volume gas at STP)/(volume bulk hydrate) storage capacity is achieved at a processing pressure of 3.89-MPa (550 psig) in less than 3 hours of processing time.

For a hydrate storage process to be economical, it must be simple. Hydrate formation must be rapid. Labor must be minimal. Preferably, there would be no moving parts in the hydrate formation-storage tank that would reduce maintenance, labor, operating difficulties, and capital investment.

Surfactant in the water solution simplifies the process by three ways: (1) Hydrates form rapidly in a quiescent system. (2) Hydrate particles migrate to the cell walls where they self-adsorb and self-pack. (3) Interstitial water forms hydrates to leave minimal un-reacted water. In the first simplification, hydrates form so rapidly it is anticipated that with proper design of the formation-storage vessel, a formation-decomposition cycle including turnaround time could be achieved within a 24-hour period. By forming hydrates in a quiescent system, the need to impose water flow, movement, or mechanical stirring is eliminated. Consequently, complexity of the formation/storage tanks would be reduced; in fact, hydrate formation-storage-decomposition could be accomplished in the same vessel. Surfactant allows reuse of the process water: after hydrate decomposition, the water and surfactant would remain in the storage tank and the next formation cycle would proceed by re-pressurizing with gas. In the 2nd and 3rd simplifications, difficult intermediate process steps of manually collecting and packing hydrate particles in a storage vessel are eliminated, because the particles form in the cell in an ordered and packed manner. After packing, the interstitial water is converted to hydrates at a high rate to improve packing efficiency.

At the conclusion of the feasibility study, an economic analysis of the conceptual large-scale process concluded that the development costs per 1000-scf for gas hydrate storage might be competitive with liquefied natural gas (LNG), salt caverns and depleted reservoirs by using at least 4, 14, and 54 cycles/year, respectively. The user costs could be competitive with conventional storage above 13 cycles/year; above 125 cycles/year, hydrate costs are superior to all.

B. CRITERIA POC DESIGN BASED ON LABORATORY FEASIBILITY STUDY

(1) Hydrate Formation Vessel

Criteria. Target operating conditions for the hydrate formation/storage tank are 35°F and 550 psig to store 5000-scf of natural gas in gas hydrates; an upper pressure limit of 650 psig is desired for safety. The formation tank scale-up must be from a 1-gallon laboratory apparatus to approximately 300-gallon proof-of-concept (POC) scale.

In the laboratory apparatus, hydrates form on the cylindrical metal walls and grow radially and symmetrically. Likewise, the POC cell must provide hydrate symmetrical formation in order to completely fill the tank with gas hydrates and also to preserve a free path for gas flow along the developing hydrate front. (That is, in the vertical, cylindrical laboratory cell, hydrates formed on the walls; as the free-water level dropped, gas hydrates accumulated longitudinally down the cell. Therefore, the hydrate buildup on the solid surfaces progressed lengthwise as well as radially. Even as the cell became full, a “doughnut” hole remained from top to bottom of the cell allowing free gas movement.)

Symmetry can most easily and confidently be achieved in a vertical vessel, although a horizontal tank design was considered that might have given the desired symmetry.

The formation tank must be constructed to ASME standards for pressure vessels and fabricated by a coded shop.

(2) Heat Exchanger/Adsorption Surfaces

Criteria. Surfactant catalyzes gas hydrate formation. The hydrate particles are carried with the surfactant to adsorb on a cold-metal surface at the gas-water interface. The rate of hydrate formation is dependent, among other factors, on the metal surface area at the water-gas interface, the rate of heat transfer from hydrate collection surfaces, and the rate of mass transfer to the metal surfaces. Latent heat of formation for the hydrates is relatively large, so there is a substantial heat component to be removed, and this is considered to be the limiting rate step in the process. Therefore, one must provide in the POC formation tank adequate surface area for heat transfer; additionally, the same metal surfaces must provide a platform for gas hydrate attachment and support. A heat exchanger serves to both remove heat of hydrate formation and to collect hydrate mass.

A primary scale-up criteria chosen for the POC unit was a volume/surface ratio equal to or less than the laboratory apparatus, which was approximately 1/1.

The hydrate-formation heat exchanger must be constructed to ASME standards for pressure vessels and fabricated by a coded shop.

(3) Refrigeration and Heating System

Criteria. The refrigeration must supply 70-gpm coolant of 28°F to 32°F in order to form 5000-scf of natural gas in gas hydrates during a 6-hour period. A 6-hour formation period was chosen because of increasing refrigeration equipment costs to accommodate shorter formation times.

To decompose the gas hydrates, it is necessary to warm the cold fluid circulating through the heat-exchanger system. At a pressure near atmospheric inside the hydrate tank during decomposition, hydrates will decompose slowly unless heat is added. The rate of decomposition can be managed by the temperature and flow rate of the circulating fluid. If the process were to be used in a Power Plant, 70°F to 100°F would be convenient and economical for the hydrate decomposition step.

(4) Other Process Equipment

Other aspects of the process considered in the initial design are the following.

Gas disposal. Flaring or combusting liberated gas in a burner/boiler was considered. The boiler/burner was chosen in which some of the steam generated could be returned to decompose additional hydrates.

Gas supply. To avoid the cost of a compressor for natural gas, as well as the associated hazards of compressor leaks, a bank of compressed natural gas cylinders was purchased. Gases were premixed to our specifications in the cylinders. Discussions were made with NexAir, the primary supplier of compressed gases to the university, to supply the bank of cylinders.

Surfactant-water preparation. The most economical and simplest system was to lease a water deionizer and manually premix the water-surfactant solution in a holding tank and to purchase one centrifugal pump to fill the formation tank.

(5) Summary Initial Design

To achieve the scale-up from the 1-gallon laboratory apparatus to the 300-gal proof-of-concept (POC) model, careful considerations to the design of the hydrate formation tank and the formation heat exchanger were necessary. A design was developed with the following criteria: (1) Provide a heat exchanger to remove the latent heat to form hydrates from 5000-scf of natural gas and to add that approximate amount of latent heat at the end of the storage to decompose the hydrates. (2) Provide a heat exchanger with surface area and configuration to adsorb and support hydrates formed from 5000-scf of gas. (3) Select tank and heat exchanger materials of construction having strength and thickness for a maximum process pressure of 650 psig and an operating pressure of 550 psig. (4) Provide a configuration of the heat exchanger that would give a symmetrical buildup of hydrates on the exchanger to allow free gas movement until the tank became full of hydrates. (5) Form the hydrates in a practical period of time. (6) Provide safety pressure relief valves. (7) Provide measurements of temperature, pressure, and mass flow rates. (8) Provide means of visual observation of the tank's contents during hydrate formation. (9) Construct according to ASME standards for pressure vessels.

C. FINAL POC DESIGN

(1) Description of POC Design

After completing the hydrate formation tank design, the drawings and specifications were submitted for bids to ASME pressure-vessel-coded machine shops as required by the university.

The design provides for the capture and storage of 5000 standard cubic feet of natural gas in gas hydrates during an 8-hour processing period. The hydrates form in a pressure vessel at an operating pressure of 550-psi; the maximum design pressure is 650-psi. Formation temperature is 35^{o}F. The vertical, cylindrical pressure vessel of approximately 6 ft length and 36 in. outside diameter (0.75 in. wall thickness) has a bottom dome welded in place and a top dome joined to the cylindrical vessel by bolted flange. Thirty finned heat exchanger tubes extend from the top dome to near the vessel bottom. Each of the 30 tubes has attached 8 fins of 1.5" height extending longitudinally for 6 ft.

At the beginning of the hydrate-formation process, water-surfactant (sodium dodecylsulfate) solution covers the top of the finned tubes. As hydrates form, the ice-like hydrates collect on the finned tubes and grow symmetrically from the tubes in radial and longitudinal directions as the water level decreases. After 8 hours at processing pressure and temperature, the non-stirred vessel becomes filled with solid hydrates except for passageways left open for gas movement at the midpoint between any four adjacent finned tubes.

Temperature and pressure measurements are allowed by use of multiple ports designed into the vessel. Limited visual access to the inside of the pressure vessel is achieved with fiber optics lighting and borescope.

(2) Assembly Overview.

The pressure vessel and heat exchanger assembly are presented in Figure 1. For simplicity, only 4 of the 30 finned tubes of the heat exchanger are shown in this view. Note that the bottom dome is welded in place to the pressure vessel, while the top dome is connected to the vessel and sealed by flange and gasket. Heating or cooling fluid circulates through the 30 finned tubes and then flows in series through the jacket surrounding the cylindrical section of the pressure vessel.

(3) Hydrate-Formation Vessel.

The pressure vessel operates at 550 psig and is designed for a maximum pressure of 650 psig. Relief valves ensure pressures do not reach designed maximum pressure. In Figure 2 are cutaway views of the pressure vessel. The 304L stainless-steel shell is 34.5 inches inside diameter and 36.0 inches outside diameter. The working length is 72 in. The vessel will be used in the vertical position. Note that the top of the ellipsoidal dome is Teflon coated on the inside to prevent hydrate buildup on exit ports.

Detailed sketches of the top and bottom domes are given in Figure 3. A top view of the vessel showing jacket ports, lift loops, and support lugs is given in Figure 4.

A jacket for heating or cooling fluid circulation surrounds the pressure vessel and has baffles that direct the flow of circulating fluid through the jacket. The jacket wall is made of 1/8" thick 304L stainless steel. The gap between jacket and pressure vessel is 1". Four slotted-disc baffles direct the heat-transfer fluid in a spiral path along the outside of the pressure vessel.

Instructions for the welding of ports onto the pressure vessel and jacket are presented in Figure 5.

(4) Heat-Exchanger/Hydrate-Accumulator.

Thirty finned heat exchanger tubes extend into the pressure vessel: 15 tubes for entering fluid and 15 for exiting fluid. The 30 tubes are brought into 3 concentric doughnut-shaped ring headers; 12 outlet tubes exit the ring headers and those 12 outlet tubes extend through the top dome of the pressure vessel. See Figure 6.

The two inner ring headers serve the inlet fluid, and the outer ring header serves the outlet fluid. Elbows of 180^o connect inlet and outlet tubes near the bottom of the vertical pressure vessel.

Figure 7 further describes the configuration and arrangement of the 3 ring-headers. The purposes of the ring headers are to act as manifolds to distribute entering and exiting heat transfer fluid flowing through the finned tubes.

Note the symmetry of the finned tubes. Hydrates should build symmetrically from the tubes and fins. At the end of the process, hydrates from adjacent tubes should touch but leave flow paths to the exit port at the top of the vessel. Refer to Figure 8.

A means to center the heat exchanger in the pressure vessel, to stabilize the heat exchanger during transportation to the test site, and to support the heat exchanger is illustrated in Figure 9.

(5) Specifications.

The specifications for the pressure vessel and heat exchanger assembly that were submitted with the bid request are given in Table I.

TABLE I. Specifications of Hydrate Formation Tank

A hydrate formation tank is to be used to form and decompose gas hydrates at 650 psig of maximum design pressure, 20 °F to 110 °F of temperature. Water and natural gas are to fill the volume of the pressure vessel and then form hydrate solid at 550 psig, 35 °F. Ethylene glycol aqueous solution is to circulate in the internal heat exchanger and the external jacket to keep the desired temperature in the tank. The hydrate formation tank has the following main components: pressure vessel, internal heat exchanger, and external jacket.

General requirements:

1. Pressure vessel and internal heat exchanger must be fabricated according to the 2001 edition of ASME Boiler and Pressure Vessel Code, section VIII, division 1.
2. Code stamps on vessel and on internal heat exchanger are required.
3. Pressure vessel and internal heat exchanger must be leak checked.
4. Internal vessel surfaces should be clean using appropriate method.
5. Pressure vessel and heat exchanger should be assembled before shipping.

6. Customer reserves the right to witness all pressure testing.
7. All calculations, drawings are required upon delivery.
8. Vessel heads to be 2:1 ellipsoidal.
9. All flanges to be raised face with standard dimensions. Body flanges to be raised face according to ASME code, section VIII, division 1.
10. Quote shall include body flange options A & B as follows:
    A. Flange material to be carbon steel with 1/8" stainless steel 304L overlay on wetted area
    B. Flange material to be all stainless steel 304L
11. A 3-D AutoCad model of the Formation Tank is included with this bid package. This model is for visualization purposes only. The 3-D model is not to scale. Information on the hard copy supersedes anything that may be obtained from the 3-D model.
12. Design data:

Pressure vessel:		
	Design pressure (internal):	650 psig
	Design temperature:	20 °F to 110 °F
	Corrosion Allowance:	None
	Paint on external surface:	None
	Radiograph:	Limited amount as required in ASME code
Heat Exchanger:		
	Design pressure (external):	650 psig
	Design temperature:	20 °F to 110 °F
	Corrosion Allowance:	None
	Radiograph:	Limited amount as required in ASME code
Jacket:		
	Design pressure	Calculated by fabricator. Minimum 45-psig internal. See Fig. 5.
	Design temperature	20 °F to 110 °F
	Corrosion Allowance:	None
	Paint on external surface:	None
	Radiograph:	Limited amount as required in ASME code

13. Materials:

Vessel		
	Shell/heads	304L stainless steel
	Body Flanges	To be quoted for options A & B
	Bolts	Bolting material and number to be specified and provided by fabricator
	Gaskets	Gaskets for body flanges to be spiral wound ss 304/Teflon. Dimensions to be specified by fabricator. Fabricator to supply 3 each body-flange-gaskets.
	Insulation	External surface prepared for insulation
	Supports	Vessel supports shown in Fig. 2 and Fig. 4
	Lifting Loops	Shown in Fig.2 and Fig. 4
	Fittings	304L stainless steel

All Materials to be stainless steel 304L with the following exception:

-The body flange to be quoted for options A & B under item 10 of general requirements.

In Table II is a list of the ports that are to be constructed on the hydrate formation vessel.

TABLE II. Specification of Ports

1) Ellipsoidal dome (top)
    a) 9 ea, ½" FNPT drilled through:
    b) 1 ea, 1" schedule 80 pipe with flange
    c) 1 ea, 2" schedule 80 pipe with flange
    d) 12 ea, 1" pipe hole

2) Jacket
    a) 2 ea, 2" FNPT drilled through

3) Ellipsoidal dome (bottom)
    a) 1 ea, 1" schedule 80 pipe with flange
    b) 1 ea, 1 ½" schedule 80 pipe with flange
    c) 4 ea, ½" FNPT drilled through
    1 ea, 2" schedule 80 pipe with flange

D. CONSTRUCTION

(1) Machine Shop Selection and Fabrication

Public bids were requested for the hydrate formation tank according to State requirements. The sealed bids were dutifully evaluated and Hebeler Corporation's bid of $41,900 was chosen. The $41,900 included tank shell, heat exchanger, dome top and bottom, inlet and outlet ports, leak and pressure checks, labor and testing, and an ASME stamp verifying construction meets pressure-vessel standards. Construction was begun about two weeks after the bid was accepted.

Headquarters of Hebeler Corporation is Tonawanda, New York. Hebeler specializes in process equipment and turnkey systems; they design and fabricate a wide variety of pressure vessels, heat exchangers, piping systems and turnkey modular process systems. They offer fabrication to ASME codes.

Construction of the hydrate tank was at their Vicksburg, Mississippi, plant. The Vicksburg facility has 72,000 ft^2 of inside space and 10 acres of yard space.

(2) Test Bay Construction

A test bay to accommodate the hydrate tests was constructed at the DIAL research facility on the campus of Mississippi State University. A roof, concrete pad, and control room were constructed to serve the hydrate project as well as other projects in adjacent bays; the facility has three test bays. The bay has open sides and a high roof (approximately 25 ft) and a floor area of approximately 1000 ft^2 for the hydrate process.

E. INSTALLATION

(1) Photographs of Installation

In Figure 10 is a front view of the 5000-scf gas-hydrate formation vessel that serves formation, storage, and decomposition of hydrates. The vessel will be used in the vertical position as seen in Figure 10.

In Figure 11 is a west-side view of the facility. In the front of the facility can be seen DIAL's mobile data collection and process control center. This mobile unit was replaced later in the project with permanent housing for the control room. The equipment can be seen mounted in the open on a concrete pad under a roof. Note item 3, compressed gas supply. Banks of gas cylinders will supply natural gas to the formation tank. NexAir Corporation will premix the gases used in the tests to specified compositions. A constant pressure regulator will maintain a constant 550-psi on the formation vessel, admitting more gases as hydrates form. Item 4 is the Drake 12-ton chiller; item 1 is the glycol solution surge tank; item 6 is the surge tank for dissociated gases; item 5 is the boiler to combust dissociated gases.

A back view of the process can be seen in Figure 12. In the photograph can be seen more clearly Item 4, the chiller.

A flow chart for the chilled water loop of the process is presented in Figure 13. The instrumentation, piping, and equipment are depicted for circulating glycol-water solution from the chiller, splitting the flow to go through formation tank and its jacket, returning flow to a surge tank and back to the chiller. The surge tank is protected from over-pressure in case of gas leakage from the formation tank into the heat exchanger fluid. When decomposing gas hydrates in the formation tank, water-glycol solution circulates in like manner, but heat exchanger H-404 supplies the heat for dissociation.

(2) DIAL Installation. Insulation.

Insulation was installed on the lines and process vessels. Electricity and water lines were run to the newly constructed test bay. Instrumentation and data acquisition systems were installed and calibrated.

F. CHECKOUT OF FACILITY

(1) Chiller

The chiller of 12-tons refrigeration capacity was purchased from Drake, Inc. See Figure 14. Glycol-water solution circulates from the chiller through the heat-exchanger/adsorber plates inside the formation tank and then in series through the exterior jacket of the formation tank.

(2) Burner/Boiler

One problem at the beginning of the project was to find means to dispose of gases stored in the gas hydrates. It would be impractical to recover and reuse the hydrocarbon gases. A corporate donation to DIAL of a used boiler/burner provided means to dispose of stored gas and demonstrate steam generation from the burning. This piece of equipment was to be used jointly with another project. A photograph of the boiler as received before refurbishing is presented in Figure 15.

The boiler refurbishing was accomplished at the beginning of the project. A photograph of the refurbished boiler is presented in Figure 16.

A series of tests verified the boiler's proper working order prior to operation of the hydrate system. One test evaluated the boiler-burner by burning from the pressurized system free gas without first forming hydrates. A second run formed hydrates and the stored gases were then released to the boiler/burner for evaluation during combustion.

Boiler Tests Without Hydrates. The objective of this preliminary test was to perform a checkout of the computer system, startup, vessel cooling, boiler operation, and shutdown. The boiler operation was of primary importance. Intangible benefits from the test were for the operators to become familiar with the running of the equipment and safety procedures.

Natural gas from the house line and natural gas from the hydrate formation tank were supplied to the manifold [E] in Figure 17. The house line gas insured a constant fuel supply to maintain the pilot light of the boiler [F]. Combustion gases were vented to the atmosphere. As seen in Figure 17, exiting steam generated in the boiler-burner was split into two lines to either provide energy for further hydrate decomposition or provide steam for external applications.

Note that hydrates were not formed in this procedure. Only free gas from the formation tank and surge tank were supplied to check out the boiler. Refer to Figure 17 for the simplified flow chart that helps explain the general procedure.

Water level in the formation tank was between the 64" and 58" thermocouples; free gas (natural gas) used in the boiler tests occupied the headspace above the liquid water level.

The temperature versus time trace of the run is presented in Figure 18. This temperature trace refers to the period after the tank cooling, during free gas burning, and returning steam to the heat exchanger of the formation tank. In Figure 18, Trace (1) shows a rapid increase of temperature in the glycol entering the formation tank jacket that corresponds to opening the valve of the steam line. Trace (4) and (5) indicates the first temperature response in the formation tank in the gas phase. Both thermocouples (4) and

(5) are stationed above the water level in the gas. The faster response of the gas phase reflects the lower heat capacity of the gas compared to water and possibly some convection currents in the gas phase.

Although Traces (2) and (3) are both in the water phase, a slower response by Trace (2) reflects its location in the bottom dome area that is below the heat exchanger; as expected, the Trace (2) in the bottom of the tank never reaches as high of a temperature.

This preliminary test to perform a checkout of the computer system, startup, vessel cooling, boiler operation, and shutdown gave the following results. 1. The boiler and regulators performed satisfactorily. Gases from the formation tank were burned. 2. Steam was readily generated from the burned gases. 3. Generated steam was split into two streams to either reject to the atmosphere or circulate through the formation tank. With a fraction of the steam generated, temperature of the water in the formation tank could be rapidly raised. The good heat transfer indicated that decomposition of hydrates could be readily controlled with circulating heating fluid. 4. The run indicated that a gas flow meter is needed upstream of the burner to help monitor cumulative amount of gas entering the burner.

Burner Tests with Hydrates. Two successful burner-boiler tests were conducted for equipment checkout.

In the first test, after purging the system of air, the hydrate formation tank was partially filled with water and pressurized with natural gas to a point well below the hydrate formation temperature. Free gas from the headspace was then burned and steam generated in the burner-boiler. Controls and test performance of the burner-boiler were good.

In the second test, gas hydrates were formed and gases from the decomposed hydrates were then burned to create steam in the boiler. Eleven batches of natural gas were added to the formation tank by first admitting enough to establish 550 psig in the tank, forming hydrates to reduce the tank pressure to about 500 psig, and then readmitting natural gas to reestablish 550 psig in the formation tank. (Overall, 475-scf of gas in hydrates and 475-scf of free gas were processed.) The generated steam was either used to decompose more hydrates or to exhaust to the atmosphere; heat transfer to the hydrates through the internal heat exchanger was excellent. (Steam heated glycol in a secondary heat exchanger, and then the glycol was circulated through the internal heat exchanger.)

