NATURAL GAS HYDRATES STORAGE PROJECT
PHASE II. CONCEPTUAL DESIGN AND ECONOMIC STUDY

FINAL REPORT
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ABSTRACT

DOE Contract DE-AC26-97FT33203 studied feasibility of utilizing the natural-gas storage property of gas hydrates, so abundantly demonstrated in nature, as an economical industrial process to allow expanded use of the clean-burning fuel in power plants. The laboratory work achieved breakthroughs: (1) Gas hydrates were found to form orders of magnitude faster in an unstirred system with surfactant-water micellar solutions. (2) Hydrate particles were found to self-pack by adsorption on cold metal surfaces from the micellar solutions. (3) Interstitial micellar-water of the packed particles were found to continue forming hydrates. (4) Aluminum surfaces were found to most actively collect the hydrate particles.

These laboratory developments were the bases of a conceptual design for a large-scale process where simplification enhances economy. In the design, hydrates form, store, and decompose in the same tank in which gas is pressurized to 550 psi above unstirred micellar solution, chilled by a brine circulating through a bank of aluminum tubing in the tank employing gas-fired refrigeration. Hydrates form on aluminum plates suspended in the chilled micellar solution. A low-grade heat source, such as 110°F water of a power plant, circulates through the tubing bank to release stored gas. The design allows a formation/storage/decomposition cycle in a 24-hour period of 2,254,000 scf of natural gas; the capability of multiple cycles is an advantage of the process.

The development costs and the user costs of storing natural gas in a scaled hydrate process were estimated to be competitive with conventional storage means if multiple cycles of hydrate storage were used. If more than 54 cycles/year were used, hydrate development costs per Mscf would be better than development costs of depleted reservoir storage; above 125 cycles/year, hydrate user costs would be lower than user costs of depleted reservoir storage.

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EXECUTIVE SUMMARY

The feasibility of storing natural gas in gas hydrates was demonstrated in the laboratory during Phase I of this contract. Although 180+ (vol gas @ STP in hydrates)/(vol hydrates) at equilibrium was known to be possible prior to the study, serious problems had to be overcome to realize the potential in a practical process: (1) Free water when trapped between forming hydrate particles become isolated from gas and unreactive. (2) Mechanical stirring required for rapid formation created scaleup problems. (3) Hydrate formation was too slow in an unstirred system to be practical. (4) Filtering and packing hydrate particles from a cold, pressurized slurry is difficult, requiring excessive labor for an economical process.

In Phase I of the study, these problems were resolved in the laboratory by using a 242+ ppm of a surfactant sodium dodecyl sulfate that formed micelles to solubilize the hydrocarbon gas: (1) Rates were increased by a factor of greater than 700. (2) Hydrates formed subsurface and the surfactant moved the particles to the stainless steel walls to be adsorbed. (3) Entrained water in the interstices of adsorbed hydrate particles rapidly converted to hydrates. Consequently, hydrates were formed to 86% of theoretical gas capacity in a quiescent system which self-collected and self-packed in the test cell within 3-hours of hydrate initiation.

Based on the laboratory findings, Phase II prepared a conceptual design and an economic analysis of a large-scale process, which are contained in the subject report. To process 2,254,000 scf-natural-gas/cycle, 3 carbon-steel tanks are proposed of 10 ft diameter by 60 ft length designed for a 550 psig operating pressure with retrievable aluminum adsorption plates supported in the tank. A refrigerated brine heat-transfer medium for hydrate formation flows through 500 aluminum tubes, 3/4" diameter, 14 Birmingham Wire Gauge (BWG). The tubing extends parallel through the length of the tank. Water from the power plant at 110^{o} F would flow through the tubing to decompose the hydrates. A vacuum-enclosed fiber-glass insulation on the tank exterior cuts heat gain costs to a minimum during storage. A natural-gas-fired refrigeration system is integral to the design to reduce costs and to utilize methane-rich gas above the hydrates.

A single formation/decomposition cycle can be achieved within 24 hours: 7 2/3 hours for the formation in each of 3 storage tanks filled in series and 1 hour for the decomposition. The limiting factor in filling each tank with hydrates is the heat-transfer rate to remove the latent heat of hydrate formation, not the formation rate or mass transfer rate of the hydrates. The aluminum plates and aluminum tubing arrangement allows relatively rapid hydrate-filling of the tanks even though it is the pacing step in the process. Consequently, a daily cycle of formation/storage/decomposition would be possible.

An economic analysis of a large-scale process concluded that the development costs per 1000 scf for gas hydrate storage can 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 can be competitive with conventional storage above 13 cycles/year; above 125 cycles/year hydrate costs are superior to all.

I. INTRODUCTION

A. Needs for Gas Storage

Natural gas offers clean-burning fuels, abundant domestic supply, existing distribution infrastructure, and a low-price energy source. For some applications, however, use is limited by current storage choices of mainly salt caverns and depleted gas reservoirs, choices that geologically exclude some major markets. Compressing and liquefying natural gas encounter safety and economy problems. Therefore, the subject work was undertaken to study the feasibility of a novel way to store natural gas, namely, occluded in gas hydrates.

Natural gas storage in gas hydrates is novel in the sense that industry has never made use of the potentially high gas storage capacity of hydrates. However, it is not novel considering that some 100,000- 300,000 trillion cubic feet (tcf) of natural gas (Collett, 1996; Kvenvolden, K.A., 1993), multiple times the entire conventional supply of hydrocarbons, are estimated to be naturally stored in gas hydrates onshore and offshore in the United States. Historically, hydrate research has dwelt on preventing hydrate occurrence in the oilfield, while research on utilizing hydrate storage properties for industry has been negligible. It was therefore appropriate to engage in this feasibility study.

As the first serious attempt to utilize the unique properties of hydrates to store natural gas, the objective was to determine the technical feasibility of commercial storage and, if found feasible, develop a conceptual design and determine an economic viability of a large-scale process.

B. Advantages of Gas Hydrate Storage

Prior to the subject study, the known advantages of gas hydrates for storing natural gas were the following: 1. Gas in excess of 180 (vol gas @ standard conditions)/(vol of hydrates) could be packed into the gas hydrate crystals. (2) Natural gas stored in hydrates would be inherently safer because gas is essentially encased in ice. (3) Natural gas stored in hydrates would be released slowly, in case of storage tank rupture. (4) Gas could be stored in hydrates at relatively low pressures. (5) Vast quantities of gas are stored in naturally-occurring hydrates. These properties suggested a possibility of safe storage of natural gas aboveground at sites whose geology limits conventional underground storage.