The boiler test with decomposed hydrate gases was also successful. Hydrates could be readily dissociated with circulating heat–transfer fluid warmed by generated steam. Some foam was created with decomposing hydrates and carried over with exiting gases to the surge tank, but it was not a serious problem. Some hydrates sluffed off the top of the heat exchanger at the end of the run but caused no apparent problem. Overall, the tests were very encouraging.

In the second test, 975-scf of decomposed and free gas was burned. All systems of the process worked as desired in the two test runs.

(3) *Instrumentation, Chiller, Formation Vessel*

The hydrate formation tank was hydrostatically tested to 850 psig, and it was verified to be a leak-proof vessel. The refrigeration system was tested and was found to perform as designed: (a) The set-point temperature of 28°F was attained. (b) Glycol-water solution was circulated at the designed temperature, pressure drop, and mass flow rate, and (c) The 210 gallons of water in the hydrate formation tank was cooled from ambient temperature to operating temperature within 3.0 - 3.5 hours.

As a first test for gas storage, a partial-capacity run was made. Gas hydrates were formed in the POC vessel. First, about 210 gallons of deionized water/SDS solution were cooled to 33°F - 35°F in the hydrate formation tank. Then, natural gas (95.1% methane, 3.5% ethane, 1.4% nitrogen) was added to bring the pressure in the tank to 550 psig. Hydrates were formed immediately. When pressure had decreased to 475-psig due to hydrate formation, more natural gas was added to return vessel pressure to 551.6-psig. A series of five batches of gas were thus added. The test was stopped when about 15% of the designed storage capacity of the vessel had been reached.

After addition of the 5th batch of gas, enough free water was drained from the test cell to lower vessel pressure to 303.5-psig, below the equilibrium pressure for the prevailing gas mixture, whereupon hydrates began decomposing. Hydrates continued decomposing until 342.6 psig, the equilibrium pressure, was reached.

Data from the test run showed: (a) Hydrates were formed with negligible induction time. (b) Hydrates were formed rapidly. (c) Hydrates were collected on the adsorbing plates. (d) Temperature was maintained on the system by the refrigeration unit by adequately removing latent heat of hydrate formation.

IV. RESULTS AND DISCUSSION

A. POC TEST RESULTS

(1) Storage Capacity

Run Hyd-10. The POC system is designed to store 5000-scf of natural gas by pressurizing with natural gas a vessel containing SDS surfactant solution and then allowing hydrates to form and to self-pack on a stainless-steel heat exchanger. Natural gas used in Run Hyd-10 was composed of 95.1% methane, 3.5% ethane, and 1.4% nitrogen. The design of the POC system is such that as hydrates form on the exchanger-collector, the water level drops until the designated volume of the formation tank fills with gas hydrates.

The objective of this test was to evaluate functioning of the system and in so doing perform a 75% of full-scale run of the system including startup, vessel cooling, boiler operation and shutdown. The goal was to form hydrates in the test under a driving pressure of 550 psig and about 35^{o}F. The storage capacity would be indicated by the test results.

Estimate of Gas Stored Run HYD 10. The estimate of gas stored in the hydrates is based on an analysis of the bank of compressed gas cylinders and their pressures. See Table III.

TABLE III. Mass Balance of Natural Gas Used in the Process

Where Gas Located	Quantity of Gas, SCF
Total Gas Withdrawn from Gas Bank	4054
Gas Dissolving in Formation Tank Water	9
Free Gas in Formation Tank Head-space	484
Gas Occluded and Stored in Gas Hydrates	3561

The test stored 3,561-scf of gas in gas hydrates, or 4045-scf in the hydrates plus headspace free gas. The storage compared to an expected 3,750-scf to be stored based on the water level at the beginning of the test; this is 95% of design based on hydrate storage. The storage of occluded gas was 5% short of expectations for the following three possible reasons.

1. The initial water level covered 75% of the heat exchanger surfaces; hydrates form on exchanger areas covered by water. Therefore, 25% of the designed storage capacity was not used in the test.
2. Much of the three test segments were conducted with decreasing pressures. That is, batches of gas were added, and the pressures were allowed to decline as hydrates formed. The process design was for a constant pressure of at least 550 psig. Lower pressures hurt storage capacity as well as formation rate. The impact of the lower pressures on storage capacity is that fewer cavities in the hydrate crystal are filled with gas at lower pressures.
3. The natural gas utilized in the test was composed of 95.1% methane, 3.5% ethane, 1.4% nitrogen and no propane. This mixture necessitates higher pressures to form

hydrates and has higher equilibrium pressures at our operating temperature. In this regard, the methane-ethane mixture afforded a stricter test than that designed.

Gas Injection Sequence. Because of cost, the cheaper composition of 92.21/4.33/3.31/0.15 methane/ ethane/ nitrogen/ oxygen was used in Run #14 to supplement the 92.09/4.15/3.76 methane/ethane/propane. A bank of 12 cylinders containing 2894-scf of the propane gas was purchased. The two gas compositions were injected in a sequence of injections according to Figure 19.

The hydrate formation vessel was initially pressurized with the propane-containing gas. Note that the bank pressure declined at the end of the test to about 600-psi for each gas composition.

Cumulative Gas Stored in Run HYD-14. The natural gas stored in the hydrates of Run #14 was calculated from the continually monitored pressure decline in the banks of feed gases during processing. The compressibility factor equation of state was used with compressibility factor z calculated to be 0.91. The cumulative gas stored in gas hydrates as a function of time is presented in Figure 20.

The cumulative gas stored was 5289-scf. Even at the time of terminating flow of gas into the vessel, hydrates were still forming, as observed in Figure 23; after shutting off feed gas flow at the end of the test, hydrates continued to form as indicated by the decline of pressure in the vessel to eventually approach equilibrium. These observations mean that the cumulative gas stored ultimately exceeded the 5289-scf reported.

Especially significant was the fact that hydrates collected on metal surfaces of the heat exchanger for its entire length, and in doing so the accumulated hydrate solids left access of gas to the free solution in the bottom of the tank.

Chiller, burner-boiler, and controls in the process worked satisfactorily. Ambient temperature on-site external to the equipment sometimes reached 90^{o}F+ during Run Hyd-14, but the system operated satisfactorily despite these severe temperature constraints.

Data of water-column height provide more information on the hydrate formation during Run #14. See Figure 21. The anomalous blip in the trace between 47 and 65 hours indicates downtime because of feed line blockage. However, the water column height precisely follows hydrate formation. Note the abrupt decline in water level at hydrate initiation of about 19 ½ hours. It is interesting to observe in Figure 21 that all of the free water (except for probably a small quantity of water pooled in the bottom dome which is un-insulated and is below the heat-exchanger) was taken up by hydrates within the 45-hour mark. However, it can be surmised that hydrates continued to form after the 45-hour mark. In other words, significant hydrate particle-to-particle interstitial water remained to continue hydrate formation until system pressure decreased to its equilibrium value. This result in the POC corresponds to laboratory results encountered during the feasibility study. An important aspect of the surfactant-hydrate process is that this interstitial water continues to react because of the porosity and permeability of the hydrate particles, thus improving efficiency of storage-tank space utilization.

Reactions in Hydrate-Formation Vessel. The goal was to form hydrates in the formation vessel at 550 psig. Some interruptions to this goal were realized by a period of hydrates blocking inlet flow lines, switching flow lines between the two different feed-gas compositions (i.e. the 95.1% methane, 3.5% ethane, 1.4% nitrogen and the 95.1%

methane, 3.5% ethane, 1.4% nitrogen, and isolating the vessel to observe rate of pressure decline (an indication of hydrate formation rate). The progress of Run #14 can be followed from Figure 22, which presents a plot of hydrate formation vessel pressure versus time.

The formation vessel was initially pressurized with the 3.76% propane mixture at about +18.67 hrs, where time zero was designated earlier when the chiller was turned on. Therefore, two downtimes are noted on Figure 22 when hydrates were not being formed: around +20 hrs and between 49 hrs and 65 hrs when feed-line blockage occurred.

Effective hydrate forming times during the process are when the pressure was near the 550 psig operating pressure.

Rate of Gas Storage in Hydrates, Run HYD-14. The goal of 5000-scf of gas stored in the hydrates was reached in 48.1 hours of operating. Therefore, this corresponds to storing 104-scf/hr or 1.73-scf/min.

The test was terminated after 54.33 hours when 5289-scf of gas had been stored. After the feed gas had been shut off at 54.33 hours, hydrates continued to form as gas reacted with interstitial water; the pressure in the formation vessel lowered and approached equilibrium as the hydrates continued to form after the feed gas supply had ended. See Figure 23.

It can be seen in Figure 23 that pressure declined at a rate of about 0.94-psi/min immediately after shutting off gas input to the formation tank at the end of the run. The pressure declined because interstitial water continued to react with the gas. After leaving the equipment in this stagnant mode over the weekend, pressure declined to 290.6 psig, i.e., 305-psia, which is near the equilibrium pressure. At these equilibrium conditions, composition of free gas left in the system was calculated to be approximately 99.9% methane and 0.1% propane, a composition that checks fairly closely with laboratory results.

Therefore, more than 5289-scf could have been packed into the system if gas injection had been continued.

(2) Rate of Hydrate Formation

Heat Transfer Area. The peaking of localized temperatures as the hydrate front passed Figure 24 illustrates that the propane-containing gas provides a ΔT sufficient for hydrates to continue forming even at the peak temperature.

The data of Figure 24 reveal the important conclusion that operating temperatures in the formation vessel must be better maintained along the hydrate formation front to realize a maximum rate of hydrate formation; the peak temperatures show that heat-transfer area of the heat exchanger are less than needed. Control of peak temperatures to values lower than recorded in Run HYD-14 would be best achieved by increasing heat-transfer area of the heat exchanger.

Bottom Gas Injection. This was a short test to substantiate the improvement in hydrate formation rate afforded by bubbling feed gas from bottom of the vertical formation vessel through the cold solution; hydrates form at the water-gas-metal interfaces above liquid solution. Gas was injected through two bottom-injection ports. One port accommodated a ¼-inch spray nozzle and the second port accommodated a porous, Teflon, gas-diffuser plug through which flowed feed gas from a bank of compressed gas; the gas diffusers protruded into the cold solution of the formation tank.

Gas was input through the top port of the formation tank until pressure reached 524 psig. Gas flow was shut off and the refrigeration turned on to cool tank contents from ambient temperature toward a hydrate-forming temperature. The cooling condition was maintained until pressure drop indicated hydrate initiation, whereupon gas was injected through the bottom nozzles.

The hydrate formation rate increases at progressively colder temperatures below the equilibrium value. That is, magnitude of distance to the left of equilibrium represents a driving force for rate of hydrate formation. This can be seen in the Vysniauskas and Bishnoi Equation (1). (Vysniauskas, A., & Bishnoi, P.R., 1983, A kinetic study of methane hydrate formation. *Chemical Engineering Science,* 38, 1061- 1972.)

$$r = Aa_s \exp(-\Delta E_a / RT) \exp(-a / \Delta T^b) P^\gamma \qquad (1)$$

In Equation (1), the rate of hydrate formation r is determined by the degree of super-cooling ΔT below equilibrium, the absolute temperature T of the system, the pressure P of the system, the overall order of reaction γ with respect to pressure, the constants a and b, the lumped pre-exponential constant A, the surface area a_s of gas-water interface, the activation energy ΔE_a for hydrate formation, and the universal gas constant R.

The second injection was begun about 6.41 hours after starting refrigeration to the system. It is seen in Figure 25 that a greater ΔT below the equilibrium condition existed during the 2nd injection. In this case, TT207 in the bottom-dome water had reached a considerably lower temperature than during the first gas injection, approximately 37°F, although that temperature was still decreasing.

Hydrates formed during the start of the 2nd gas injection period to the extent that a hydrate formation rate could be estimated. In Figure 26 are plotted data of formation tank pressure versus time. Gas injection began at about 6.41 hours and the pressure declined until about 6.68 hours. During the pressure decrease the amount of injected gas, given as cumulative standard cubic feet, increased. The amount of injected gas was calculated from the decline in the gas feed-bank pressure.

From the times and gas flow rates of Figure 26, the hydrate formation rates of Figure 27 were calculated.

The hydrate formation rate in the first five minutes of injection was calculated to approach 11-scf/min. The hydrate formation rates calculated for this gas injection are very encouraging, especially considering that the gas composition contained no propane.

The short test of this report period injected gas through a spray nozzle and a diffuser in the bottom of the hydrate formation tank. After an abortive run in which bottom-water temperature had not been allowed to reach a low enough temperature, the next injection gave a peak hydrate formation rate of about 11-scf/min over a 5-minute injection period. Insight was gained on injection procedure.

(3) Temperature History Run HYD-14

The placements of the thermocouples in the Formation Tank are shown in Figure 28.

A localized temperature increase is a reliable means to determine where hydrates are forming at a given time. With the embedded thermocouples in the formation vessel, a peak temperature/time was found from the recorded data. The result is given in Fig. 29.

It is evident from Figure 29 that peak temperatures traveled down to the next level of thermocouples in about 5 minutes. Not shown is the peak temperature of the 4th thermocouple placed near the bottom of the vessel; it is not included in the graph because of considerable downtime from line blockage before hydrates reached the bottom. Although not shown in Figure 29, the thermocouple 12 inches from the bottom of the vessel reached a peak, localized temperature of 42.6^{o}F.

The complete temperature traces of the four thermocouples during Run #14 are presented in Figure 30.

Downtimes as well as hydrate formation times are included in the traces of Figure 30 and in order to pinpoint only operating times on this graph, also consult Figure 22.

The progressive and orderly traverse of the hydrate front down the length of the formation vessel indicates progressive collection of hydrates on the heat-exchanger fins and vessel walls as designed. If the water column also drops during this progression of the hydrate front, there would be more substantiation of the desired pattern of hydrate collection.

The temperature spikes during the process at each of the four thermocouples in the formation tank, presented in Figure 29, raise a question. How close do the operating temperatures at these points approach the equilibrium line? The answer is important because larger separating distances mean faster formation rates. In Figure 24 the operating pressure/temperature during the time the hydrate front passed each thermocouple is superposed on the equilibrium lines for both gas compositions used in the test.

(4) Gas Compositions

In all previous POC test runs, feed-gas composition was that given in Table IV. Values in the table are based on three gas chromatograph analyses. Note there is no propane in the mixture.

TABLE IV. Natural Gas Composition Used in Initial Tests

Species	Sample #1 Conc. %	Sample #2 Conc. %	Sample #3 Conc. %
CH_4	95.15	94.38	92.21
C_2H_6	3.49	4.48	4.33
C_3H_8	0.00	0.00	0.00
N_2	1.36	3.31	3.31
O_2	0.00	0.15	0.15

In Run HYD-14, a gas containing propane was purchased. The gas had the composition given in Table V. Values in the table are based on three gas chromatograph analyses.

TABLE V. Composition of Natural Gas Used in Run HYD-14.

Sample #	**Methane**	**Ethane**	**Propane**
1	92.20	4.12	3.68
2	91.99	3.92	4.09
3	92.09	4.41	3.50
AVG	92.09	4.15	3.76

The gas containing no propane was used because of a substantially lower cost. The use of the cheaper feed gas with no propane allowed setting an upper limit on processing requirements; that is, the gas containing no propane requires higher pressures to form hydrates at a given temperature.

The costs and capacities of different gas compositions from the local supplier (NexAir) are given in Table VI. (Note that a bank of 12 cylinders is used for a hydrate test run in which the 12 cylinders simultaneously feed into a manifold serving the hydrate formation vessel.)

TABLE VI. Relative Costs Feed Gas with Propane.

Propane, %	Cost/bank, $	Pressure Cylinder, psig	SCF in Bank
1	2411	2400	4172
3	2411	2250	3469
4	2411	1688	2894
0	1140	2400	4320

One technical advantage of the gas containing propane can be seen from Figure 31, which compares hydrate pressure/temperature equilibrium values for some gas mixtures that have been used in the hydrate tests. The operating pressure/temperature in the POC process is (550 psig) /35^{o}F, and at these values it is quite evident that $T_{eq} – T_{op}$ is much greater for the gas containing propane. Hydrate formation rate is a strong function of this temperature difference.

(5) Decomposition Process

After forming gas hydrates and storing about 5300-scf of natural gas in Run Hyd-DOE-14, the hydrates were decomposed and released gases burned in a boiler/burner. A small portion of the generated steam was returned to supply latent heat for dissociation of the remaining hydrates. During the dissociation process, the processing events given in Table VII could be followed on pressure and temperature traces.

TABLE VII. Events During Hydrate Decomposition of HYD-14

Time, hrs	**Press, psig**	**Processing Event**
0.6	280	Burning of gas in burner/boiler begun.
1.2	115	Some steam admitted to heat exchanger to warm fluid flowing through fins/jacket.
2.2	38	Flare went out. All systems shut down. Flows stopped.
4.5	320	All systems reinstated. Steam back on.
12.3	19	System shut down overnight. Remaining hydrates decompose overnight.
25	240	After prolonged shutdown, free gas ejected and flared.
25.2	12	No pressure increase after this point. All hydrates decomposed.

Pressure Trace Analysis of Dissociation. A formation-tank pressure versus time trace is helpful to understand the impact of different processing steps on hydrate dissociation. See Figure 32. Also, see Table VIII. Initially, the tank contents were at an equilibrium state for the given temperature, pressure, and free-gas composition. At about 0.6 hours after the designated decomposition starting point, free gases from the formation tank were expelled and flared in the burner/boiler; consequently the tank pressure dropped from about 280 to 115 psig. Over the subsequent 1.2 to 2.2 hours period, a small part of the generated steam was diverted, and its heat was exchanged with the glycol/water solution circulating through formation-tank jacket and internal heat-exchanger/adsorption-plates. As a result, pressure rose or fell in the hydrate formation/storage vessel, depending upon relative rates of dissociation and manual gas venting. At +2.2 hours, the flare inadvertently went out, requiring the system to be shut down until +4.5 hours. During that period, free gas increased in the formation tank until equilibrium was reached at the higher pressure. After reestablishing the venting, burning, and dissociation at +4.5 hours, decomposition continued steadily until +12.3 hours. Most of the hydrates dissociated and the gas burned during this period of 7.8 hours while maintaining a pressure of about 19 psig in the formation/storage tank. At the end of 12.3 hours point, the system was shutdown overnight for a 12.7-hour period, and during the shutdown all remaining hydrates decomposed. The liberated gas raised the pressure from 19 psig to about 240 psig. This free gas was vented and burned in a few minutes at +25.2 hours.

TABLE VIII. Events Explaining Formation-Tank Pressure History Fig. 32.

Time, hrs	Press, psig	Event
0.6-1.2	280- 115	Gas flaring begun. Free gas vented and burned. Tank press declines.
1.2- 2.2	115- 320	Pressure builds in formation tank from steam. When pressure declines venting rate increased.
2.2- 4.5	38- 320	Pressure increases to near equilibrium point because of decomposition while system is shutdown.
4.5- 12.3	320- 19	Major decomposition while steam is on and gases vented/flared. Pressure declines as gases are rapidly vented/burned.
12.3- 25	19- 240	Remainder of hydrates dissociate and pressurize formation tank overnight while system shutdown.
25- 25.2	240- 12	Free gas vented and burned in burner/boiler.
25.2+	12	Pressure in formation tank did not increase beyond this point. Therefore, all hydrates had decomposed.

Temperature Heat-Transfer-Fluid Analysis of Dissociation. The glycol-water solution that circulates through the formation tank is split to provide parallel flow through the tank jacket and internal exchanger/adsorption-plates. Upon exiting the tank, the streams are rejoined and either is cooled in the chiller or heated from burner/boiler steam. The temperature trace in Figure 33 is that of the combined fluid exiting the formation/storage tank. Again, time refers to the elapsed hours after beginning the dissociation process and synchronizes with the events of Table VII and Table IX.

The major decomposition period between +4.5 and +12.3 hours shows an increase of circulating fluid temperature from about 60^{o}F to 152^{o}. Abruptly at +12.3 hours, the fluid flow was stopped, and temperature decreased rapidly to about 62^{o}F because of no further heat exchange with the steam as well as the cooling effect of hydrate decomposition (latent heat for decomposition taken as sensible heat from the fluid).

TABLE IX. Events Explaining Heating-Fluid Temperatures Figure 33.

Time, hrs	Temp, F	Event
1.2- 2.2	40- 70	Heating fluid temp rises as consequence of steam contact.
2.2- 4.5	70- 60	Heating fluid temp levels out and then declines after system shutdown.
4.5- 12.3	60- 152	Temp rises rapidly when steam is turned back on. Hydrates decompose rapidly. Gases flared in burner.
12.3- 25.2	152- 62	Remaining hydrates decompose overnight during shutdown. Non-circulation and hydrate decompositions lower fluid temp.
25.2- 25.8	62-65	All free gas flared. No change in fluid temperature.

Temperature Inside Formation Tank During Decomposition. The four thermocouples placed inside the formation tank near the adsorption collection plates give a temperature history near the hydrate decomposition front. The thermocouples were placed as follows: 8" from top dome in free-gas headspace, 13" from top dome just below top of vertical heat exchanger, 32” from top dome, and 12” from bottom dome. The responses of the four thermocouples are presented in Figure 34.

The first recognitions of steam being added to the system were in temperatures of the free water in the bottom of the dome and temperatures of the free gas in the headspace. The first movements of temperatures in those places were some three hours after steam had been applied, and temperature in the free water increased first (no hydrates were in the bottom dome of the vessel, but some hydrates were in the top dome). The next thermocouple response was from TT202, 13” from the top-dome, signifying that the hydrates first decomposed near the top of the heat exchanger/collection plates, and then the decomposition front traversed downward.

In the final period between +12.3 and +25 hours, the four thermocouples converged on the same equilibrium temperature.

In Table X are listed major events that are evident in the four thermocouple responses of Figure 34, and these events help explain Figure 34.