Also, prior to the subject study, the following known negative factors diminished feasibility prospects: (1) The formation of hydrates in a quiescent pure water-hydrocarbon gas system was extremely slow at hydrate-forming temperatures and pressures in laboratories. (2) A dynamic process was complex for scale-up, especially if a mechanically-stirred reactor became necessary to achieve acceptable formation rates. (3) The slurry separation and packing of hydrate particles formed in a stirred reactor seemed economically prohibitive. (4) Excessive free water typically trapped between hydrate particles would diminish gas-packing density, thus increasing storage tank size and cost. (5) A storage process for hydrates had never been demonstrated.

C. Results of Feasibility Study

Phase I of the contract demonstrated in the laboratory the feasibility of a hydrate storage process. A review of those results follows.

(1) Experimental

A stainless steel cell of 3900 cm^3 was constructed and equipped with two RTD probes, pressure transducer, and relief valve. Cooling coils were placed inside the cell and around the exterior walls; a gas mass flowmeter, a constant pressure regulator, and a computerized Omega data-collection system were installed. Video capture of hydrate formation was made with still photographs taken through a 2" thick, 3" diameter pure quartz disk sealing the top of the cell and with an invasive fiber optics/camera system viewed through sapphire-windowed ports in the side of cell; activities inside the cell could be viewed on a monitor screen and/or filmed with VHF video cassette recording.

(2) Hydrate Storage Capacity and Formation Rate

A breakthrough occurred early in the laboratory work that provided answers to multiple problems regarding commercial storage of gas hydrates. A surface active agent was found to solve the problems of achieving high storage capacities in a short period of time while facilitating packing the hydrate particles from an unstirred system. Consider the results presented in Fig. I.C.1 of three experimental runs made to determine attainable capacity; temperature was held constant at 275.4 K (36^{o}F), and a sodium dodecyl sulfate (SDS) surfactant concentration was maintained at 286 ppm; procedure and other conditions except pressure were repeated. Hydrates were formed in the cell until all of the water became tied up in the hydrate structure, i.e., interstitial water also formed hydrates. Individual runs were made at pressures of 3.89, 3.47, 3.11, 2.76 MPa (550.2, 503.6, 451.2, and 400.5 psig), where the chosen pressure was kept constant throughout each run with a constant pressure regulator, and the rate of gas occluded was measured with a gas mass-flowmeter. Such a constant-pressure procedure in a semi-continuous process would be preferred in an industrial operation.

The results presented in Fig. I.C.1 show that 155 (vol gas)/(vol bulk hydrate) storage capacity is achieved at a processing pressure of 3.89 MPa (550 psig). Furthermore, as a result of surfactant in the water, this much gas is incorporated into the hydrates in less than 3 hours of processing time, a rate of hydrate formation about 700 times faster than in a pure water system. The 155 vol/vol represents 86% of the theoretical storage capacity if all cavities were filled, including hydrates formed from interstitial water.

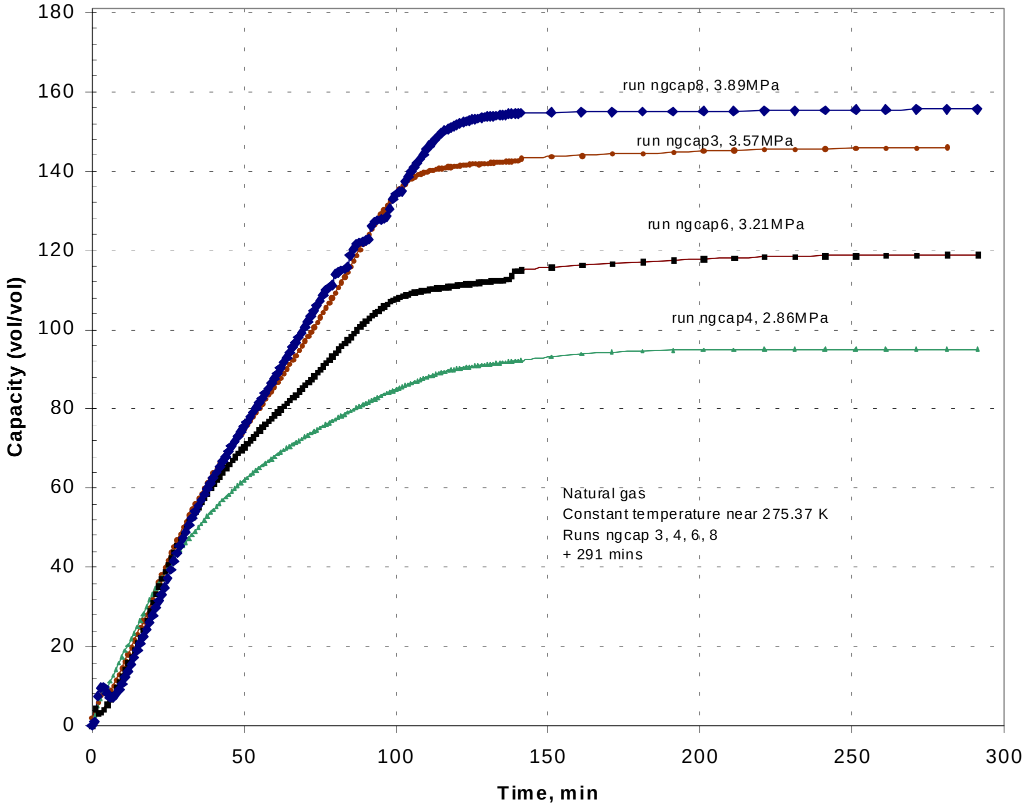


Fig. I.C.1. High storage capacity in less than 3 hours

At a common time after hydrate initiation is taken, 291 minutes for example, the storage capacity is seen to increase with pressure as given in Fig. I.C.2. Therefore, a processing pressure of 3.89 MPa (550 psig) is suggested for a large-scale process.

It was found in later experiments that aluminum was better than stainless steel or copper as a surface to adsorb and retain hydrate particles as they form from micellar solution. Fortunately, aluminum also would have a lighter weight, better heat conduction, and more favorable economy as adsorption plates in a large-scale process.

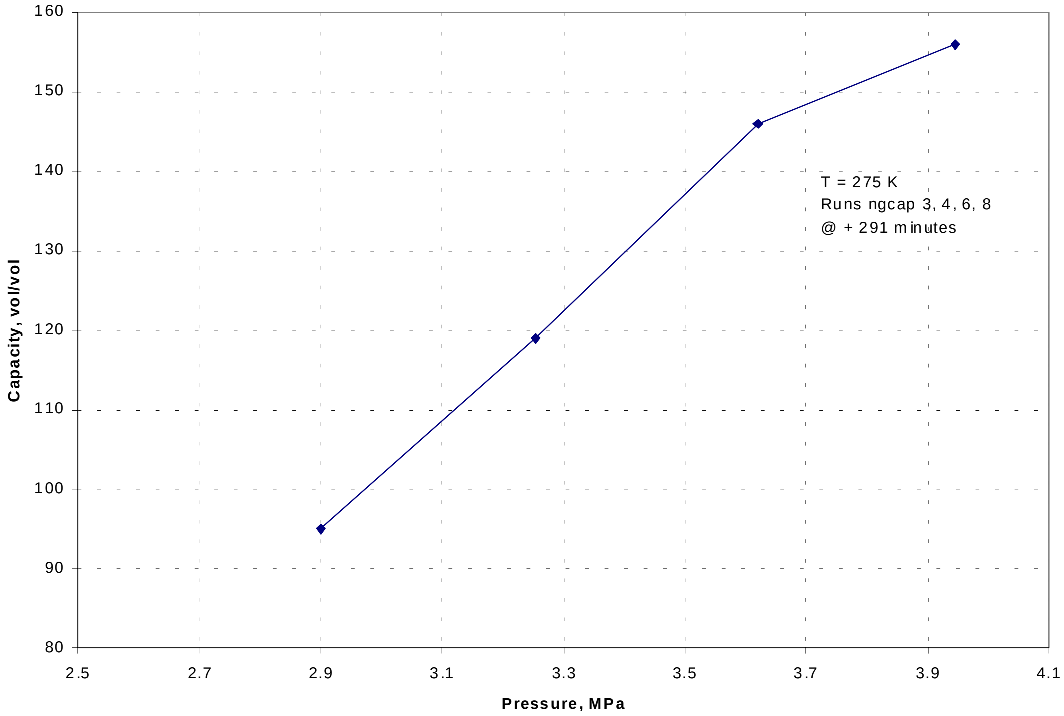


Fig. I.C.2. Processing pressure of 550 psi chosen

The rate of hydrate formation was increased by adding surfactant to achieve the critical micellar concentration (CMC). The formation rate became elevated to the extent that the reaction rate would no longer be controlling. Instead, the heat-transfer rate of removing latent heat of formation would limit rate of filling a storage tank in a large-scale process.

(*3*) *Packing of Hydrate Particles*

The inherent problem of packing hydrate particles in an industrial size process was addressed. It was found that SDS surfactant facilitates the packing of hydrate particles as formed. By situating a camera at the water-gas interface, VHS film captured the formation of the hydrate particles subsurface and their movement (specific gravity is less than 1) from the water slurry to the surface of the water. Near the water surface, the particles moved to the stainless steel walls to be adsorbed, building inwardly from the walls in a concentric cylinder. The natural gas hydrates symmetrically pack in the cell, leaving open only a small cylindrical void slightly off-center through which the bottom of the cell is visible. Practically, this means that an expensive processing step of separating particles from a water slurry and packing them in a storage container is preempted. Furthermore, storage space is maximized when the surfactant-laden particles build inwardly from the container walls.

(4) Conversion of Interstitial Water

The conversion to hydrates of interstitial water was achieved in a semi-continuous process with a system containing natural gas, water, and 286 ppm of SDS. Gas was continuously added to the cell to replenish gas being occluded and to maintain a constant pressure during hydrate formation; gas flow was controlled by a constant-pressure regulator and flow measured by a gas mass flowmeter. At the higher constant pressure, a greater fraction of the cavities fill than if gases were added batchwise. Natural gas in our test cell was maintained at 3.89 MPa (550 psig). Hydrates were allowed to form until all of the free water initially in the bottom of the cell was dissipated into the hydrate structure or as free water in the interstices; then the free water remaining in the interstices was converted to hydrates. Results showed that within 3 hours, 86% of theoretical capacity was achieved. Hydrate formation rates remained high as interstitial water was converted.

(5) Process Simplification

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

Surfactant in the water solution simplifies the process four ways: (1) Hydrates form rapidly. (2) Hydrates form in a quiescent system. (3) Hydrate particles migrate to the cell walls where they self-adsorb and self-pack. (4) Interstitial water forms hydrates. In the first simplification, hydrates form in the presence of surfactant greater than 700 times faster than in a quiescent, pure-water/gas system. Therefore, with proper design of the formation-storage vessel, a formation-decomposition cycle including turnaround time could be achieved within a 24-hour period. In the second simplification, surfactant causes hydrates to be formed in a quiescent system, eliminating the need to impose water flow, movement, or mechanical stirring. 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 repressurizing with gas. In the third and fourth simplifications, difficult intermediate process steps of 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.

The simplifications greatly enhance the prospects for an economical large-scale process.

(6) Critical Micellar Concentration for Hydrate Formation

Critical micellar concentration (CMC) refers to a threshold level of surfactant concentration in water necessary for micelles to form, and above which some physical properties of a solution abruptly change. To determine concentration levels needed to influence hydrate formation and to give insight into the mechanism of hydrate formation, surface tension was measured for numerous concentrations of SDS/water solutions; the CMC at 298 K (77°F) and 1 atm for our solution occurred near 2700 ppm of SDS.

However, when using the same surfactant in the chilled and pressurized test cell, hydrates rapidly formed at lower SDS concentrations than 2700 ppm, indicating a lower CMC. In explanation, CMC is a function of temperature and the amount of gas dissolved in the water. In order to get a better estimate of CMC at test conditions, multiple runs were made with a pressurized and chilled water/ethane system in the test cell while varying SDS concentration. The results are given in Fig. I.C.3.

In Fig. I.C.3 the very sharp break in the curve at 242 ppm represents the CMC at ethane hydrate-forming conditions for SDS. Hydrate induction time gave the most sensitive indication of the breakpoint, although amount of gas occluded at a specific time would also have sufficed.