TABLE X. Events Explaining Temperature History of Figure 34.

Time, Hrs	T, Top	T, 13” <Top	T, 32” <Top	T 12” >Bottom	Event
1.2- 2.2	32	32	32	32	No change in temp even after steam applied.
2.2- 4.5	32	32	32	32	No change in temp during shutdown.
4.5- 12.3	32-97	32-36	32-35	32-130	Major period of steam applied and decomposition.
12.3-25.2	97-62	36-62	35-64	130-62	All hydrates decompose overnight. Equilibrium achieved inside form tank.

Temperature History of Heat Exchanger/Collection Plates During Dissociation. The temperature traces of heat transfer fluid entering and leaving the heat exchanger (denoted as “fins”) are presented in Figure 35 and associated major events are presented in Table XI. Note the two temperature spikes of the entering fluid where steam was injected. Also note that the temperature of the leaving fluid is slightly lower that the entering fluid when hydrates are dissociating but the same when not dissociating.

TABLE XI. Events Explaining Figure 35 and Figure 36 Temperature Histories.

Time, hrs	T, ^{o}F Enter	T, ^{o}F Exit	Event Comments
1.2- 2.2	36-70	35.5-60	Temp difference reflects sensible heat increase to entering fluid and subsequent loss to decomposing hydrates.
2.2- 4.5	70-60	60-60	During shutdown, entering and exiting fluid temperature equalized.
4.5-12.3	60-200	60-149	A few degrees temp difference maintained over this long period of decomposition.
12.3-25.2	200-67	149-67	During shutdown overnight, the two temperatures equalize. All hydrates decompose.

In Figure 36, a very similar temperature history is recorded for the heat transfer fluid entering and leaving the formation tank jacket. Similar interpretations are made for the traces in Figure 36 as in Figure 35.

Status of Hydrate Decomposition Step in the Storage Process. Most of the hydrates were decomposed during the two periods of 1.2 to 2.2 hours and 4.5 to 12.3 hours when steam was intermittently applied to the circulating heat-transfer fluid. Therefore, the hydrates containing the 5300-scf of gas were essentially decomposed, gases vented, gases burned, and steam generated during those 8.8 hours. There was no indication that decomposition during the 8.8 hours represented any maximum rate of decomposition. On the contrary, it appeared that hydrates could have been dissociated faster.

The heat-transfer surfaces of the heat-exchanger/adsorption-plates accommodate cooling for hydrate formation and also allow heating for decomposition. Because of much larger driving force of temperature difference of heating medium and equilibrium temperature of the hydrates, the decomposition becomes easy to perform, as expected. For example, even 110^{o}F effluent fluid from an electric utility power-generating cycle should be adequate to decompose the hydrates. In the subject experiment, only a fraction of the steam generated was needed to decompose the hydrates; the quantity of steam returned to heat circulating heat-transfer fluid was not measured.

The apparatus was designed so that hydrates would form symmetrically around the fins and heat-exchanger tubes arranged vertically in the formation/storage vessel. Some open space would then exist from the top to the bottom of the tank that would allow gas access along the exchanger length. The arrangement was to also allow free flow of exiting gases through the top of the formation/storage tank. This appears to have resulted during the decomposition, as no high-pressure pockets developed within the hydrates that interrupted flow of exiting gases. Data indicate that hydrates decomposed from top to bottom in candle-burning fashion, or at least the decomposition gradient was steep from top to bottom of the tank.

Decomposition rate proved to not be a limiting factor in the overall hydrate formation/storage/decomposition process. No problems were encountered.
hydrates (5300-scf of natural gas) was accomplished in about 8.8 hours. Gases were vented through a partially opened valve in the storage tank, then flowed to a surge vessel, and finally flared in the boiler burner. A small fraction of the steam was

Decomposition Conclusion. The decomposition of the full storage tank of
used to supply latent heat for further hydrate decomposition. Most of the hydrates were decomposed with total pressure in the storage tank reduced to about 19 psig.

As planned, flows of gases from the storage tank were unhindered in the design of the heat-exchanger/adsorption-plates.

The results indicate that a low-grade heat source would probably be adequate to decompose the hydrates.

The boiler/burner operated satisfactorily and performed the triple function of flaring gases, generating steam, and supplying latent heat for complete hydrate decomposition.

Hydrate decomposition rates could be regulated by controlling temperatures of the circulating heat-transfer fluid.

Breaking Foam. Laboratory tests were conducted to break foams generated when gas hydrates decompose in a surfactant-based process. From the feasibility study, foam was noted as a potential problem. When the hydrates form from a water-surfactant solution, hydrate is excluded from the structure of the hydrate crystal and is relegated to the interstitial spaces around the hydrate particles—possibly attaching to the outer surfaces of the hydrate particles. Upon decomposition of the hydrates, outer layers of hydrate go to liquid water and cold gas is evolved. Foam is produced because the liquid water-surfactant contacts evolved gas. These liquid-gas emulsions are easier to form at colder temperatures. The SDS surfactant is in the liquid film of the bubble and stabilizes the foam. Raising the temperature of the exiting stream proved to be the best remedy to foaming in the laboratory. However, expanding decomposition gases into a holding tank in the POC process prior to burning gases in the burner/boiler did not present a foam problem in the scaled-up tests.

(6) Bottom Injection

Previous tests in this grant indicated that injecting feed gas through the chilled water-solution from the bottom of the formation tank substantially increased hydrate formation rate. Also, bottom injections of the gas through a small spray nozzle and/or through a Teflon gas-diffuser were evaluated. Positive results were obtained when the nozzle and diffuser were operated in tandem; hydrate formation rate became 10 to11-scf/min during the first 5-minutes of gas flow. (These results were obtained with a 95.15/3.49/1.36 methane/ethane/nitrogen gas mixture.) Operated singly, some hydrate plugging was evident, especially in the Teflon gas-diffuser. However, these results substantiate previous positive short tests with bottom injection.

B. LABORATORY TEST RESULTS

(1) Eliminating Foam

Ten experimental runs were made to check the foam-removal effectiveness of anti-foaming agents, demister knockout, and temperature.

Anti-Foaming Agent. Foam from the SDS-water solution was readily generated in the 2000 ml flask and the overflow passed through a second 2000 ml flask half-filled with Tergitol XD. Foam was generated above the anti-foaming solution, and in about 4 minutes overflowed the top outlet port of the 2nd flask. The Tergitol XD was ineffective in eliminating foam.

The test was repeated and foam was directed beneath the surface of a Tergitol 15-S-3 water solution. Again, foam formed above the anti-foaming solution and overflowed the top outlet port in about 2 minutes. The foam created above the Tergitol 15-S-3 was more stable than that above Tergitol XD of the previous run.

Again, a test directed foam beneath the surface of Polysorbate 60 solution. Foam buildup over Polysorbate 60 was slower than the previous two runs with Tergitol. Also, foam that developed over the Polysorbate broke down faster than with Tergitol of the previous two runs. Although not viable for scale-up from the laboratory arrangement, Polysorbate 60 might be useful in breaking the foam in another or POC arrangement.

A fourth test used the fluorosurfactant Zonyl FSP as an anti-foaming agent in a laboratory arrangement similar to the previously discussed experiments. The vigorous motion of gas bubbles at the surface of the zonyl solution in the second flask reformed the foam. Zonyl FSP was ineffective in breaking the foam.

The fluorosurfactant was sprayed through a mister that produced about 100 μm diameter liquid drops; the Zonyl FSP was sprayed onto the surface of a stagnant SDS-generated foam. There was no appreciable breaking of the foam.

Demister-Type Liquid Knockout. A stainless steel screen was placed in the overflow line of the first series 2000 ml vacuum flask. The screen thickened the foam and made it more stable. It was concluded that the least amount of shear possible must be put on the water-gas-surfactant stream to minimize foam generation.

Raise Exiting Foam Temperature. SDS-water-gas foam was directed through the tubes of a glass heat exchanger. Selected temperatures were imposed on glycol-water flowing through the heat-exchanger shell-side. As temperatures were increased from 80°F to180°F, the foam was progressively broken. Gas within each bubble expanded with temperature to stretch the surrounding liquid film until that film ruptured. It became apparent that heating the exiting gas stream was the best direct way of reducing foam during hydrate dissociation.

Several other helpful procedures became evident in the laboratory tests: (1) Minimize shearing of exiting stream. (2) Make exiting lines as large diameter as practical. (3) Make the exiting lines as short as possible. (4) Dump the exiting stream into a holding tank. (5) Warm the exiting line that contains foam with a heat exchanger.

Warming the line with the dissociated gas is also beneficial from the standpoint of increasing this feed gas temperature that is going to the burner/boiler to increase efficiency of the steam generation.

In the POC process, a holding tank or surge tank collected dissociated gases before the gases went to the burner/boiler. Although no heating of dissociated gas was performed in the POC tests, dumping into the surge tank and possibly larger exit lines than used in the laboratory apparently reduced foam. Foam was generated in the large-scale tests, but dissociated liquid from the foam could be drained from the POC surge tank. The foam proved to be manageable in the large-scale runs with these two relatively minor adjustments.

Conclusions on Eliminating Foam. The following conclusions may be drawn from the laboratory tests and the concurrent POC tests.

1. Anti-foaming agents were not effective in breaking the foam.
2. Shear must be minimized in the product line transporting the foam and dissociated gas. Short product piping should be designed. Large-diameter piping is desired.
3. Heating the foam proved most effective. Breaking of the foam improved as temperatures of the stream were raised. At 180^{o}F adequate foam dissipation occurred in the laboratory.
4. The larger product lines of the POC process and the dumping of the product line into a surge/holding tank helped dissipate the foam in the large-scale process so that it was manageable. No interference of foam with burning gas in the boiler/burner was encountered.

(2) Surfactant Adjustment Tests

Biosurfactants have been found to catalyze gas hydrate formation in porous media (Rogers et al., 2003). Especially effective has been Surfactin, a lipopeptide bioproduct of the *Bacillus subtilis* bacterium, a microbe commonly found in soil. Surfactin is one of the more powerful surface-active agents (Nakano et al., 1988), and it is used in medicine as an anti-blood-clotting agent and also as an antibiotic. The *Bacillus subtilis* has been identified as a microbe active around gas-hydrate outcrops on the floor of the Gulf of Mexico (Lanoil et al., 2001). The Surfactin that *Bacillus subtilis* produces has been found to be one of the most effective surfactants in promoting gas hydrate formation in sand/bentonite packings (Rogers, et al., 2003). The objective was to perform laboratory tests determining if Surfactin, a powerful surface-active agent generated by the *Bacillus subtilis* bacterium, would improve gas-hydrate formation rates if used in conjunction with the synthetic surfactant SDS commonly used in the POC hydrate storage process.

Bacillus subtilis of the ATCC 21332 species was cultured in the laboratory. When the critical micellar concentration of the biosurfactant Surfactin was reached, an inert gas was bubbled through the broth to generate foam. Surfactin was concentrated in the foam's films that allowed recovery of the biosurfactant by passing the foam through distilled water.

The Surfactin that was collected was mixed with the SDS synthetic surfactant to determine if the combination improved hydrate formation rates in the gas storage process. The pure Surfactin was also compared to the SDS effect on hydrate formation. Gas hydrates were formed in the laboratory test cell under pressure and temperature conditions of the POC gas-storage process. Hydrate formation rates, induction times, solution surface tensions, and pressure drops during hydrate formation were compared for the different surfactants and their combinations.

Surface Tension. A primary property distinguishing surfactants is the surface tension exhibited in water solution. In promoting gas-hydrate formation, the role of surface tension is relatively unknown, but two other properties of the surfactant are important in promoting hydrate formation. One is the ability to bring together the insoluble hydrocarbon guest gas with structured water to initiate hydrate formation. Another is the ability of the surfactant to attach to a solid surface at the gas/water interface to prevent mass transfer from becoming the rate-limiting step during hydrate formation.

Data showed 300-ppm concentration of SDS in distilled water gives a fairly consistent 64.6-mN/m surface tension. That is, the 72-mN/m surface tension of distilled water is reduced by the addition of the SDS. However, Surfactin reduced the 72-mN/m surface tension of water to as low as 29.3-mN/m when the biosurfactant was added. Such a large reduction in surface tension is the reason Surfactin is characterized as one of the most powerful surface-active agents.

In fact, the surface tension of a 300-ppm SDS-water solution becomes 34.1-mN/m when a similar amount of Surfactin is mixed with it. The tests showed conclusively that surface tension could be reduced greatly by combining some Surfactin with SDS. This can be seen in Figure 37.

Hydrate Induction Times. Hydrate induction time is the hydrate-initiation lag time after establishing hydrate-forming conditions of pressure and temperature on the system. Surfactants generally reduce this time by bringing to one nucleation site the hydrocarbon gas and the structured water. (The hydrophobic group of the surfactant molecules attracts the hydrocarbon gas and the hydrophilic group attracts the water—possibly structured water. Thus, the longer time for random meeting of gas and structured water is circumvented.) Induction time, therefore, serves as one indicator of the propensity for hydrate formation.

In Figure 38 the relative induction times involving each of the two surfactants and their combination are presented.

It is evident in Figure 38 that Surfactin shortens the time by half to initiate hydrate formation in the laboratory—a positive incentive to combine some Surfactin with SDS. However, in the POC-scale test runs, induction time was not a problem. SDS was used in all of the POC tests, and hydrate initiation began immediately. The difference of induction times in the two process scales is attributed to a larger metal surface area in the POC facility.

Peak Hydrate Formation Rate. The formation rate of the gas hydrates after crystal initiation refers to the rate that free gas is occluded into the solid hydrate matrix. Therefore, it is important to maximize the formation rate for any industrial process. One way of measuring this parameter is to take the maximum rate after hydrate initiation, which can be accomplished from the pressure-temperature-time trace of the test cell contents. In Figure 39 is presented the peak formation rates realized with SDS, Surfactin, and SDS-Surfactin mixture.

The laboratory results in Figure 39 show that pure Surfactin dramatically decreases the hydrate formation rate from that realized with pure SDS. However, the mixture of the two surfactants gives about a 25% increase in the rate. The reason for the apparent paradox is the following.

SDS adsorbs readily on metal surfaces at the gas-water interface, and in doing so directs the developing hydrate mass to that solid surface. An important result of the surfactant on metal adsorption is that the liquid surface is kept clear of any hydrate film; with adsorption occurring, mass transfer is not a rate-controlling step in hydrate formation. Direct contact of free gas with the free-water surface is maintained. The data indicate that Surfactin does not readily adsorb on the metal surface. When Surfactin is the only agent present, hydrates are initiated rapidly, but a hydrate film develops on the water surface and thereafter gas must diffuse through the film barrier to react with the water.

It is implied that porous media in ocean sediments adsorb Surfactin to promote hydrates in a manner similar to metal adsorbing SDS in the test cell to promote hydrate formation. Therefore, it may be stated that the effectiveness of a surfactant depends upon its relationship with an adsorbing surface.

When SDS and Surfactin are combined, the net result is about a 25% improvement in hydrate formation rate. In other words, the SDS performs the service of adsorbing on the metal surfaces and the Surfactin plays a role to better solubilize the hydrocarbon gas and reduce surface tension. The effects are additive.

Formation Rate From Pressure-Drop Rate. One way of determining hydrate formation rate in the laboratory test cell is to calculate pressure drop with time. As free gas goes into hydrate solid solution, pressure of the test cell drops precipitously. This can be seen in Figure 40 and in Figure 39.

The Surfactin does not adsorb on the test-cell walls, and as a consequence mass transfer becomes the rate-limiting step in the reaction. Again, the rate is improved somewhat with a 50%/50% combination of SDS and Surfactin.

Total Pressure Drop. The total pressure drop in the laboratory experiment is a measure of the capacity of the hydrates to occlude hydrocarbon gas. In each experiment, the test cell was pressurized with the same amount of gas. In Figure 41 it is seen that the water solution with 100% Surfactin occluded the least amount of gas.

The 100% SDS solution and the 50/50 SDS/Surfactin solution gave the same maximum gas capacity. This means that an appreciable amount of water was prevented from forming hydrates because of the inhibiting hydrate film on the 100% Surfactin-water surface. Again, the mixture of SDS and Surfactin adsorbed on the metal surfaces and all water reacted to completion—that is, free water and interstitial water.

Conclusions on Surfactant Modification. The biosurfactant Surfactin was found to complement the action of the synthetic surfactant sodium-dodecylsulfate in promoting gas hydrates. SDS has been used in all POC test runs.

The following conclusions are drawn from the use of Surfactin as the only surfactant in forming gas hydrates:

1. Surfactin greatly reduces the surface tension of the water solution. Surface tension is reduced to less than 30-mN/m.
2. Surfactin reduces the induction time for hydrates to form.
3. Surfactin does not cause the developing hydrate crystals to adsorb on a metal surface at the gas-water interface. Therefore, a hydrate film forms on the water

surface and slows subsequent hydrate formation rate. This negative factor obviates the positive factors (1) and (2).

Surfactin used with SDS in a 50%/50% combination gives the following results.

1. Surface tension is reduced to 32-mN/m from the 64.6-mN/m of SDS alone.
2. Hydrate induction time is reduced to 92 minutes from 116 minutes in the laboratory tests.
3. Hydrate formation rates are increased by about 25% over SDS alone.

These results indicate some potential advantage in combining Surfactin with SDS in the hydrate storage process. Although Surfactin is expensive to purchase commercially, our method of preparing it in the laboratory for these tests was simple and probably could be done inexpensively on a larger scale.

C. OVERVIEW OF POC TESTS PERFORMED

A summary of the work performed on the project during each quarter of the grant duration is given in Table XII.

TABLE XII. Summary of POC Test Runs, Grant Duration.

Quarter	Run #	Comments on General Nature of the Work Performed
2nd, 3rd Qtr '02	n/a	Designing process, equipment, procedure.
4th Qtr '02	n/a	Design completed. Bids sought.
1st Qtr '03	n/a	Order equipment, select construction company, construct formation vessel
2nd Qtr '03	n/a	Test bay construction. Purchased equipment received.
3rd Qtr '03	n/a	Installation of equipment.
4th Qtr '03	HYD-1	Tests cool-down rates, leaks, instruments. Hydrates formed; limited to 15% capacity.
1st Qtr '04	HYD-02-07	Tests to verify equipment, operating procedures. No hydrates formed.
1st Qtr '04	HYD-08	Burner-boiler test. Free gas burned. No hydrates. Steam generated.
1st Qtr '04	HYD-09	Burner-boiler test. Hydrates formed. Steam generated.
2nd Qtr '04	HYD-10	75% of full-scale run; 4,045-scf gas stored.
3rd Qtr '04	HYD-11	2,766-scf gas stored. Rates calculated.
3rd Qtr '04	HYD-12	Bottom injection of gas evaluated to improve hydrate formation rate.
4th Qtr '04	HYD-13	Bottom gas injection, nozzles and diffusers. Tests hydrate formation rates.
1st Qtr '05	HYD-14.a.	Two feed gas compositions evaluated; 5,289-scf gas stored in hydrates.
2nd Qtr '05	HYD-14.b.	Decomposition of hydrates, steam generation, steam for hydrate decomposition.
3rd Qtr '05	Lab	Improving hydrate formation rates. Surfactin evaluated.
4th Qtr '05	Lab	Studies to break foam from hydrate decomposition.
1st Qtr '06	n/a	Economic analysis. Technology transfer. Final report.

During the grant, seven test runs were made in the POC process equipment that involved gas hydrate formation. This regimen allowed adequate evaluation of the process. The high cost of the natural gas to use in the tests necessitated a careful scheduling to efficiently obtain the most information from the tests. Domestic natural gas climbed from low prices at the time of the proposal to historic highs during the grant period. From the local supplier, a natural gas composition with propane (92.09/4.15/3.76 methane/ethane/propane) that form Type II hydrates cost more than twice a natural gas composition without propane that form Type I hydrates (92.21/4.33/3.31/0.15 methane/ ethane /nitrogen /oxygen). Therefore, most of the runs were made with the gas without propane, which established a more stringent set of conditions for Type I hydrates to form because of higher equilibrium pressure requirements and colder equilibrium temperature requirements. In the last POC run, HYD-14, each of the two gas mixtures was alternately injected to determine storage capacities and rates of formation yet conserve funds. Fortunately, data from the two gas mixtures indicate a range of hydrate-formation ease for variable natural gas compositions that would probably develop in industrial applications.

D. ECONOMICS OF THE SURFACTANT PROCESS

(1) Attributes of the Surfactant POC Process.

The scale-up factor from laboratory process to POC facility was about 300/1; roughly, a 1-gallon laboratory unit was scaled to about a 300 gallon hydrate formation vessel. The parameters distinguishing the surfactant-hydrate process from other hydrate storage processes proved to have the same economic impact on the large-POC-scale process as indicated at the laboratory size.

(a) The surfactant adsorption property facilitated the self-packing of hydrates as they formed on the metal surfaces of the vertical heat exchanger. This avoids potentially costly steps of manually filtering, collecting, and packing cold hydrate particles from pressurized slurries. Not only is labor saved by the surfactant procedure, but equipment costs for the circumvented unit operations are saved.

(b) The procedure with the surfactant-assisted process provides maximum control over the formation or decomposition of hydrates. Flow rates and temperatures of heat transfer fluid in the heat exchanger may be changed at will. Upon hydrate decomposition, energy is delivered efficiently throughout the stored hydrate mass by means of the exchanger/adsorption plates. Especially for decomposition, the arrangement gives superb control over stopping, starting, and limiting the amount of gas liberated from hydrates.

(c) The surfactant is cheap and can be reused.

(d) The process proceeds by maintaining operating pressure on the system by admitting more gas as hydrates form. This can conveniently be done with simple automatic process controls and eliminates labor costs.

(2) Budgeted Equipment Costs of Surfactant POC Process.

Table XIII presents the major equipment costs in the POC installation.

TABLE XIII. Major Equipment Costs of POC Facility.

Flow Chart Designation	**Item**	**Cost, $**
NG-101	Methane Gas Cylinder Bank	2,280*
PRG-102	Pressure Regulator	404
T-201	Hydrate Formation Tank	41,900
PRV-202	Pressure Relief Valve	165
PRV-208	Pressure Relief Valve	165
T-302	Effluent Surge Tank	590
PRV-302	Pressure Relief Valve	75
CH-401	Chiller	8,145
PRV-418	Pressure Relief Valve	75
T-419	Glycol Surge Tank	980
FT-501	Flow Indicator	471
T-502	IE Water Unit	633
M-506	Static Mixer	160
	TOTAL	**56,043**

*Varying cost of gas during project duration

The contract was accomplished within budget.

As expected, the main expense is the $41,900 hydrate formation vessel. However, the major cost of this R&D vessel could be lowered in a production facility by four ways: (a) Use carbon steel instead of stainless steel to fabricate the pressure vessel. (b) The vessel was designed and built with an operating pressure of 550 psig and a maximum pressure of 650 psig, while being hydro-tested to 800-psi upon completing construction. The operating pressure could be kept at 550 psig and a pressure relief system designed to lower the maximum working pressure below the 650 psig. The over-design for pressure is especially expensive in this situation because the large diameter of the vessel necessitates much thicker walls for the added pressure. (c) The design gave a bottom dome area that extended below the heat exchanger surfaces. This required additional volume and weight of stainless steel in the vessel as well as creating extraneous volume to be cooled/warmed. Note that hydrates did not form in this space below the bottom of the heat exchanger so that it was in effect superfluous. (d) Because of the sensitivity of vessel wall thickness (and consequently cost) to diameter, reduction in formation-vessel diameter with an attendant increase of length would reduce cost. Diameter/length should be optimized based on the results of the POC tests.

The four suggestions to reduce cost of the formation vessel are estimated to lower the $41,900 cost by 50 %. It is possible with the aforementioned decreases of storage vessel costs that the gas storage cost ($/Mcf) based on formation vessel cost could be acceptable for a stationary storage facility with the capital cost of the vessel amortized over many cycles of storage/decomposition.

(3) Extending Process to Gas Transport.

The POC facility for storing natural gas in gas hydrates by using the surfactant process to reduce labor and the number of processing steps was designed for stationary storage. The storage vessel as evaluated in the POC facility is too heavy for gas transport. However, the results of the subject grant suggest that alterations could be made to the process that would take advantage of the surfactant process to form and self-pack hydrates. The alterations would reduce storage costs ($/Mcf) substantially. The two necessary innovations are detailed as follows.

High-Pressure, Small-Diameter Semi-Continuous Reactors Feeding into a 1-atm Storage Vessel. Consider the benefits of multiple, small-diameter, parallel reactors in a semi-continuous process that transfers products to a 1-atmosphere storage container for transportation.

a. A small diameter formation vessel, perhaps a 4-inch diameter similar to the laboratory reaction vessel, would reduce metal requirements for high-pressure operations.
b. The small diameter reactor would allow formation pressures exceeding 550 psig, which would increase formation rate and the percentage of hydrate cavities filled with gas.
b. Reactors should be made of carbon steel to reduce costs.
c. Multiple, small reactors operating in parallel give desired throughput.
d. A semi-continuous process increases throughput to higher levels. A semi-continuous process could be automated to reduce labor.

e. The multiple, small-diameter, parallel reactors would form the hydrates but would not be part of storage or transportation. Thus, the capital costs of the reactors would be amortized over a very large amount of processed gas to reduce equipment costs for processing ($/Mcf) greatly.
f. The gas hydrate product from the multiple reactors would be stored at 1-atmosphere and –1 to –5°C. Storage container weight is then small enough for transportation to be competitive with LNG. Storage container cost is very low. Data taken in our laboratory looks promising for stable storage of methane and natural gas hydrates at 1-atmosphere storage pressure and –1 to –5°C storage temperature.

(4) Updating Economics of Large (+2.5 million standard cubic feet) Gas Storage Facility

In the feasibility study that preceded the POC scale-up, the economics was estimated of a large 2.5 MM-scf facility concept. For that concept, the economics was not appreciably altered by the POC tests, and experiences in constructing as well as operating the larger POC facility showed ways to improve costs of construction and operation.

However, the POC scale-up experience suggests a cost-cutting improvement of the concept for large, stationary storage facilities that would use the surfactant process in smaller-diameter semi-continuous reactors processing large throughput volumes of hydrates at high pressure and feeding into 1-atm storage vessels. The phenomenon of stable 1-atm storage at –1°C to –10°C that has developed[1,2,3] since the feasibility study, introduces this possibility of reducing the expense of formation vessels and storage vessels in large, stationary storage facilities.

---

[1] Stern, L.A., Circone, S., and Kirby, S.H., “Anomalous Preservation of Pure Methane Hydrate at 1 atm,” *J. Phys. Chem. B.*, **105**, 1756- 1762 (2001)

[2] Takeya, S., Shimada, W., Kamata, Y., Ebinuma, T., Uchida, T., Nagao, J., and Narita, H., “In-Situ X-ray Diffraction Measurements of the Self-Preservation Effect of CH_4Hydrate,” *J. Phys. Chem. A.*, **105**, 9756- 9759 (2001).

[3] Circone, S., Stern, L.A., and Kirby, S.H., “The Effect of Elevated Methane Pressure on Methane Hydrate Dissociation,” *American Mineralogist*, **89**, 1192- 1201 (2004).

(5) Inquiries into Utilizing the Process

Inquiries were received about utilizing the surfactant hydrate process for storing and transporting methane and natural gas. Discussions were engaged and are ongoing. Table XIV summarizes this activity.

TABLE XIV. Ongoing Discussions of Hydrate Process Utilization.

No. of Companies	Type Company	Specific Interest for Hydrate Process
1	Major	Transport natural gas in stranded field By forming hydrates. Railcar.
1	Major	Transport natural gas in competition With LNG. Ship.
3	1. Major 2. Major/small co. 3. Startup Co.	Stationary storage facility. Large facility. Safety aspects.
1	Small	Small-scale stationary, remote storage. For emergency backup gas supply.

V. CONCLUSIONS

The following major conclusions are made from data gathered from the project.

1. Gas hydrates were formed from a SDS-water solution pressurized to 550 psig at approximately 35 – 40°F in the POC scale-up of the laboratory process with the following results:
    - a. 5300+ scf of natural gas was stored in the formation vessel. This exceeded the goal of 5000-scf.
    - b. Hydrates collected on the finned heat exchanger as the water level in the vessel dropped. This self-packing in the POC vessel was as observed in the laboratory.
    - c. Rate of hydrate formation was less than planned because of fins on the heat exchanger not being to specification. Instead of individual fins intimately contacting the heat-transfer-fluid tubing all along the tubing length, the fins appeared to be spot-welded along the length. A second fault of the fins were that metal was bent in a U-tube to form two fins; this gave too narrow of a spacing between pairs of fins and negated about ½ of the surfaces planned for heat transfer and hydrate collection.
    - d. The POC design provided even heat distribution to the solid mass of hydrates to decompose them when it was desired to release the gas. Not only did the design provide even and quick delivery of heat to decompose the hydrates, but the symmetry of the heat-exchanger design provided adequate pathways for liberated gas to exit the vessel.
    - e. The burner/boiler worked superbly in combusting released natural gas and generating steam. A small fraction of the steam was recycled to the heat exchanger to release gas from hydrates. The POC proved that release rate of gas from hydrates could be controlled. Fast, slow, or intermediate rates of gas release could be established at will.
    - f. Foaming of surfactant-water solution upon gas release was not a problem.
    - g. The work was kept within budget. Construction costs were within budget. The hydrate formation tank was the most expensive item at $41,900.
    - h. The data indicated some improvements to the hydrate formation tank to reduce its cost and alleviate its impact on storage costs ($/Mcf) if placed on a commercial basis. Instead of stainless steel, the vessel should be made of carbon steel. The diameter-length of the formation vessel should be optimized to be most cost effective. Diameter would be decreased to give less cost to maintain 550 psig operating pressure. Maximum pressure for which the vessel is designed could be reduced from 650 psig by incorporating multiple pressure relief valves. Unused volume of the tank's bottom-dome

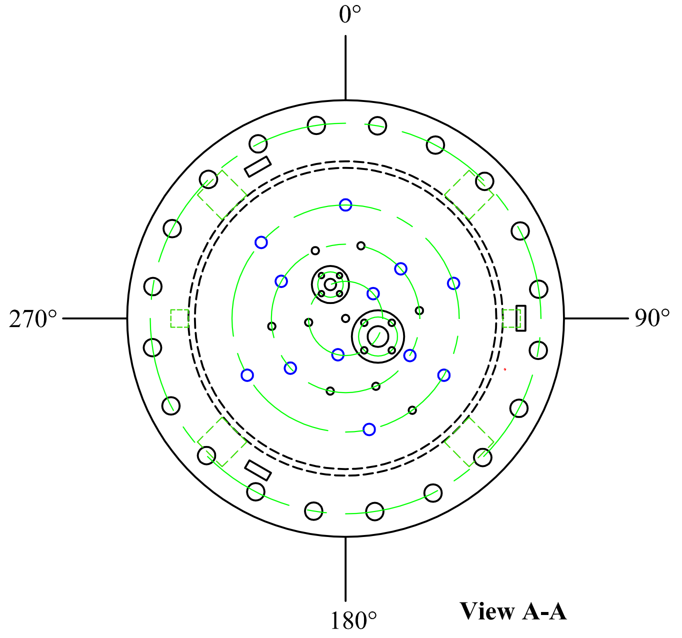
where hydrates did not form should be eliminated. The improvements are estimated to cut the $41,900 cost by 50%.

  i. Hydrates could be formed and the pressure vessel filled with hydrates by simply maintaining gas pressure on the system.
  j. Refrigeration system, refrigerant delivery to process, gas injection, insulation, vessels jacket, thermocouple and pressure measurement systems functioned satisfactorily in the process.
  k. The control room established next to the process demonstrated easy process control and monitoring.
  l. The hydrate formation vessel should have transparent viewing ports.

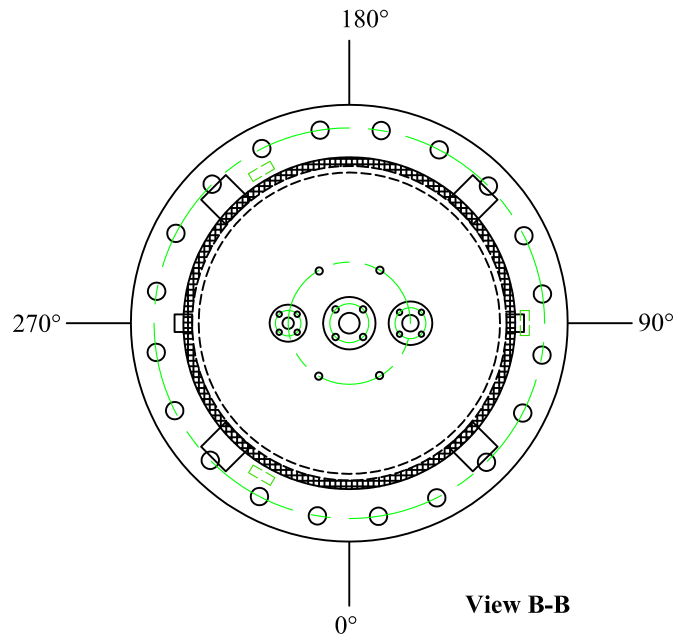
2. The process as demonstrated verified technical capability to serve stationary natural gas storage needs on a small scale. The hydrate formation vessel cost must be reduced to make the process economically attractive for stationary storage: reduce diameter, optimize diameter/length, eliminate extraneous volume in bottom dome, use carbon steel instead of stainless steel, provide pressure relief valves to reduce maximum design pressure.
3. It is recommended that the surfactant process could be competitive in gas transport by altering the POC design to parallel high-pressure, small-diameter semi-continuous reactors feeding into a 1-atm storage vessel. Technical capability exists to accomplish the semi-continuous design and 1-atm stable storage.

Figures

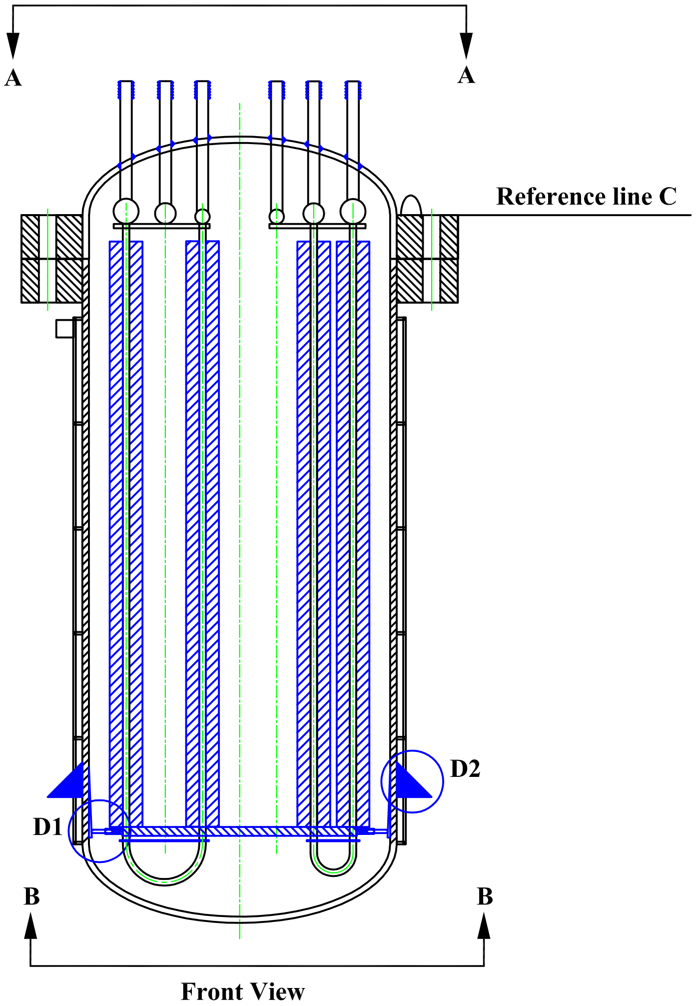
Fig. 1. Assembled Pressure Vessel and Heat Exchanger



View A-A



View B-B

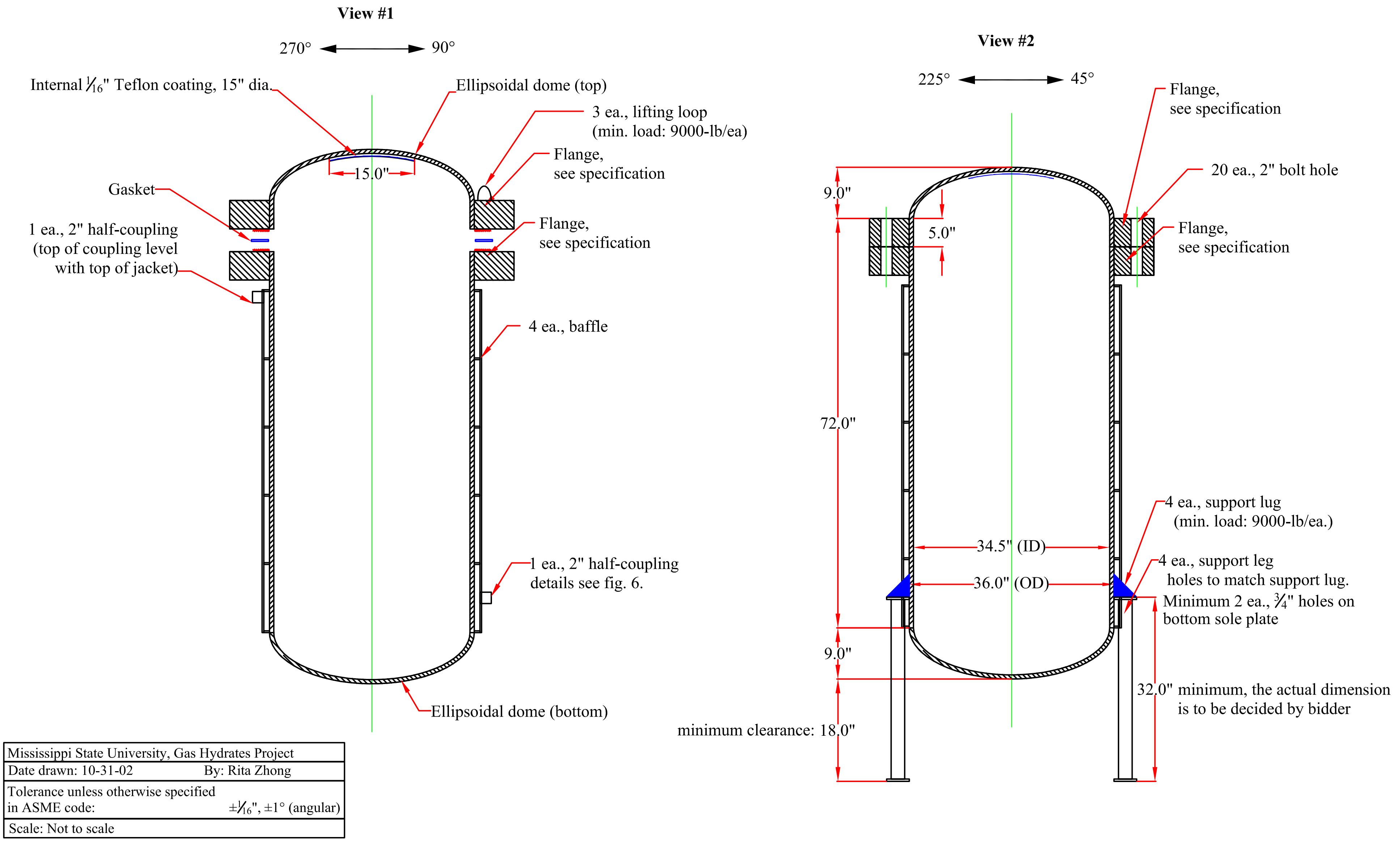


Front View

Note: 1. Assemble with insulation wire on the outside of vessel and jacket
2. Penetrations to top dome must be machined to fit heat exchanger.

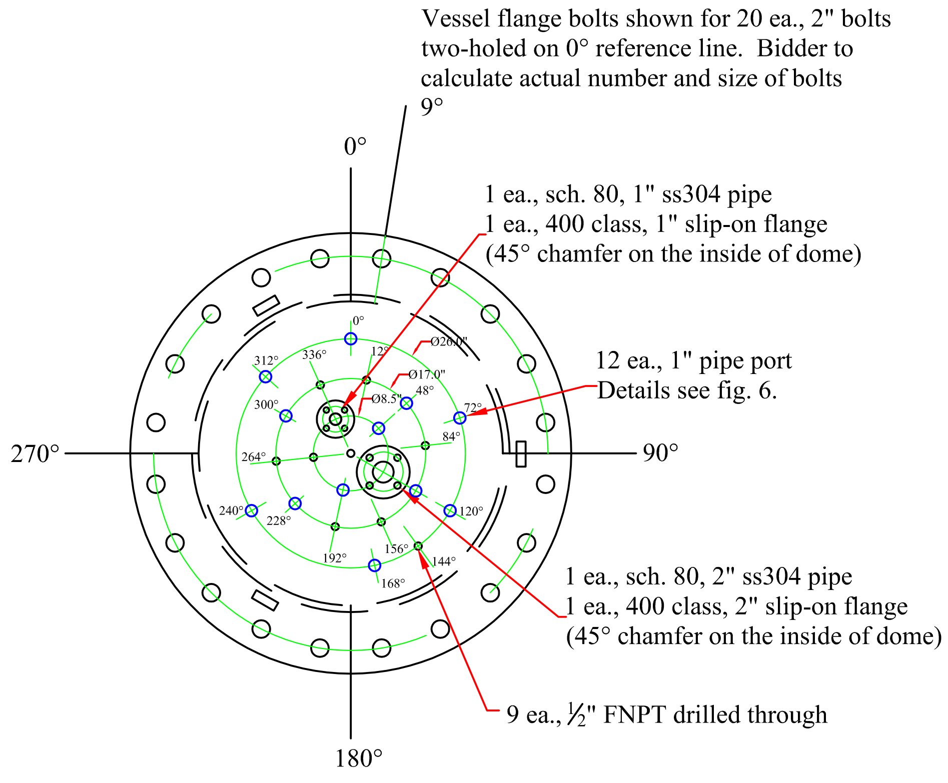
Mississippi State University, Gas Hydrates Project
Date drawn: 10-31-02 By: Rita Zhong
Tolerance unless otherwise specified in ASME code: ±1⁄16", ±1° (angular)
Scale: Not to scale