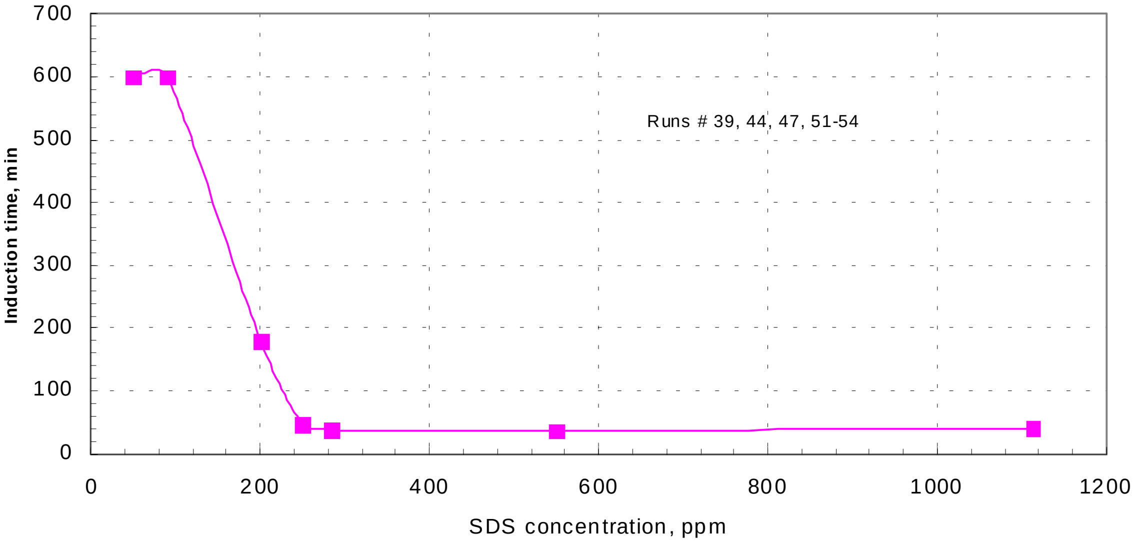


Fig. I.C.3. Critical micellar concentration threshold for hydrate formation

The conclusion from Fig. I.C.3 is that a SDS surfactant solution concentration above the CMC greatly enhances the hydrate gas-storage process. The micellar configuration is sketched in Fig. I.C. 4.

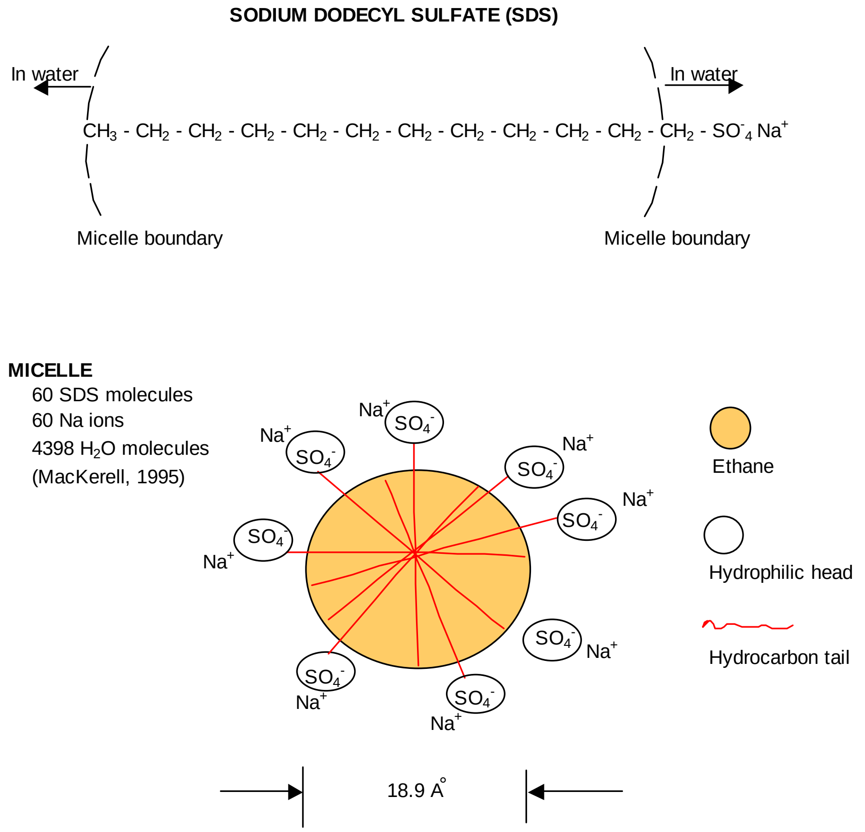


Fig. I.C.4. Micelles solubilize natural gas, forming hydrates subsurface

These experimental observations make possible a practical design for large-scale natural gas storage in hydrates in which natural gas is solubilized in the micelles and facilitates hydrate formation subsurface.

II. CONCEPTUAL DESIGN HYDRATE STORAGE PROCESS

The following is the concept of a large-scale process based on the data obtained in the feasibility phase.

A. Process Flow Diagram

A block diagram of the envisioned scaled up process for gas hydrate storage of natural gas is given in Fig. II.A.1.

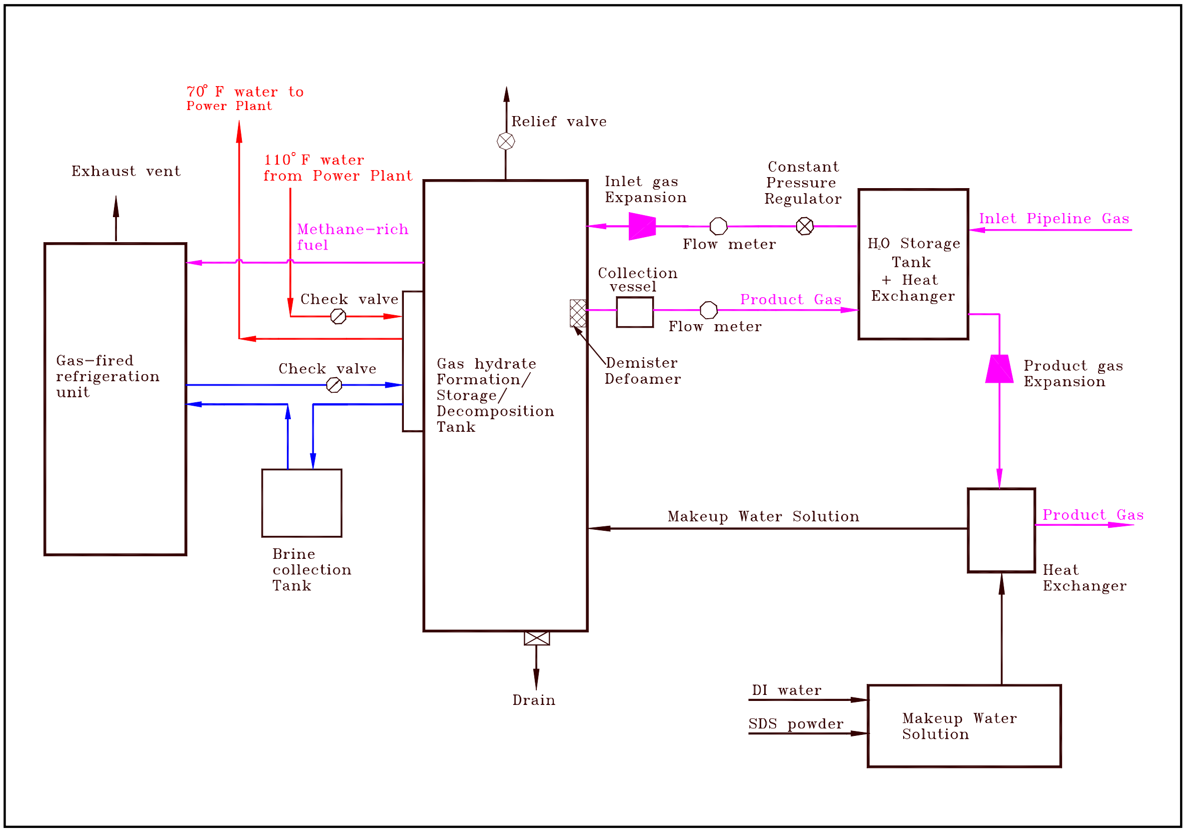


Fig. II.A.1. Block diagram hydrate storage process

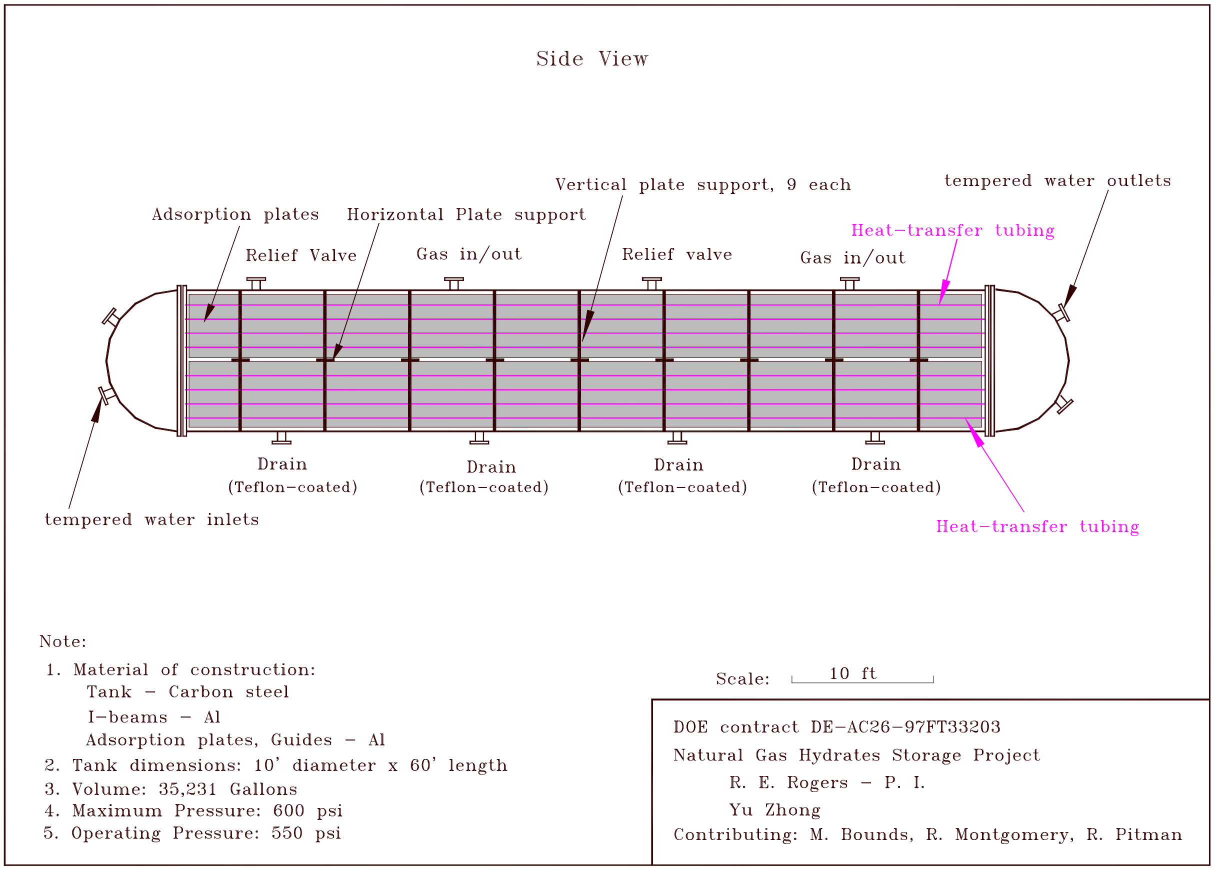
The process was designed to fill 3 tanks in series with hydrates in a 23-hour period and then decompose all 3 tanks in parallel within a 1-hour period. The formation tanks also serve for storage and decomposition. Heat transfer fluid flowing through tubing in the tank would alternately come from a refrigeration unit for formation or from the adjacent power plant for decomposition. Feed gas flows into the formation tank from a pipeline at pressures ranging from 600 to 700 psig; feed gas in the formation tank is controlled to a constant 550 psig. Makeup water to replace moisture entrained with the outlet gas is cooled by the exiting cold gas; a demister-defoamer and collection vessel remove entrained water in the exiting gas stream. A gas-fired refrigeration unit cools a circulating brine that removes latent heat of formation; the refrigeration unit uses methane-rich gases from the storage tank as fuel.

B. Formation/Storage/Decomposition Tank

(1) Storage Tank Design

Hydrate formation, storage and decomposition is performed in the same tank; it has an operating pressure of 550 psig. Laboratory studies demonstrated that hydrates form rapidly from the micelles of sodium dodecyl sulfate and, just as importantly to the success of the process, the surfactant adsorbs on a metal surface and there packs the hydrates. The laboratory work showed aluminum to be the best surface for adsorption and retention of the hydrates. This is fortunate because of aluminum's higher thermal conductivity, lighter weight, and lower cost. Therefore, aluminum adsorption plates rest on supports and traverse the length of the tank; they can be individually removed. Eighteen total vertical and horizontal aluminum supports accommodate the weight of the hydrate mass.

Aluminum heat exchange tubing extends the length of the tank and heating/cooling mediums make one-pass through each tube. Heat transfer results from conduction and convection from the tubes immersed in water and contacting the plates and supports.
The tank's drain and gas ports are Teflon coated to prevent buildup of hydrates.