Fig. 2. Vessel Cutaway Side Views

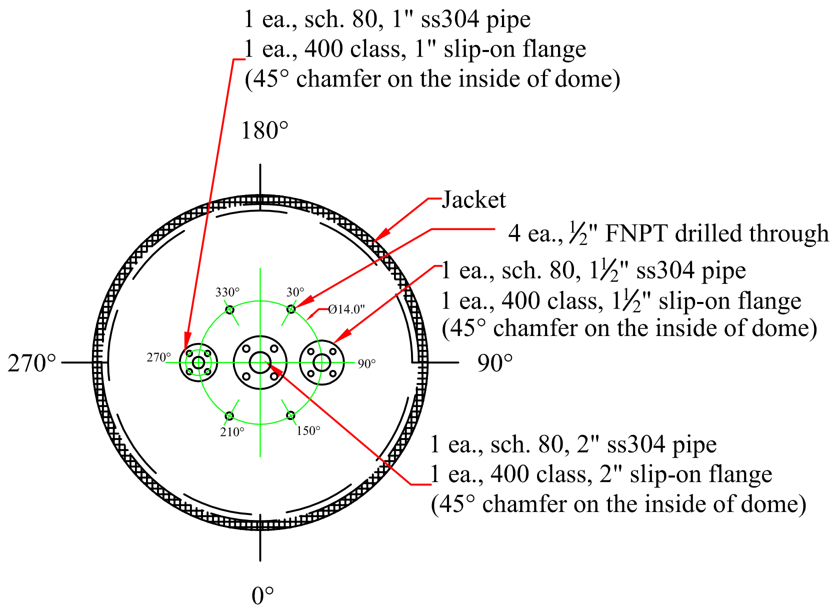


Mississippi State University, Gas Hydrates Project	
Date drawn: 10-31-02	By: Rita Zhong
Tolerance unless otherwise specified in ASME code:	±1⁄16", ±1° (angular)
Scale: Not to scale	

Fig. 3. Ports and Nozzles on Vessel Domes



View A-A

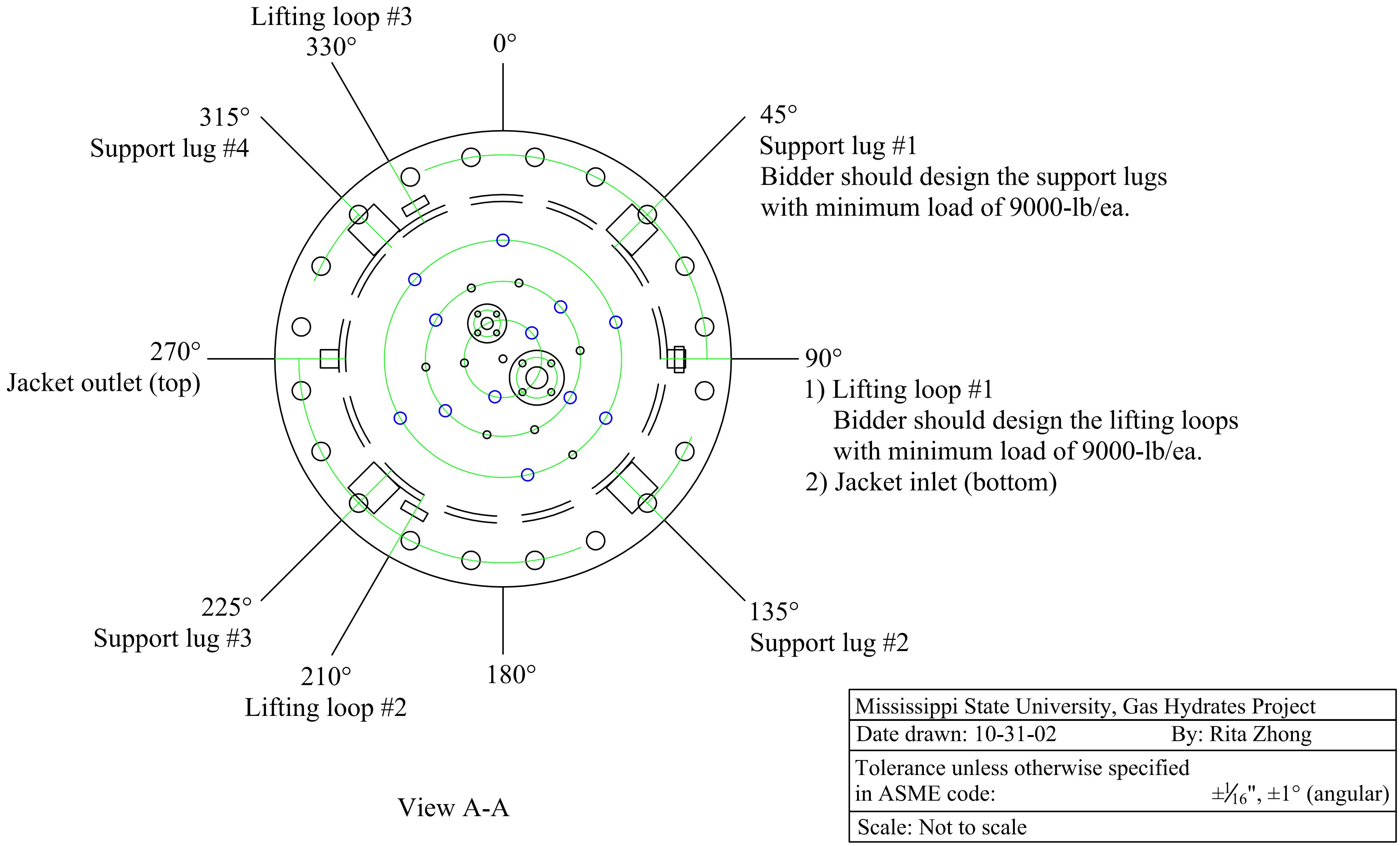


View B-B

Note: 1) Vessel flange bolt holes are two-holed on 0° reference line
All slip-on flanges bolt holes are two-holed on 0° reference line
2) Details of ports and nozzels are shown in fig.6

Mississippi State University, Gas Hydrates Project	
Date drawn: 10-31-02	By: Rita Zhong
Tolerance unless otherwise specified in ASME code:	±1⁄16", ±1° (angular)
Scale: Not to scale	

Fig. 4. Orientation of Jacket Ports, Lift Loops, and Support Lugs

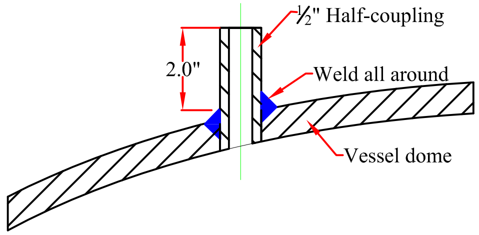


Bidder should design the support lugs with minimum load of 9000-lb/ea.

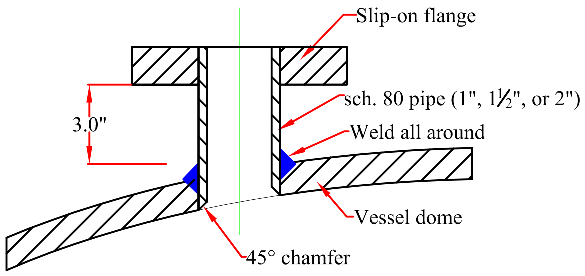
Bidder should design the lifting loops with minimum load of 9000-lb/ea.

Mississippi State University, Gas Hydrates Project	
Date drawn: 10-31-02	By: Rita Zhong
Tolerance unless otherwise specified in ASME code:	±1⁄16", ±1° (angular)
Scale: Not to scale	

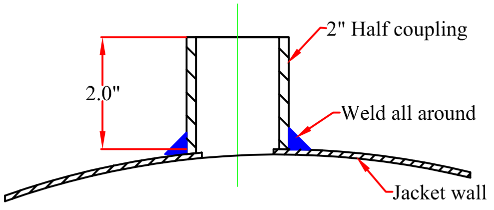
Fig. 5. Weld Details of Ports on Vessel and Jacket



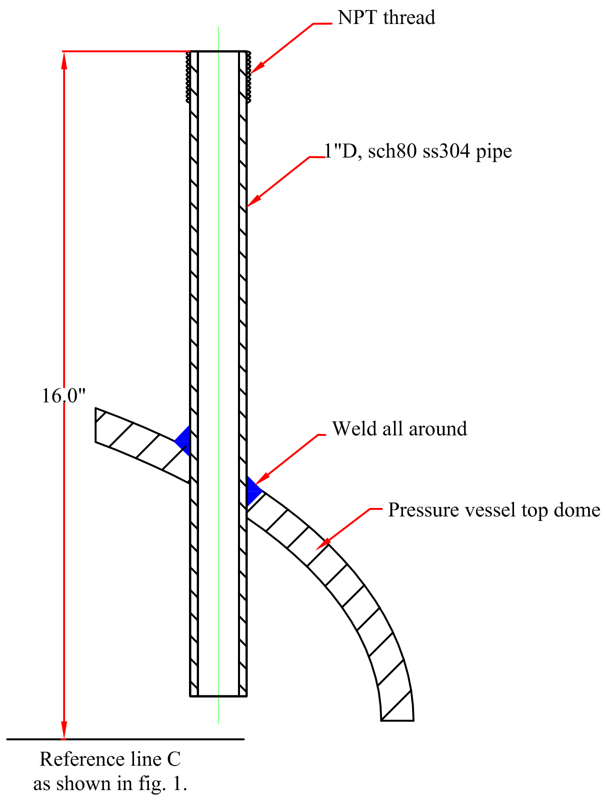
a. ½" FNPT drilled through



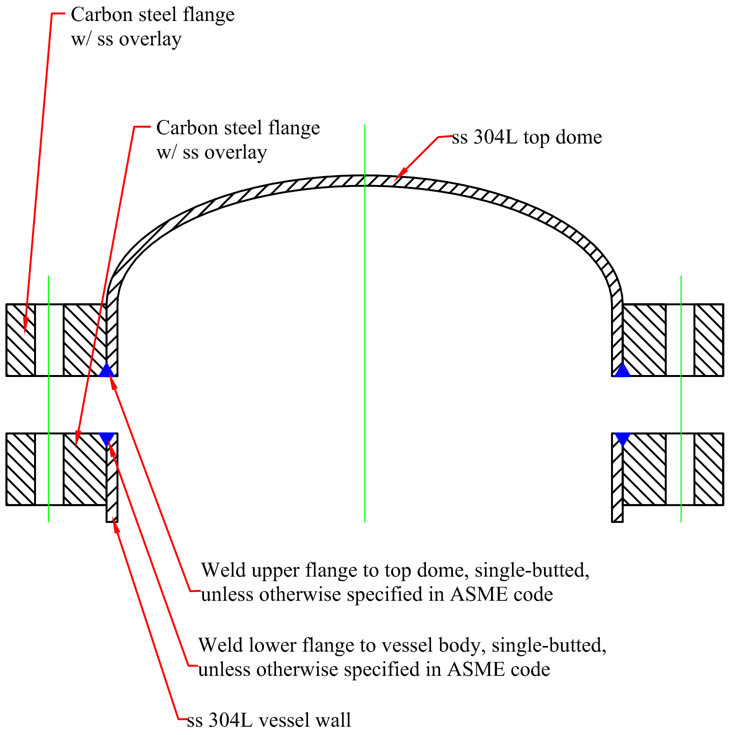
b. Flange connection (all 1" and larger ports on vessel)



c. 2" FNPT drilled through on jacket



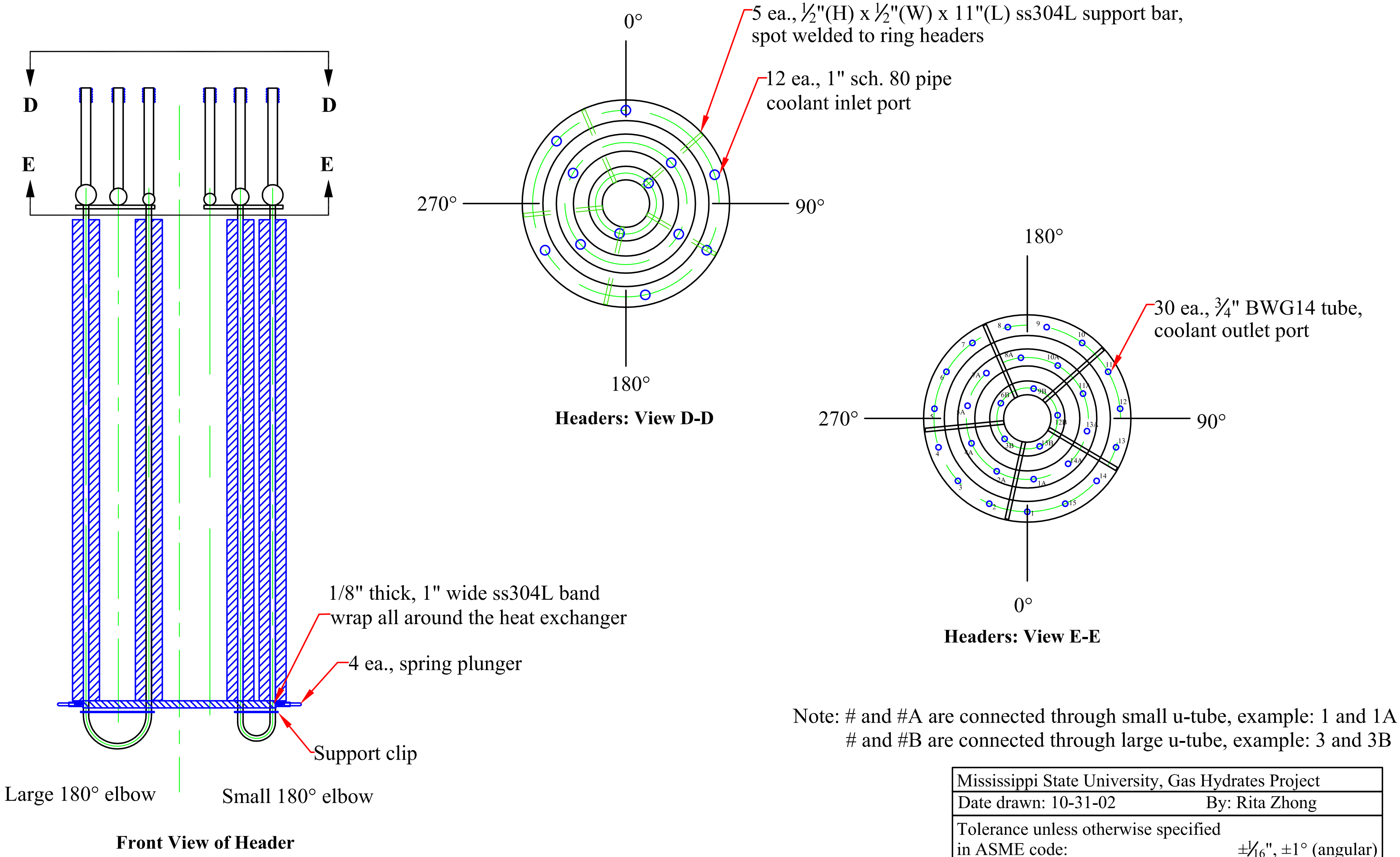
d. sch. 80, 1" pipe from heat exchanger going through vessel top dome



e. Welding carbon steel flange with ss overlay to vessel only

Mississippi State University, Gas Hydrates Project
Date drawn: 10-31-02 By: Rita Zhong
Tolerance unless otherwise specified
in ASME code: ±1⁄16", ±1° (angular)
Scale: Not to scale

Fig. 6. Heat Exchanger



Front View of Header

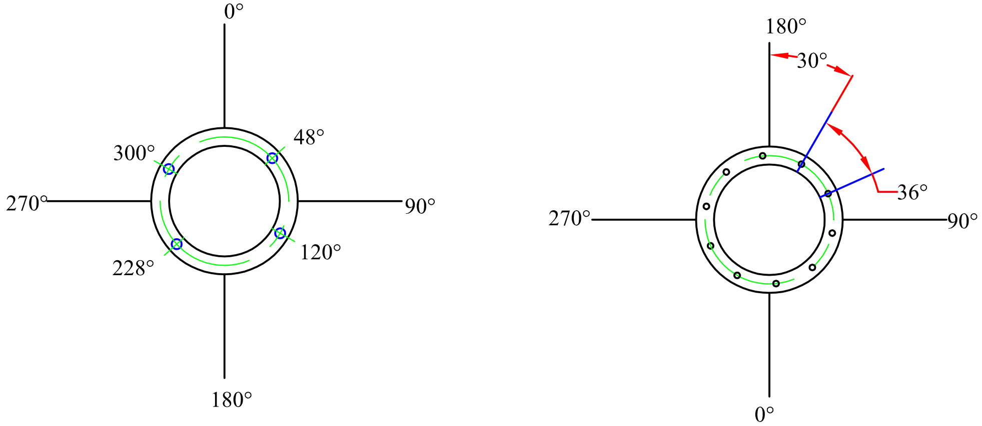
Headers: View D-D

Headers: View E-E

Note: # and #A are connected through small u-tube, example: 1 and 1A
and #B are connected through large u-tube, example: 3 and 3B

Mississippi State University, Gas Hydrates Project	
Date drawn: 10-31-02	By: Rita Zhong
Tolerance unless otherwise specified in ASME code:	$\pm\frac{1}{16}$", ±1° (angular)
Scale: Not to scale	

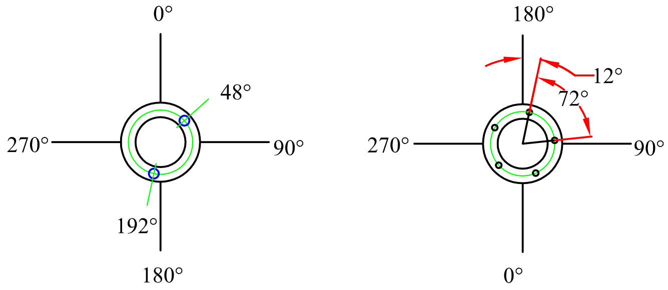
Fig. 7. Ring Headers



Top view
showing 1" pipe connection

Bottom view
showing ¾" tube connections

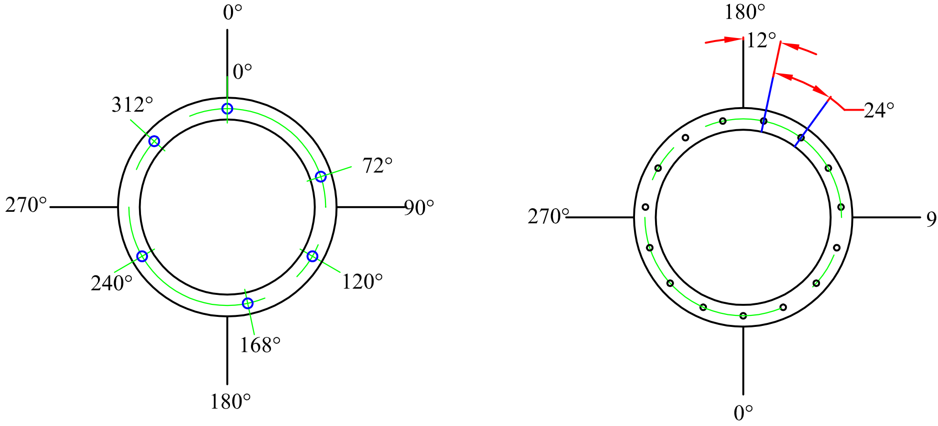
Ring Header 2: 2" D. pipe, sch. 80, bent to radius 8½"



Top view
showing 1" pipe connection

Bottom view
showing ¾" tube connections

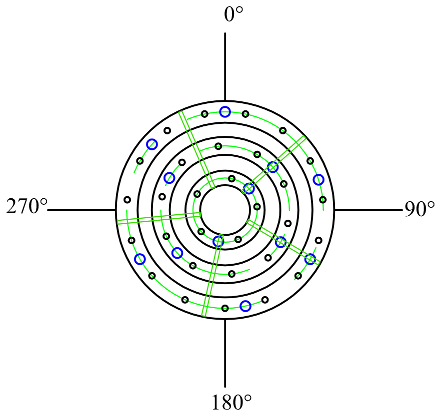
Ring Header 1: 1½" D. pipe, sch. 80, bent to radius 4¼"



Top view
showing 1" pipe connection

Bottom view
showing ¾" tube connections

Ring Header 3: 2½" D. pipe, sch. 80, bent to radius 13"



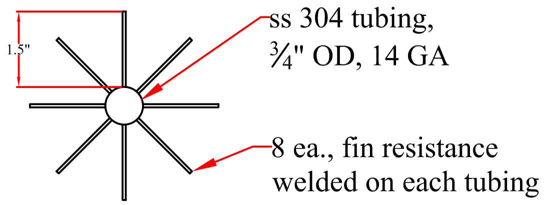
Top View
Assembled Ring Headers

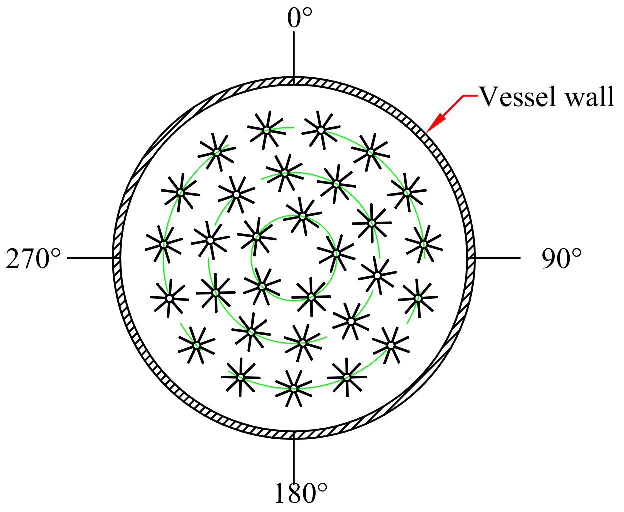
Mississippi State University, Gas Hydrates Project	
Date drawn: 10-31-02	By: Rita Zhong
Tolerance unless otherwise specified in ASME code:	$\pm\frac{1}{16}$", ±1° (angular)
Scale: Not to scale	

Fig. 8. Orientation of Fins and Tubes

Finned tube:
    Tube: Material: ss 304
        No. of tubes: 30
        Outside diam.: 3/4"
        Wall thickness: 14 GA (0.083")
    Fin: Material: ss 304
        No. of fin per tube: 8
        Fin height: 1.5"
        Fin thickness: 18 GA (0.049")
        All fins are welded on tubes via resistance welding

U-tube:
    No. of u-tubes: 5 (small)
        10 (large)
    Center to Center distance: 4.63" (small)
        8.75" (large)

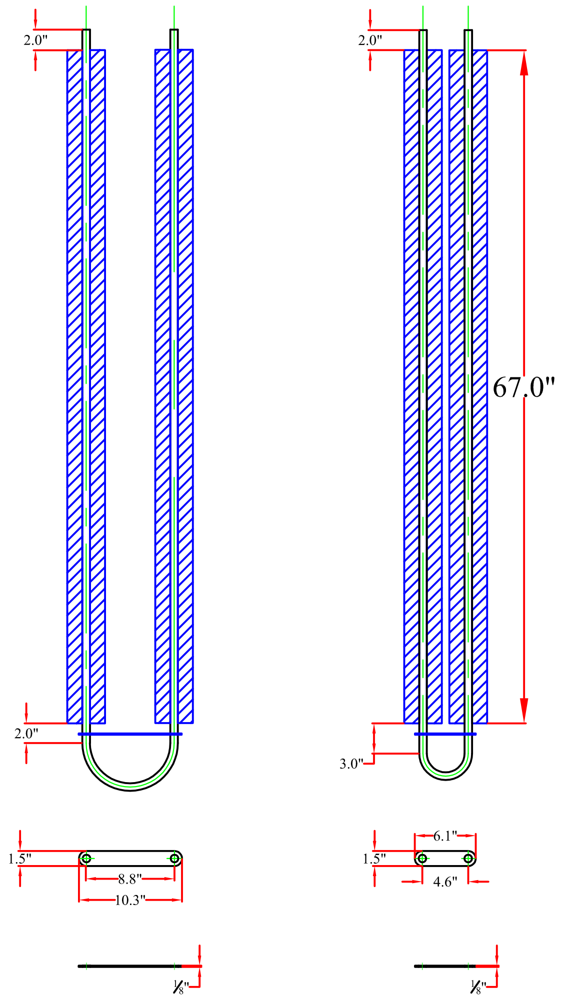




Section View of Vessel Body
with Heat Exchanger

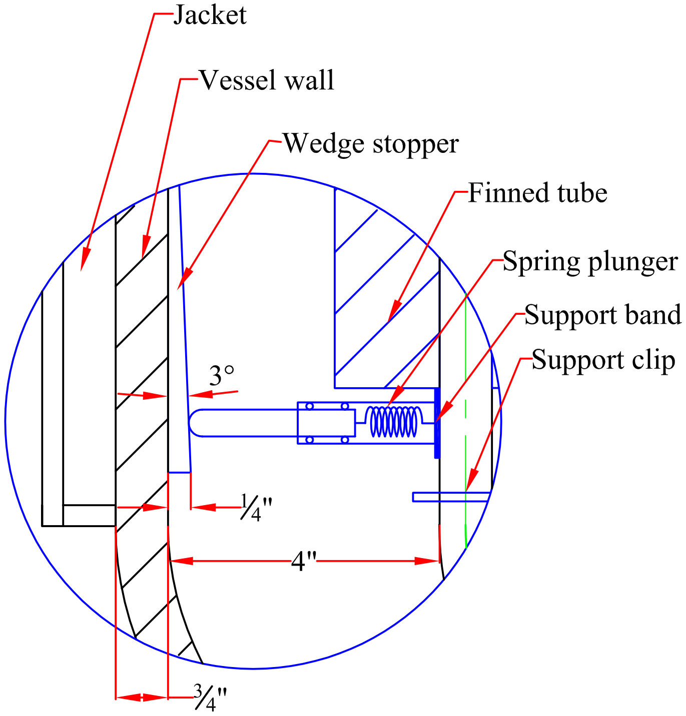
Note: Orientation of fins should be as close as possible to this figure.

Assembled u-tube



Mississippi State University, Gas Hydrates Project
Date drawn: 10-31-02 By: Rita Zhong
Tolerance unless otherwise specified
in ASME code: $\pm\frac{1}{16}$", ±1° (angular)
Scale: Not to scale

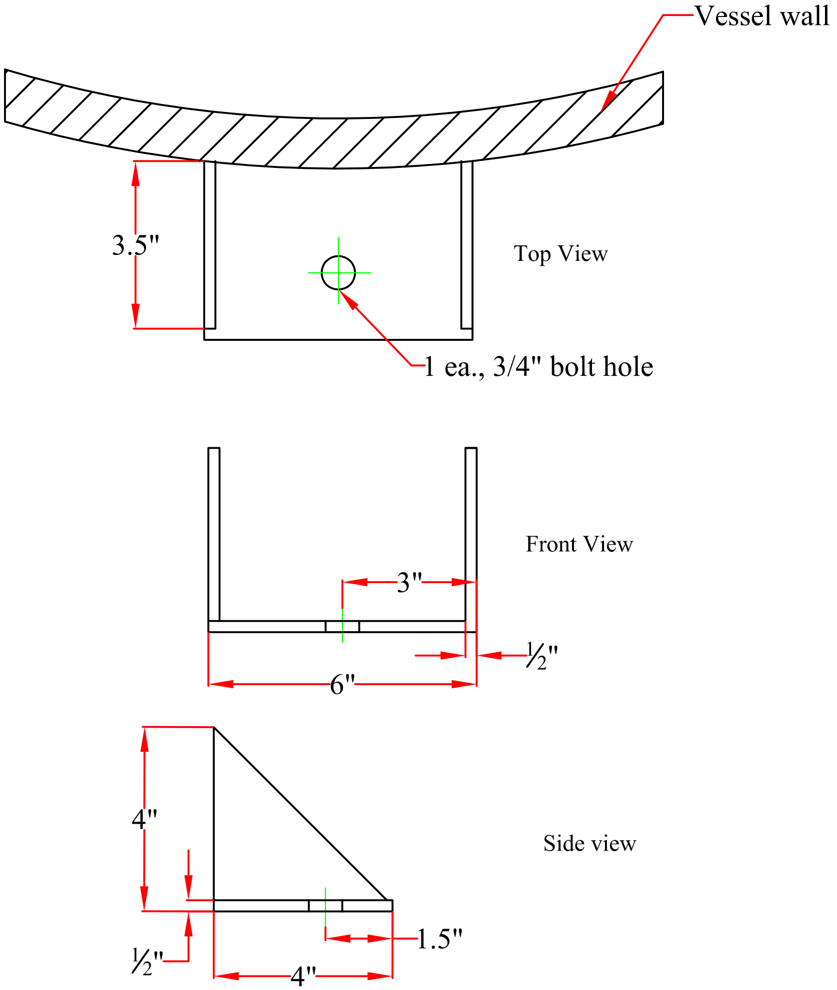
Fig. 9. Details of Spring Plunger and Support Lug



Total length of spring plunger: 4 in.
Spring travel distance: 1 in.
Spring constant: 60 lb/in

D1: Spring Plunger

Mississippi State University, Gas Hydrates Project	
Date drawn: 10-31-02	By: Rita Zhong
Tolerance unless otherwise specified in ASME code:	±$\frac{1}{16}$", ±1° (angular)
Scale: Not to scale	



This figure shows the shape of support lugs.

Bidder should calculate the thickness and dimensions of lugs to support minimum load of 9000-lb/ea. according to ASME code.

Actual dimensions of lugs should be no smaller than shown in figure.

D2: Support Lug

Fig. 10. Gas-Hydrate Formation Tank

- 1 - glycol surge tank
- 2 - hydrate formation tank
- 3 - compressed gas supply
- 4 - chiller
- 5 - boiler, gas disposal
- 6 - gas collection tank
- 7 - mobil data control center

Fig. 11. West-Side View of POC Hydrate Facility

- **1 - Glycol surge tank**
- **2 - hydrate formation tank**
- **3 - compressed gas supply**
- **4 - chiller**
- **5 - boiler, gas disposal**

Fig. 12. Back-View of POC Hydrate Facility

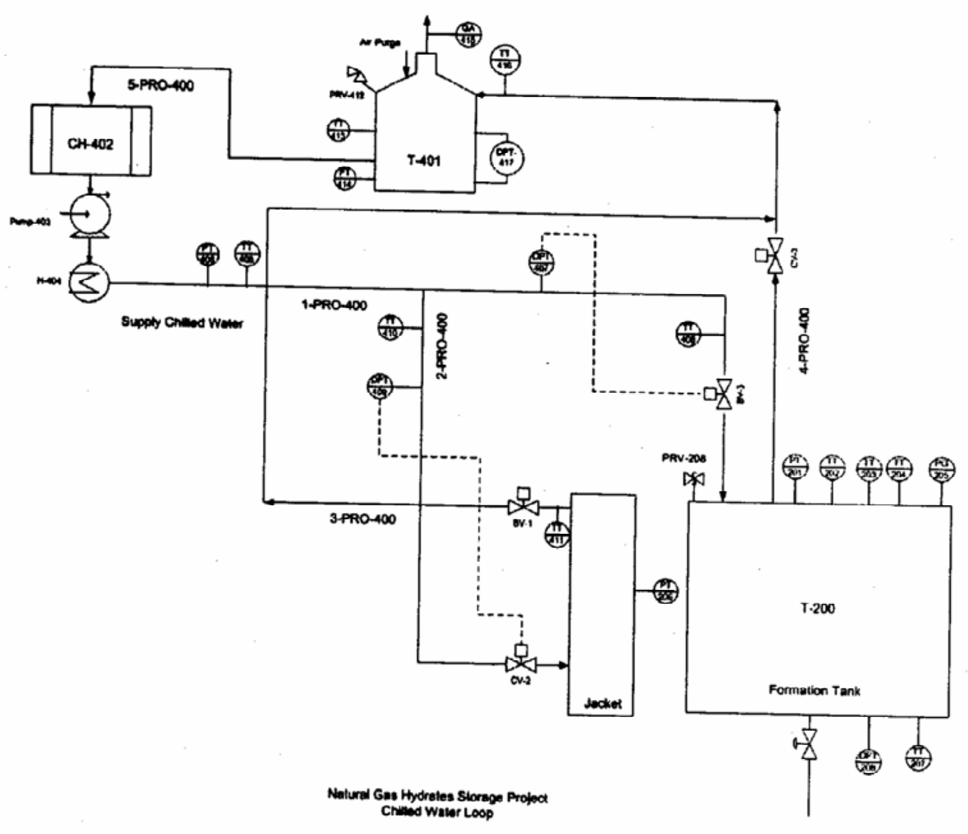


Fig. 13 Natural Gas Hydrates Storage Project – Chilled Water Loop

Fig. 14. Chiller

Fig. 15. Boiler before Refurbishing

Fig. 16. Boiler after Refurbishing.

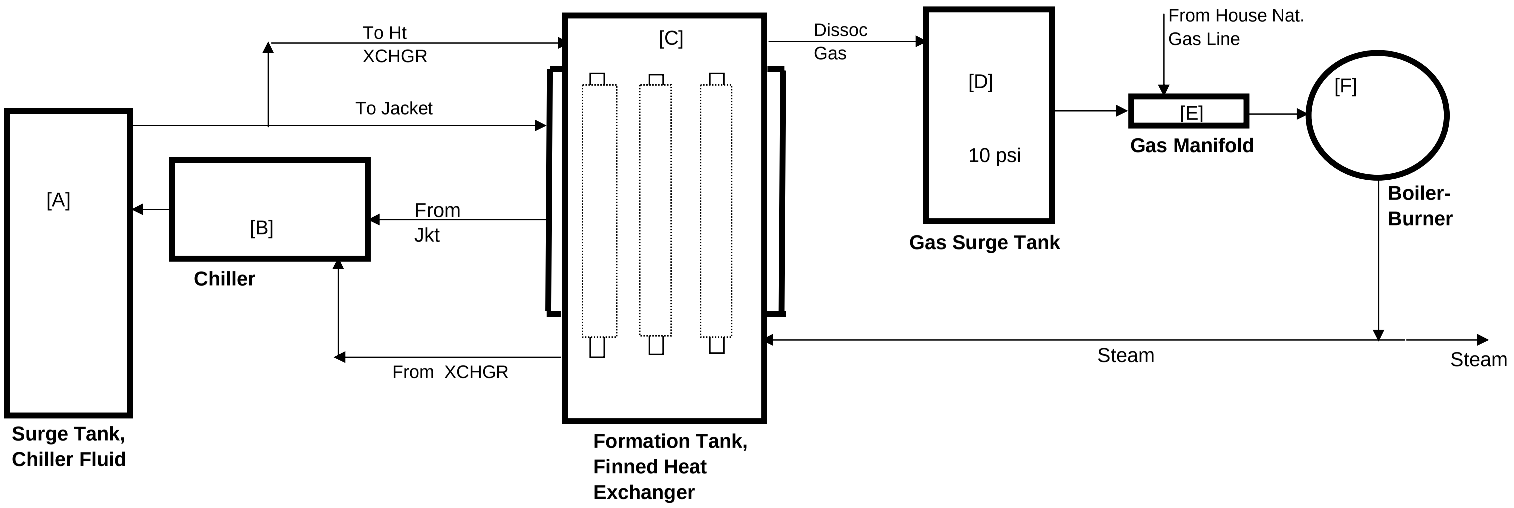


Fig. 17. Manifold on Natural Gas Supply Line.

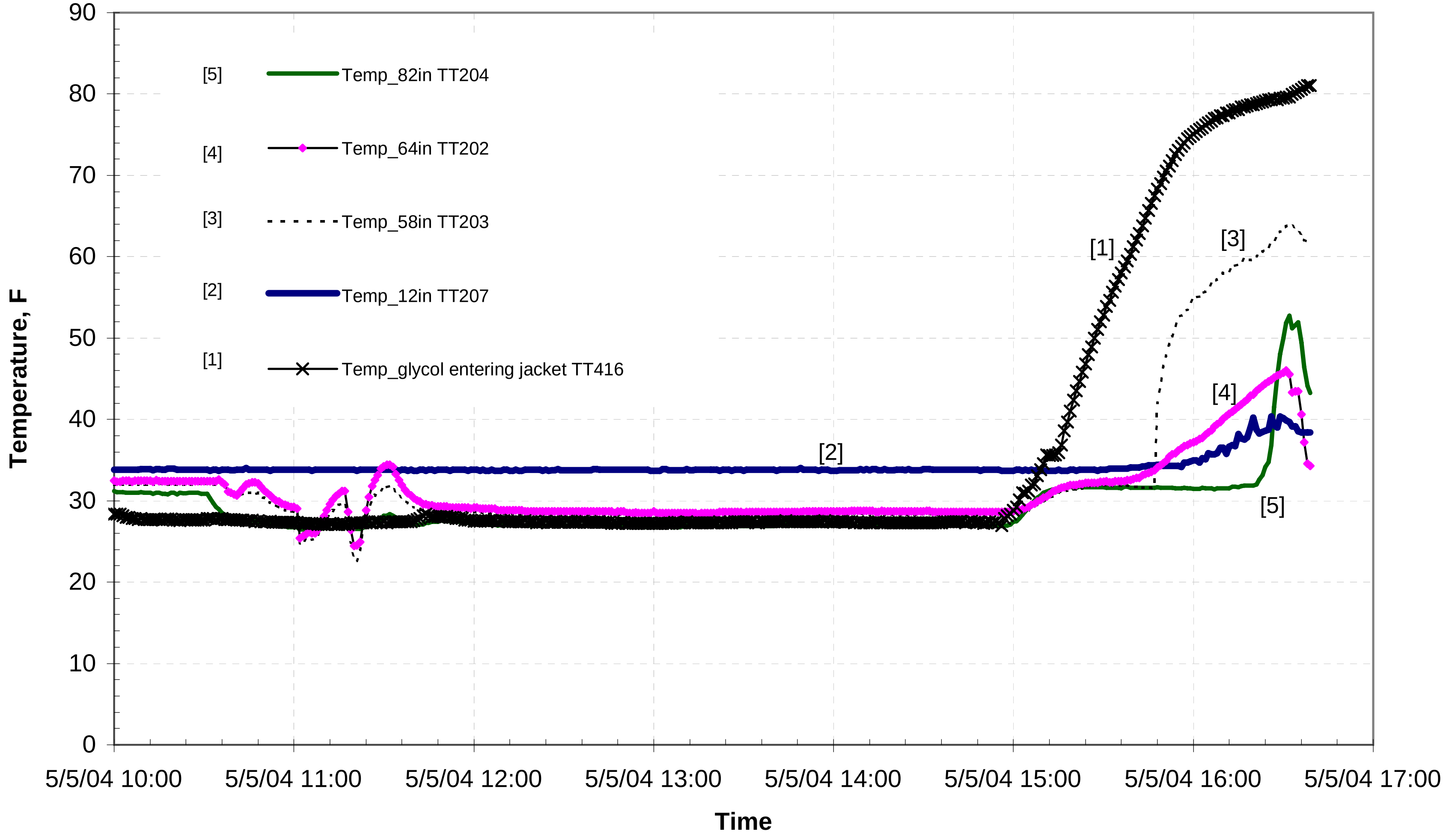


Figure 18. Temperature/Time Run HYD-08

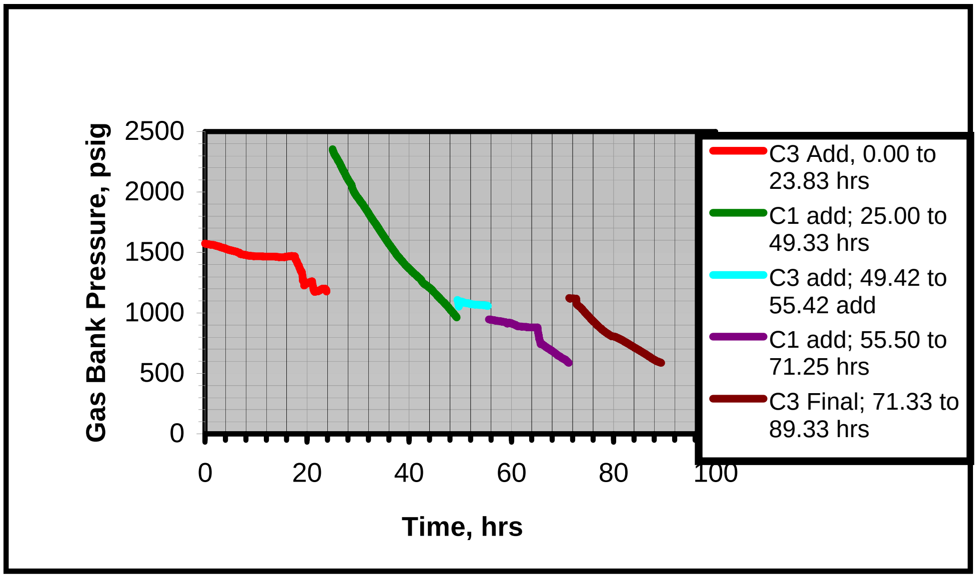


Fig. 19. Schedule of gas injections, Run HYD-14.