Note:
1. Material of construction:
Tank − Carbon steel
I−beams − Al
Adsorption plates, Guides − Al
2. Tank dimensions: 10' diameter x 60' length
3. Volume: 35,231 Gallons
4. Maximum Pressure: 600 psi
5. Operating Pressure: 550 psi

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Fig. II.B.1. Hydrate formation/storage/decomposition tank

(2) Hydrate Adsorption Plates

The rate of hydrate formation with SDS micellar solution depends upon the surface area of the adsorption plates (DOE Monthly Status Report, Aug. 1999). Therefore, for the scaled formation tank to exhibit at least a hydrate formation rate as rapid as achieved in the laboratory unit, equivalence of volume/surface area would be required. By using this scale factor, the 10-ft diameter tank would require an adsorption plate surface area at least 1879 ft^2. The proposed design, however, establishes a plate surface area of 7,995 ft^2. Although this is an over design on surface area, the additional plates are needed to support the weight of the hydrates. A sketch of the plates is presented in Fig. II.B.2.

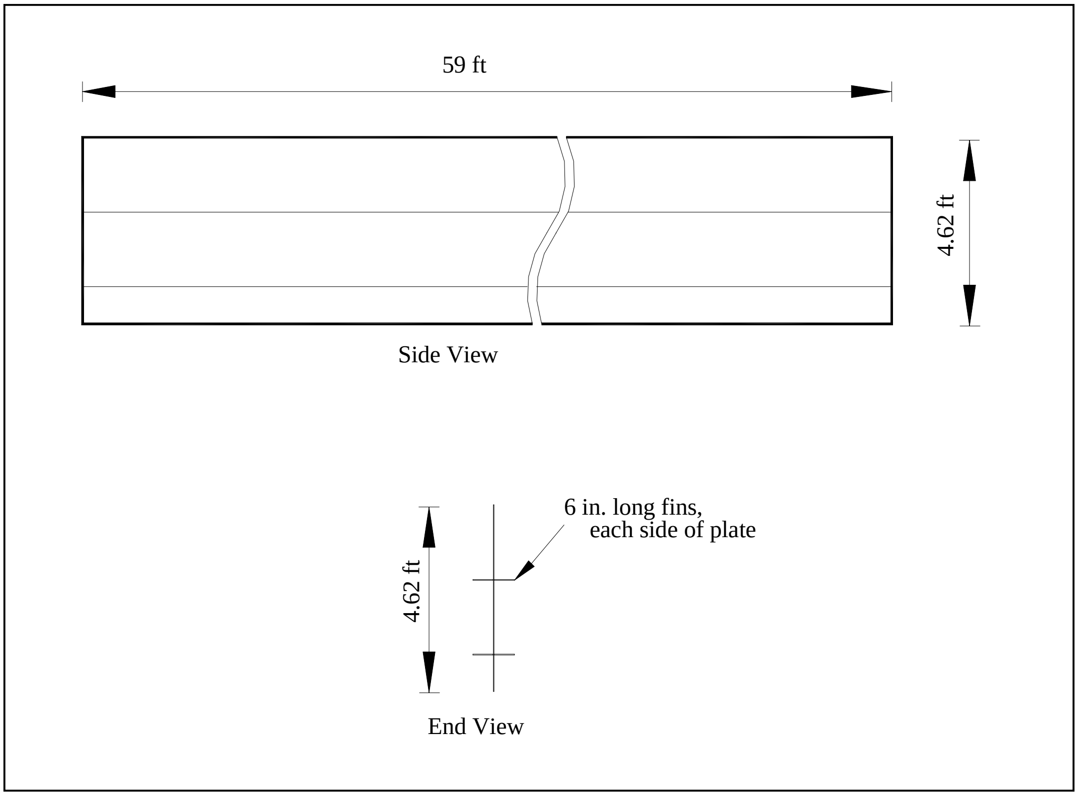

Fig. II.B.2. Sketch of largest adsorption plate.

Fins are added to support the weight of the hydrates that build outwardly from the plates, but they also provide additional surface area for adsorption. Twenty plates run the length of the tank. Each plate may be pulled separately from the tank. The heat transfer tubes run parallel to the plates and rest on the aluminum cross-supports.

In Fig. II.B.3. is sketched the pattern of plates for a quadrant of the formation tank; the sizes and numbers of plates would be repeated in each quadrant.

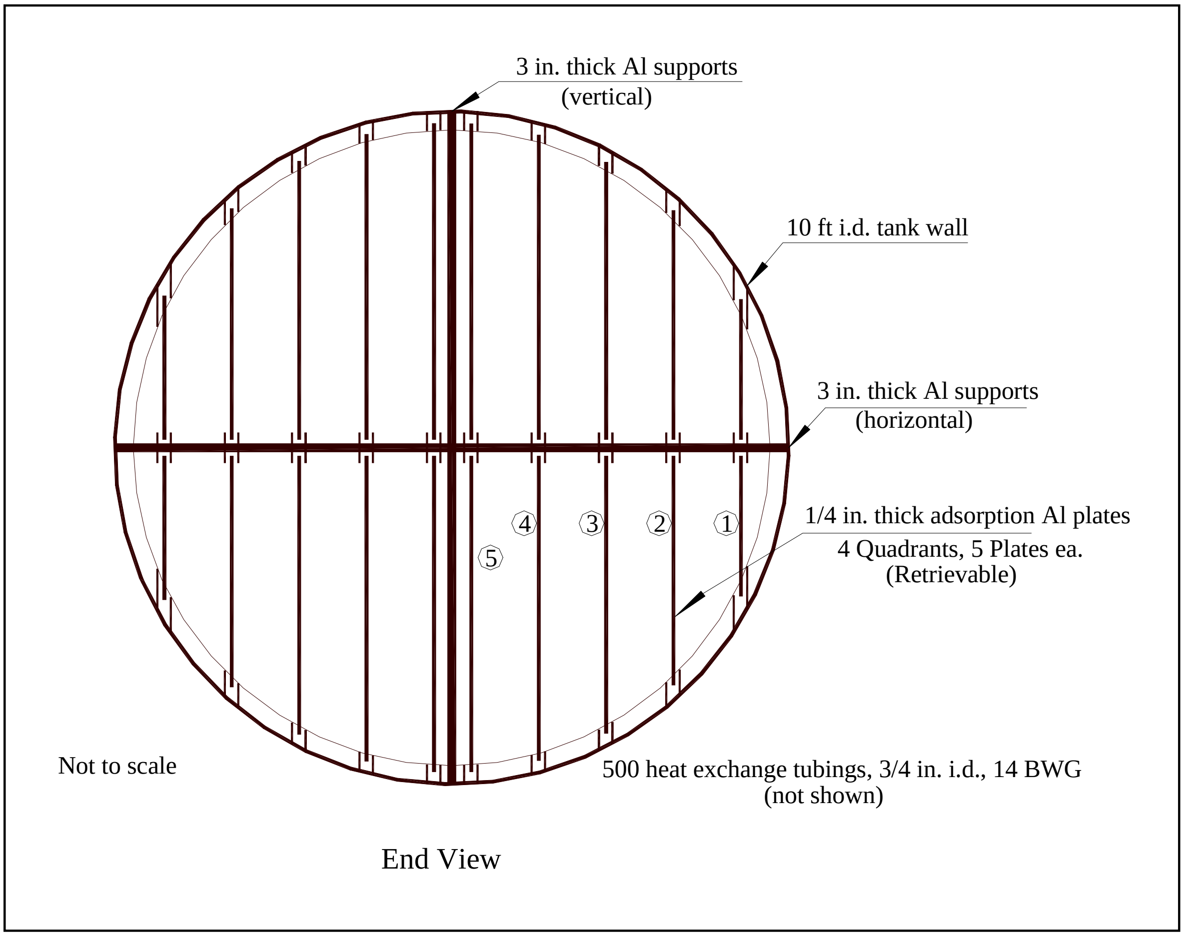

Fig. II.B.3. Plate pattern in storage tank (tubing not shown)

Note that plate guides keep the plates in place and allow each to be removed from the tank. Again, the simplicity of the design promotes economy and easy maintenance.

Each of the twenty plates would be 59 ft long and 1/4" thick aluminum. In Table II.B.1. is summarized plate dimensions.

TABLE II.B.1. Summary of adsorption plate description

Plate No.	L (ft)	W (ft)	Thick (in)	No. of Plates	Surf. Area, ft^2	Vol, ft^3/plate
1	59	2.45	1/4	4	289.2	3.01
2	59	3.53	1/4	4	416.3	4.34
3	59	4.15	1/4	4	489.8	5.10
4	59	4.50	1/4	4	530.6	5.53
5	59	4.62	1/4	4	545.5	5.68

(3) Plate Supports.

Hydrates adsorb on the plates and build outwardly, their mass kept in place by the overlapping fins. According to the laboratory runs, hydrates will fill the space between plates as the water level lowers. In Fig. II.B.4 is sketched a representation of the nine horizontal supports for the plates, each 3 in. thick aluminum alloy; nine vertical supports and the horizontal supports are paired at equal distances along the longitudinal axis. The supports are designed to withstand the hydrate load with a maximum deflection of only 0.5 in. over their entire length. Note that the aluminum heat-transfer tubing is in direct contact with the supports.

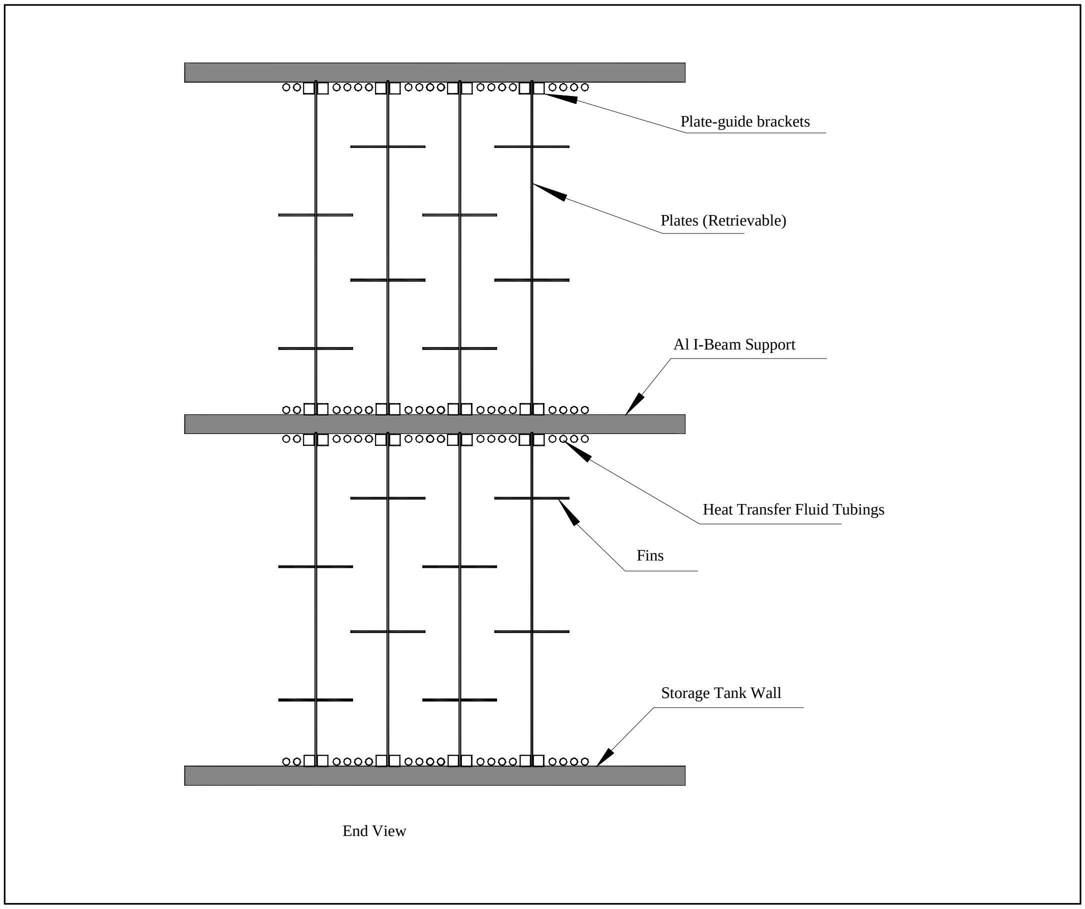

Fig. II.B.4. Plate and holder system

(4) Insulation

The hydrates would be formed and stored at a temperature between 35°F and 40°F. Heat gains would be prohibitive without exceptional insulation. It is proposed to use a super insulation employed in the insulation of liquefied gases: oxygen, nitrogen, argon, helium. The insulation has exceptionally low thermal conductivity. Small-diameter fibers of about 1 micron are bonded with melamine resin to form a fiber glass blanket that exhibits minimal out gassing under vacuum at low temperatures. (Johns Manville, Lydall Inc., 1998)

The insulation is available in 1" thick sheets and has a nominal density of l lb_m/ft^3. At a tank temperature of -153°F, the material has a rated thermal conductivity of only 0.0023 Btu/hr-ft-°F under 0.1 mm Hg of pressure.