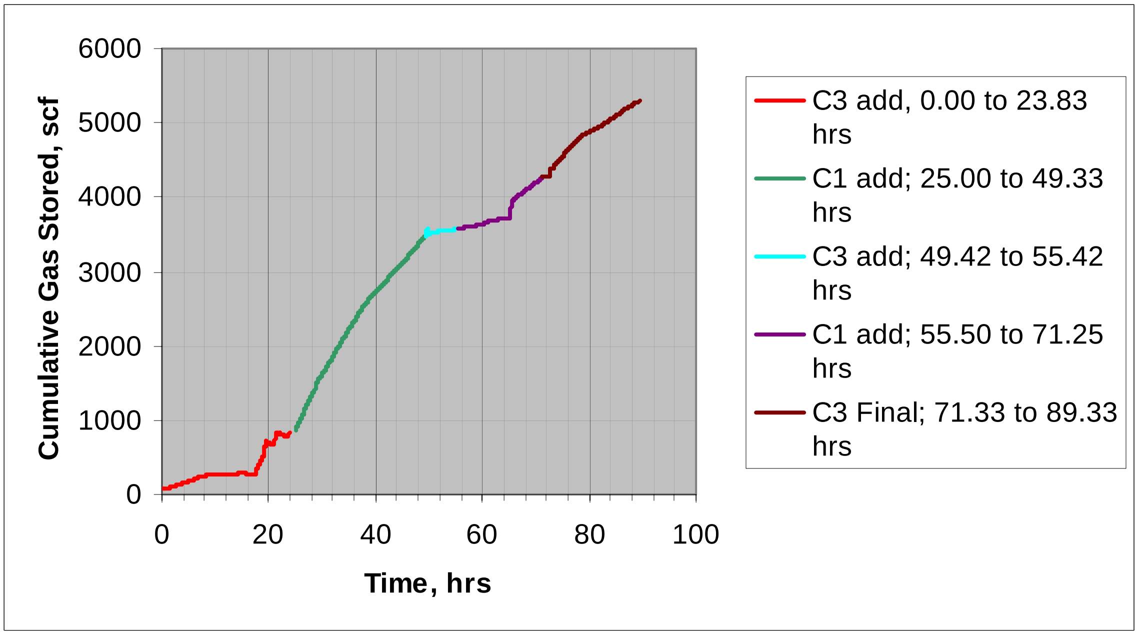


Fig. 20. POC Storage Capacity of Natural Gas in Hydrates, HYD-14

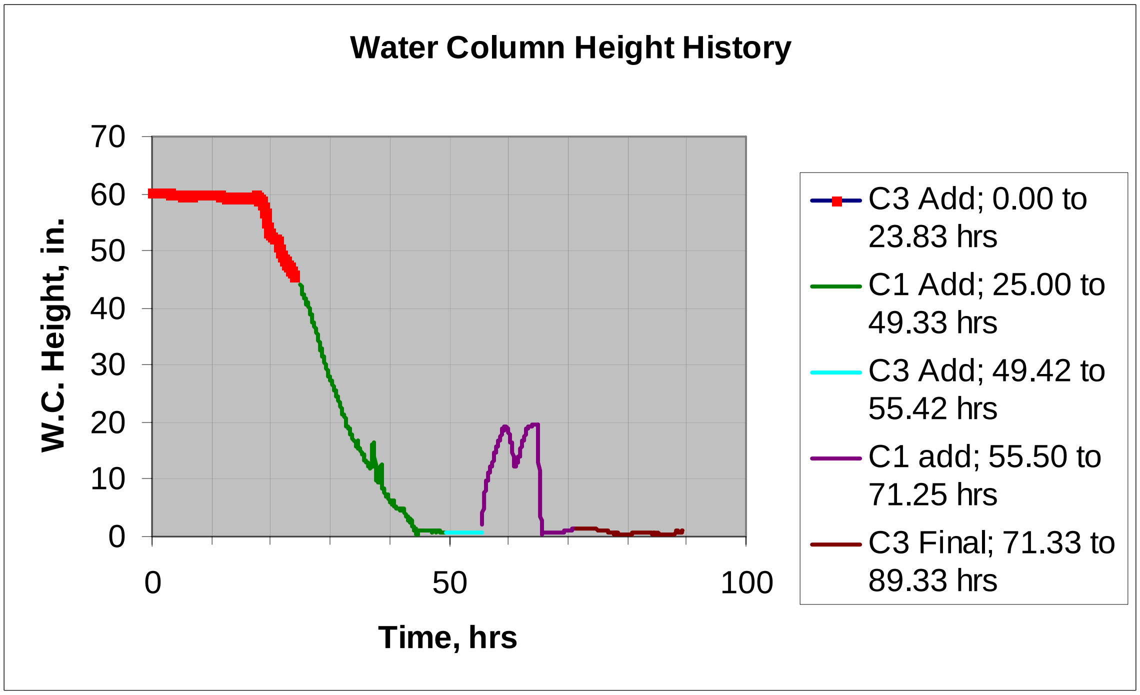


Fig. 21. Water Height Run HYD-14

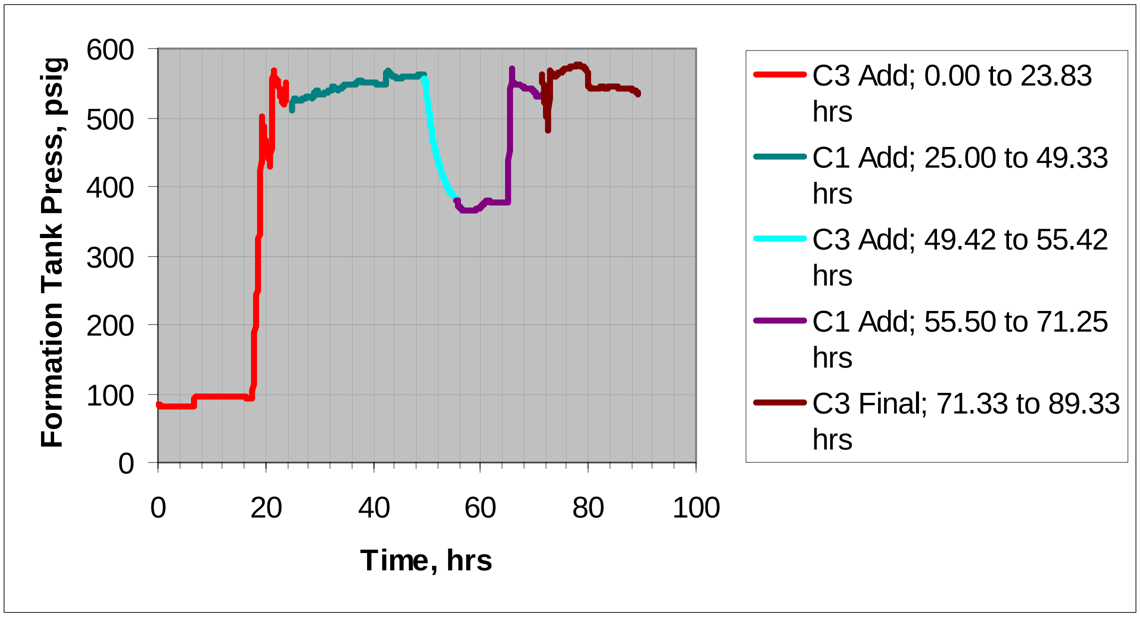


Fig. 22. Hydrate Formation Vessel Pressure History Run HYD-14.

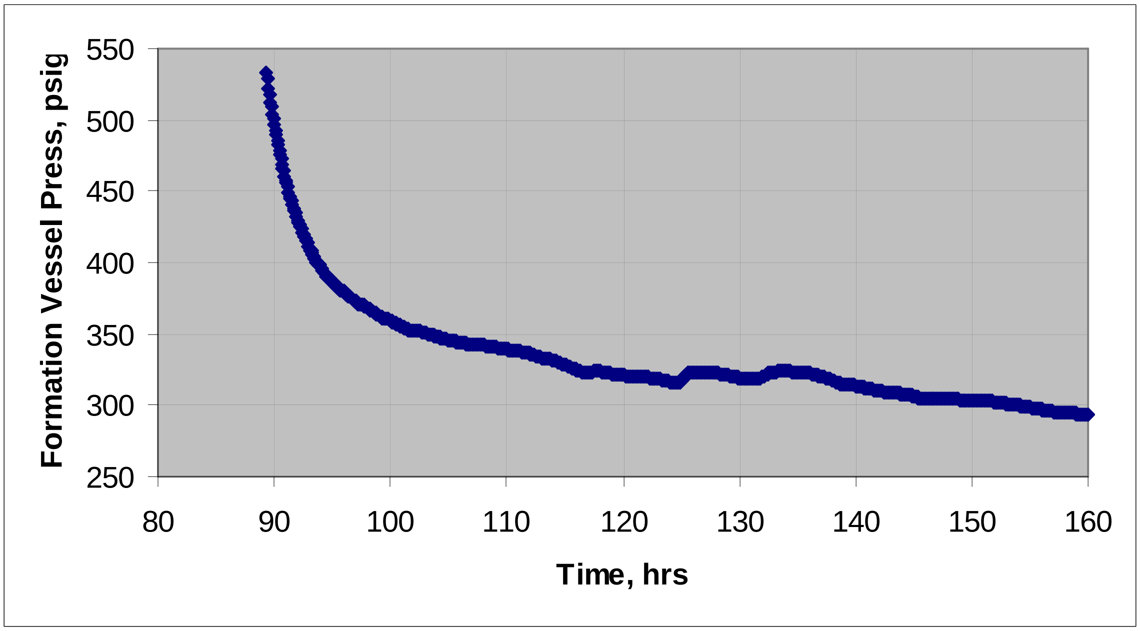


Fig. 23. Hydrate Formation after Gas Shut-Off at Test End

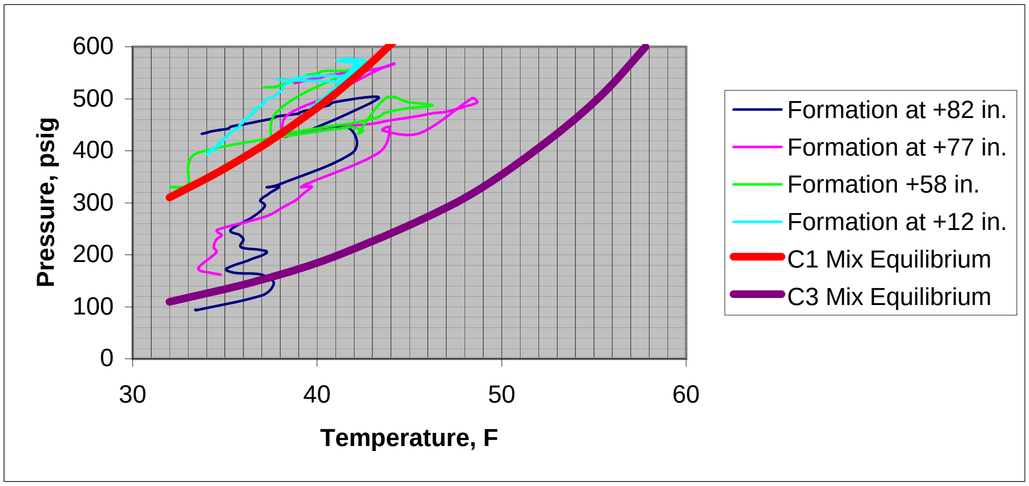


Fig. 24. Operating P/T Along Hydrate Formation Front.

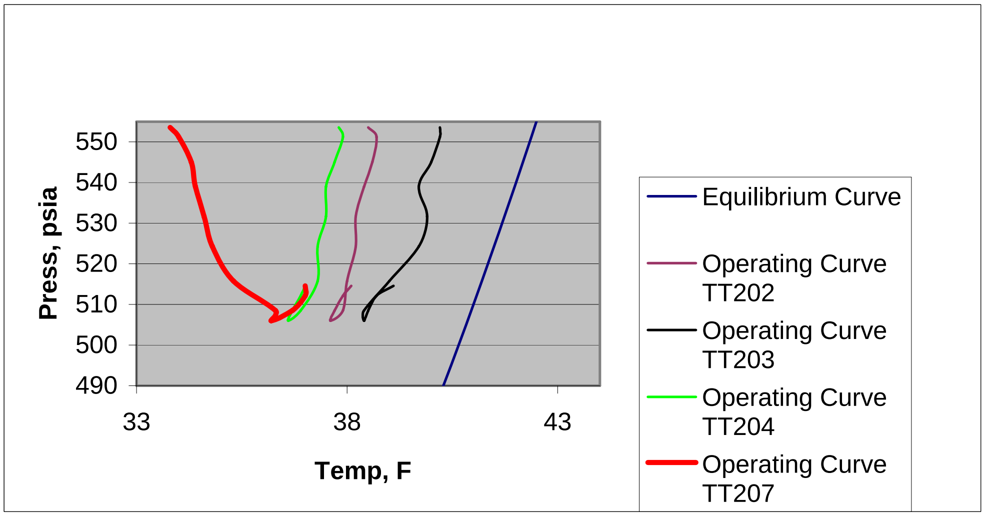


Fig. 25. Operating Curves Superposed on Hydrate Equilibrium Line for 2nd Injection.

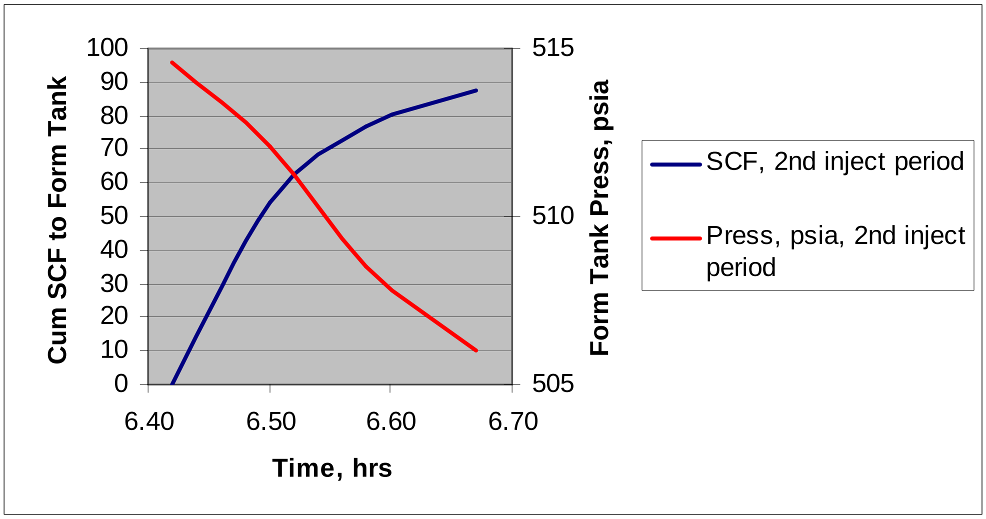


Fig. 26. Inlet Gas Flow Rate Compared to Pressure, 2nd Injection.

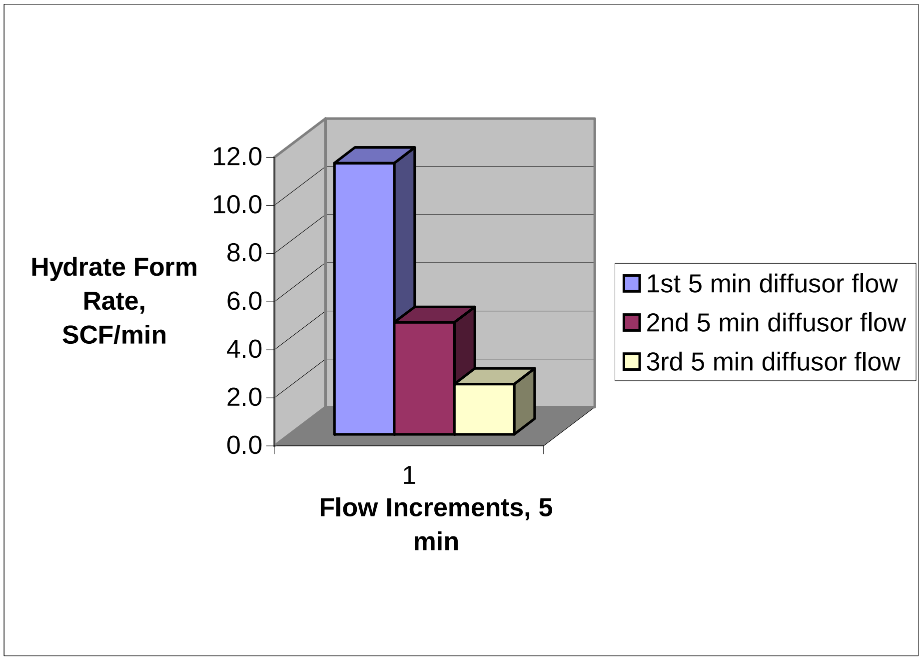


Fig. 27. Rate of Hydrate Formation, 2nd Injection.

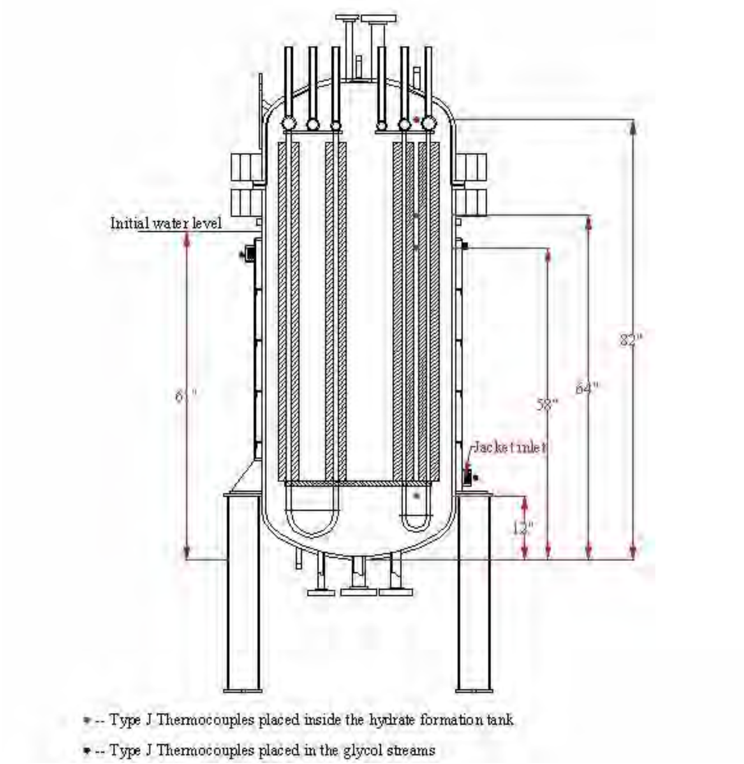


Fig. 28. Locations of Water Level and Thermocouple Placements.

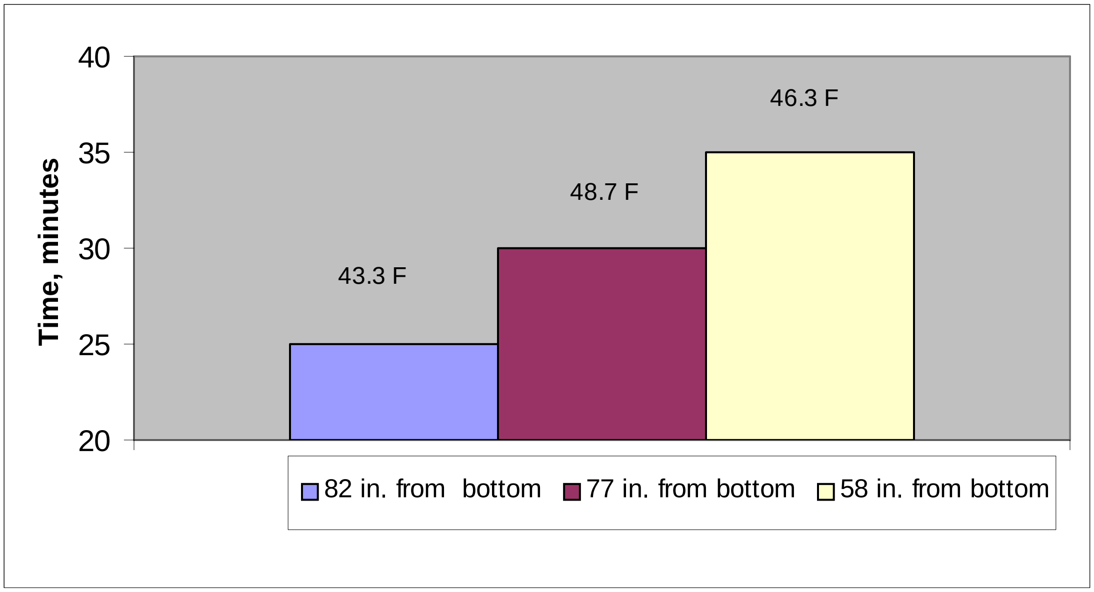


Fig. 29. Hydrate Front Movement.

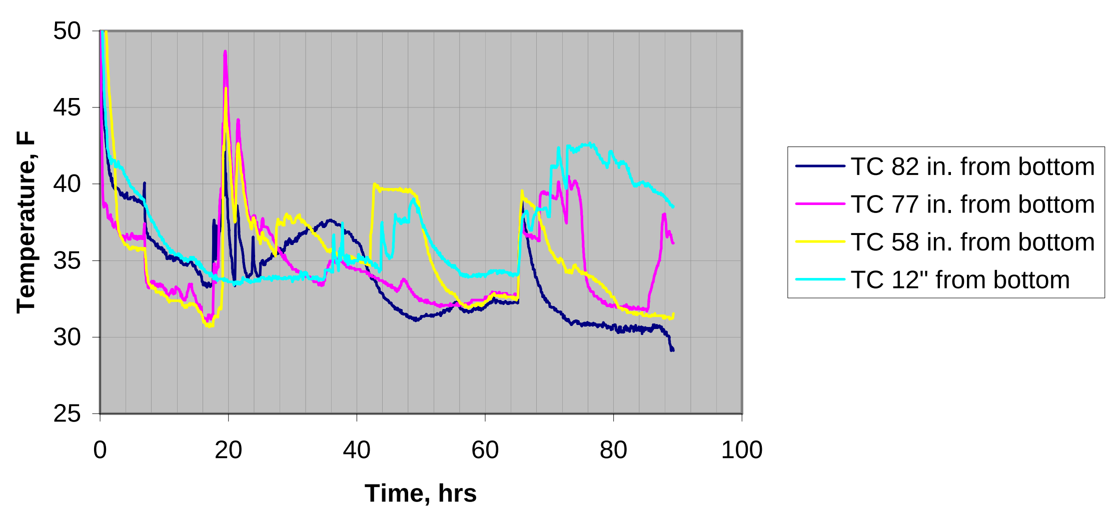


Fig. 30. Temperature History of All Internal Thermocouples.

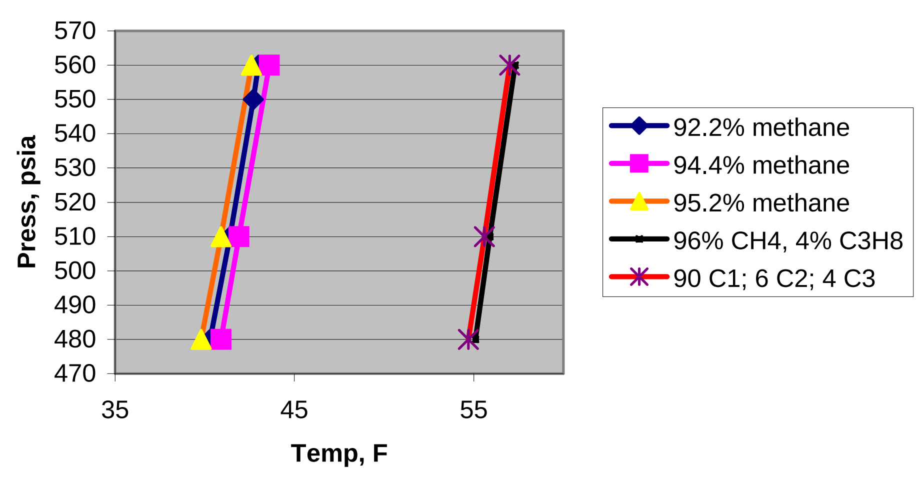


Fig. 31. Equilibrium Curves Compared Different Gas Compositions.

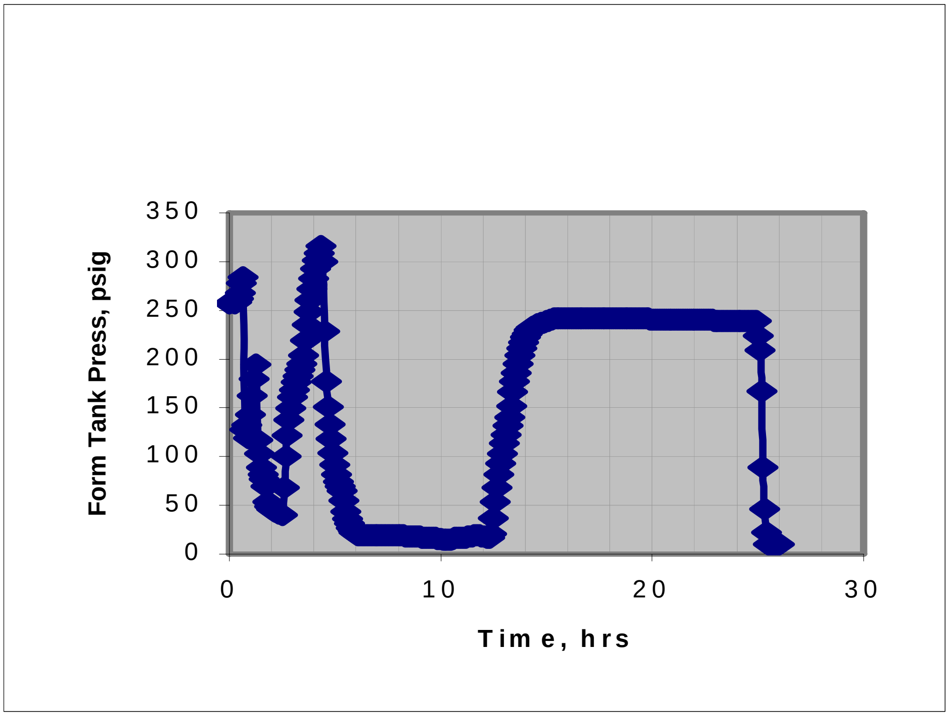


Fig. 32. Pressure History of Formation Tank During Decomposition.

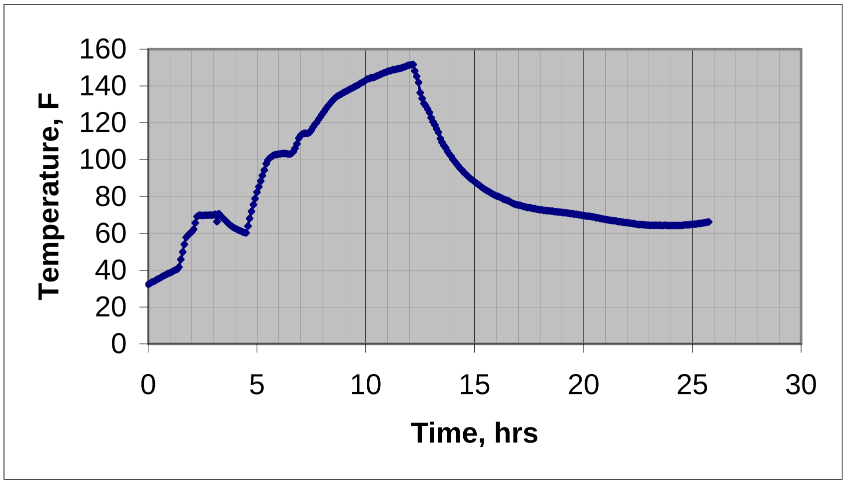


Fig. 33. Temperature History of Heating Fluid Leaving Formation Tank.

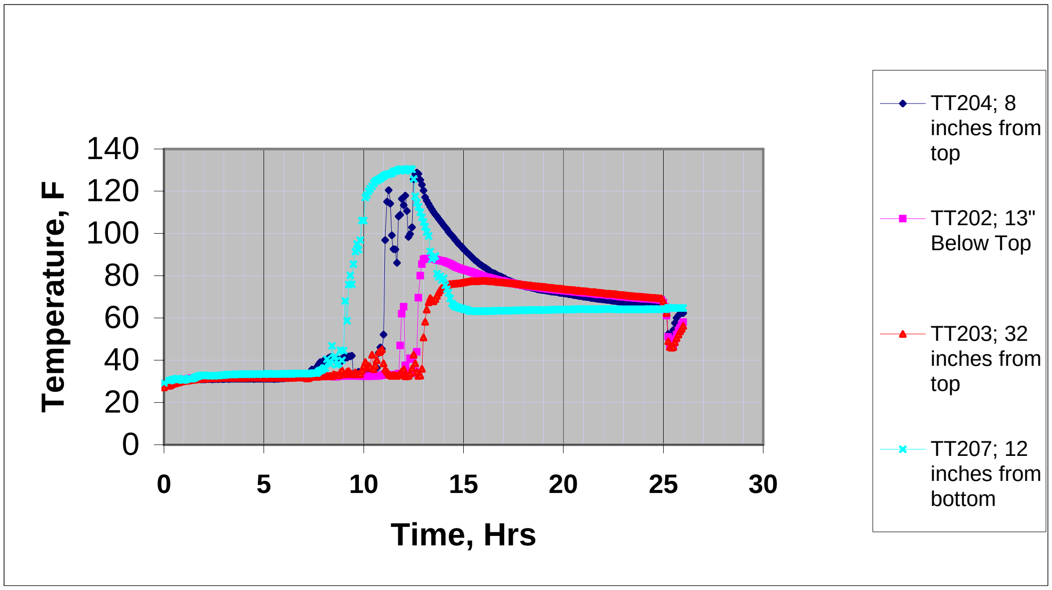


Fig. 34. Decomposition Temperature History Inside Hydrate Formation/Storage Tank.

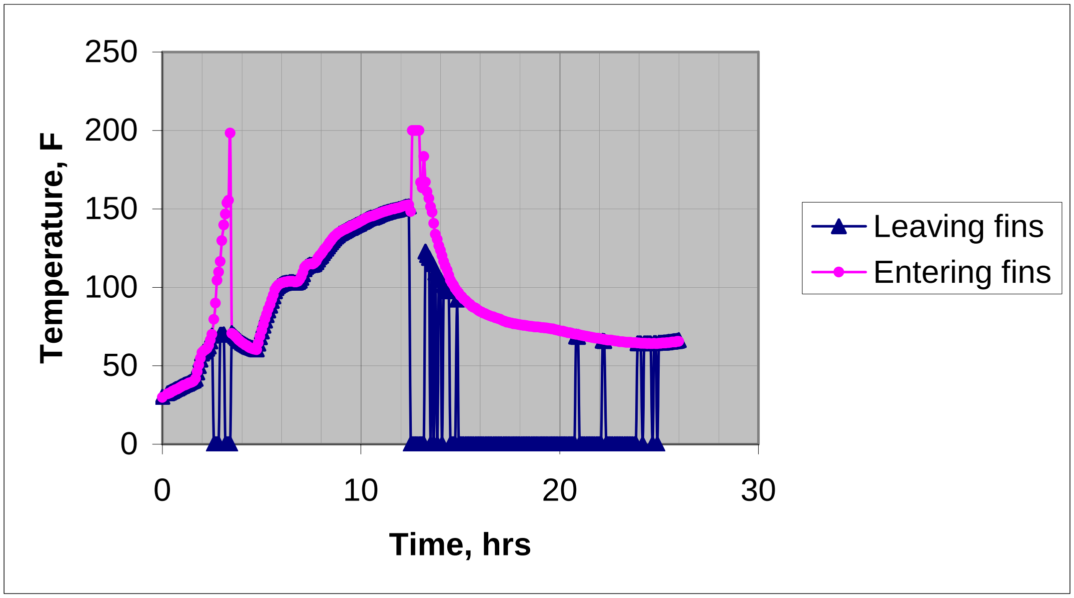


Fig. 35. Temperature History of Heating Fluid Entering and Leaving Heat-Exchanger/ Collection-Plates Inside Formation Tank.

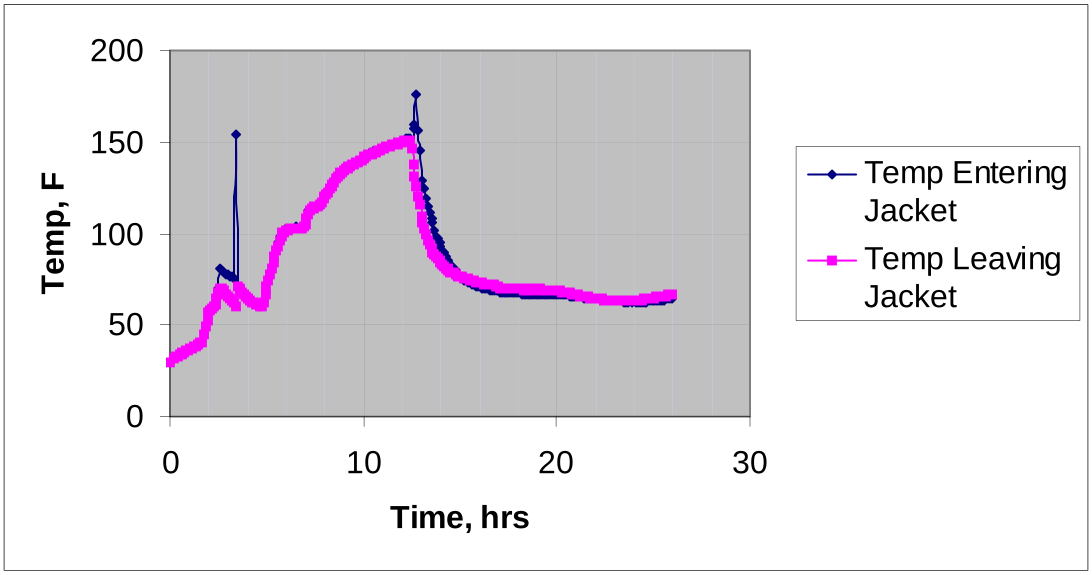


Fig. 36. Temperature History Heating Fluid Entering and Leaving Jacket

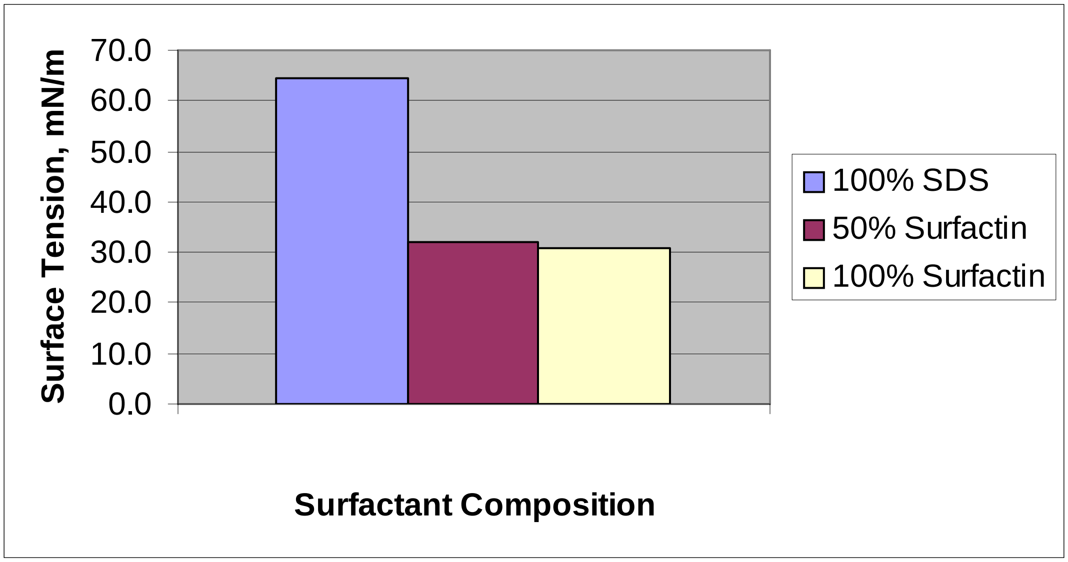


Fig. 37. Reduction of Surface Tension with Surfactin.

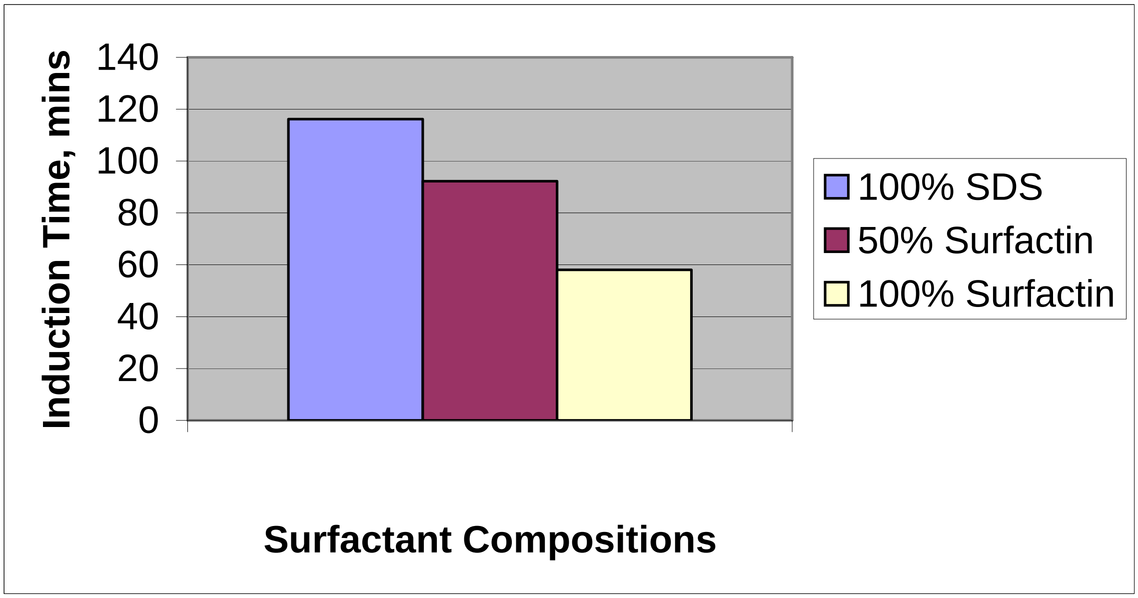


Fig. 38. Hydrate Induction Times of SDS, Surfactin, and Combination.

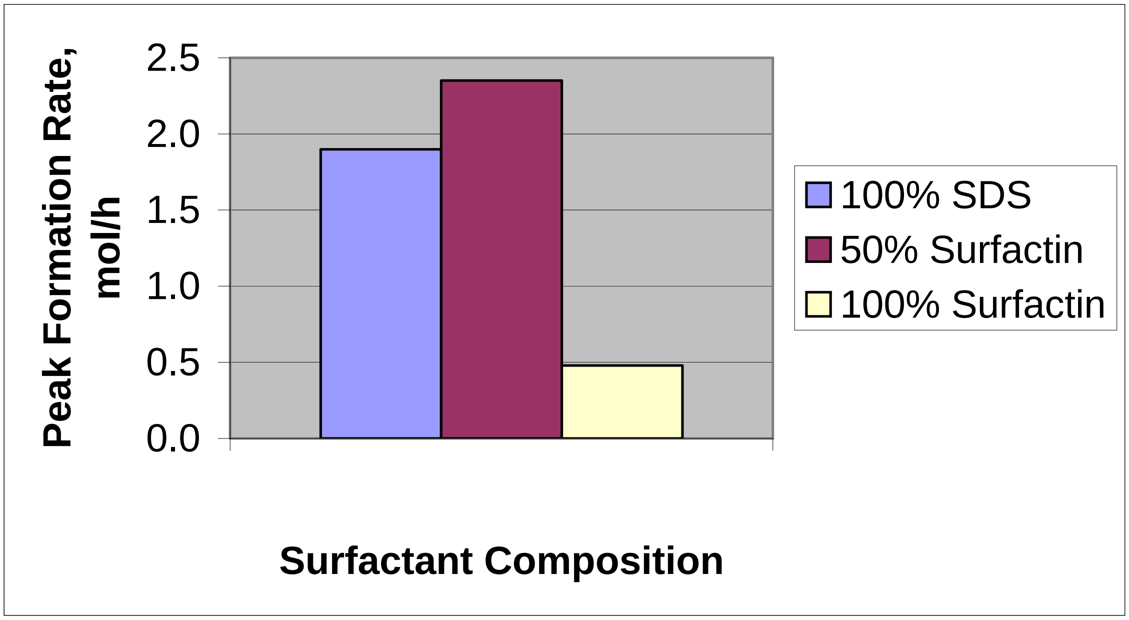


Fig. 39. Influence of Surfactants on Peak Hydrate Formation Rates.

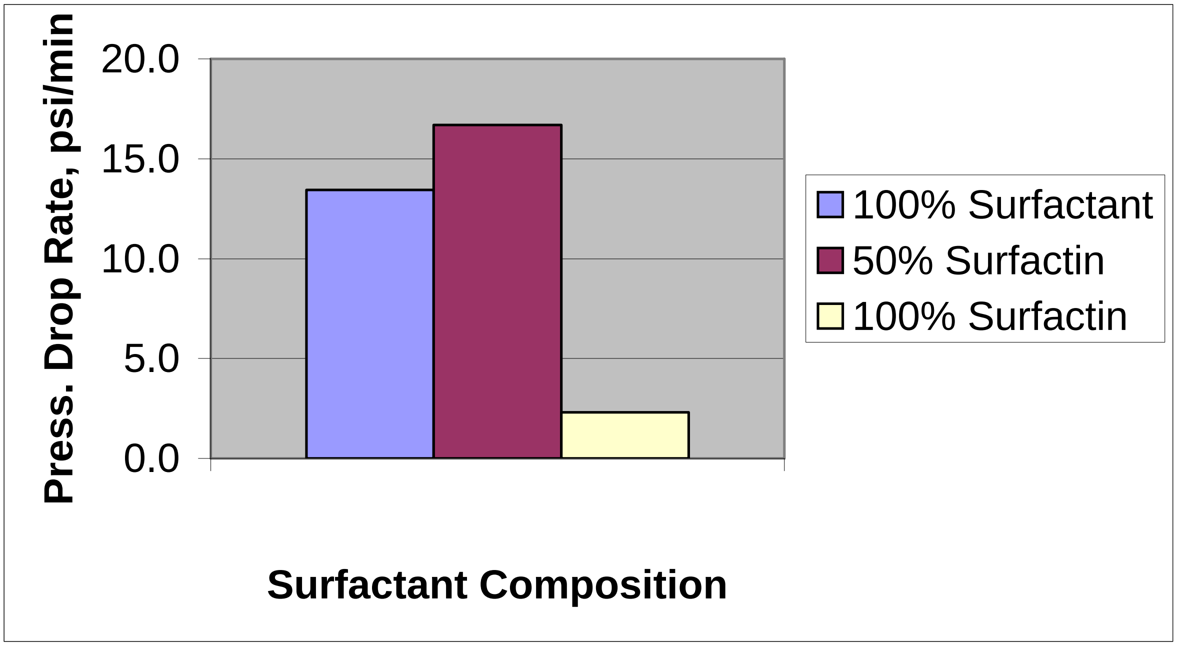


Fig. 40. Hydrate Formation Rate as Measured by Rate of Pressure Drop.

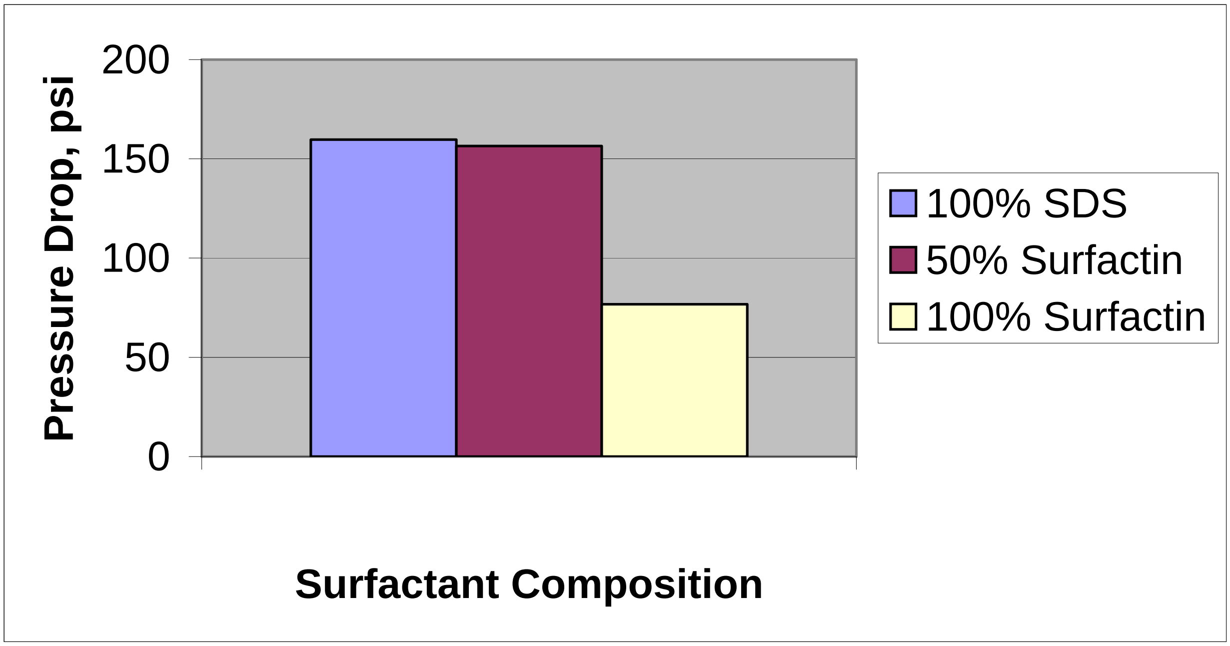


Fig. 41. Influence of Surfactant on Occluded Gas Capacity.