Three layers of the insulation to give a 3" thickness would be installed around the circumference of the approximately 60 ft cylindrical tank length and then sealed to hold vacuum.

(5) Heat Transfer Tubing

A means of forming hydrates rapidly with micellar solutions was developed in the laboratory, making a bulk storage process feasible. It was demonstrated that the rate of hydrate formation can be further increased with larger surface areas available for adsorption/packing of the hydrate crystals. Further, aluminum was found to facilitate the formation and collection the best. By inserting aluminum plates into the laboratory test cell, the hydrate formation became exceptionally fast. After making heat-transfer calculations, it became apparent that the large-scale formation rate would be limited by the heat transfer rate that dispels the latent heat of hydrate formation. Consequently, the problem of removing the heat of formation in a large scale process becomes paramount. A full tank of hydrates will require almost 50 million Btu to be removed during the formation cycle.

The large unit as designed provides aluminum plates for formation and collection of hydrates with surface area/tank-volume ratio 5 ½ times greater than the laboratory test cell. The large surface area is provided primarily to collect and support the hydrate crystals, but in so doing, it elevates the formation rate. Moreso, then, will the hydrate formation rate be limited by the heat transfer rate from these plates. Therefore, the design establishes banks of heat transfer tubes traversing the length of the 60 ft long tank. Heat transfer by convection will result from those tubes submerged in the formation waters. Conduction will also result from direct contact with the plate supports.

Heat transfer calculations were made to configure the tube bank. (See Appendix.) The following design parameters resulted from the calculations:

1. Aluminum tubing; 500 tubes; 3/4" o.d., 59 ft length; 14 BWG.
2. Diameter and wall thickness of tubing provides adequate stress against collapse for a maximum pressure difference of 550 psi in the tank and an extreme occurrence of 1 atm inside the tubing. A stress safety factor of 3 resulted.
3. Maximum fluid velocity of 7 ft/sec in the tubing.
4. Maximum pressure drop of 12 psi in the tubing.
5. Overall heat transfer coefficient of 479 Btu/ft^2-°F.
6. Chilled brine flow rate of 2,960 gal/min.

With these parameters, the approximately 50 million Btu could be removed from the tank in 7 hours--establishing the formation segment of the hydrate-storage cycle-time. This time compares with a formation time in the laboratory test cell of about 3 hours, even though the laboratory cell has a 5.5 times lower surface/volume ratio. It should be noted that there is space to add more than the designed 500 tubes to the large-scale tank design.

A sketch of the plates, heat-transfer tubes, supports, and tank are given in Fig. II.B.5.

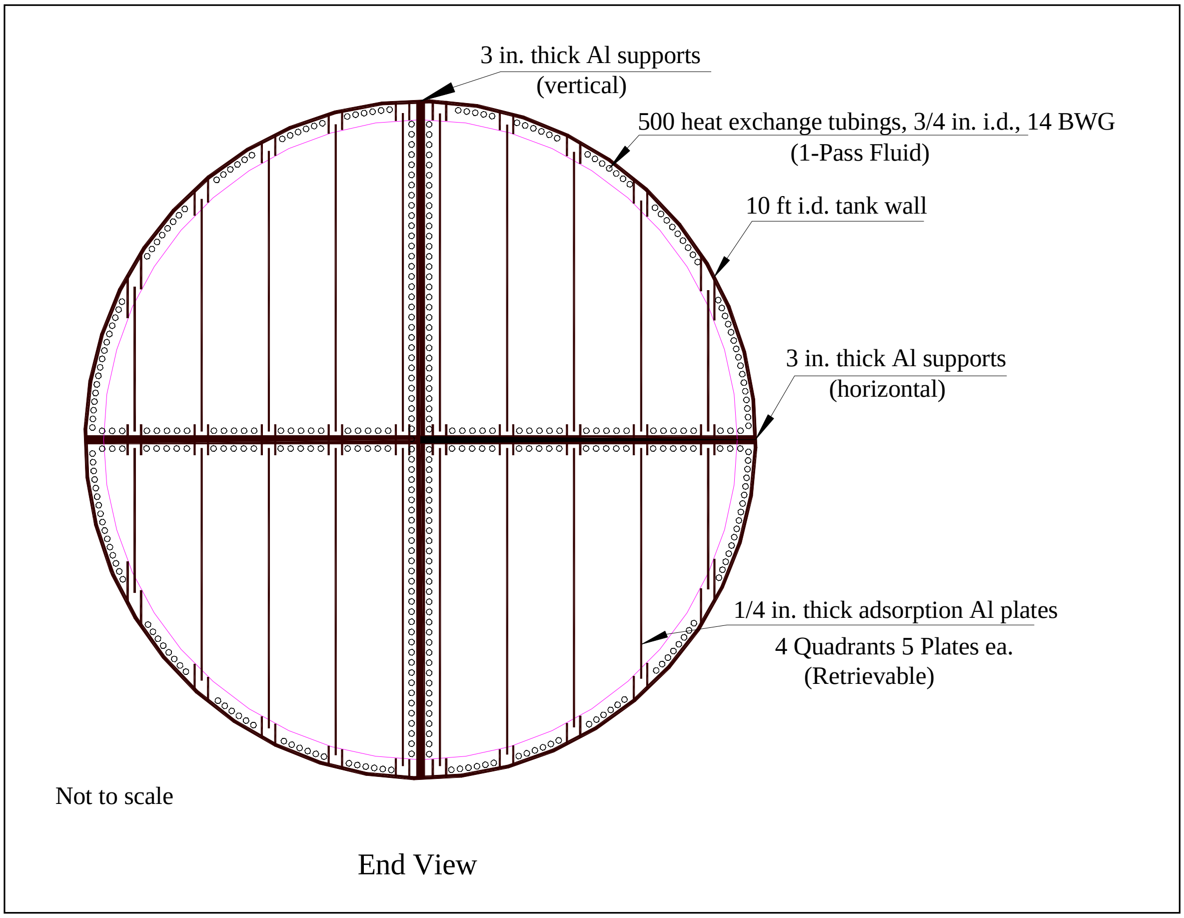

Fig. II.B.5. Heat-transfer tubing arrangement

III. MASS AND ENERGY REQUIREMENTS

The major energy and mass flowrates for a single hydrate storage tank is shown in Fig. III.1. The sketch applies to one tank out of the three tanks that are involved in a cycle of formation/storage/decomposition.

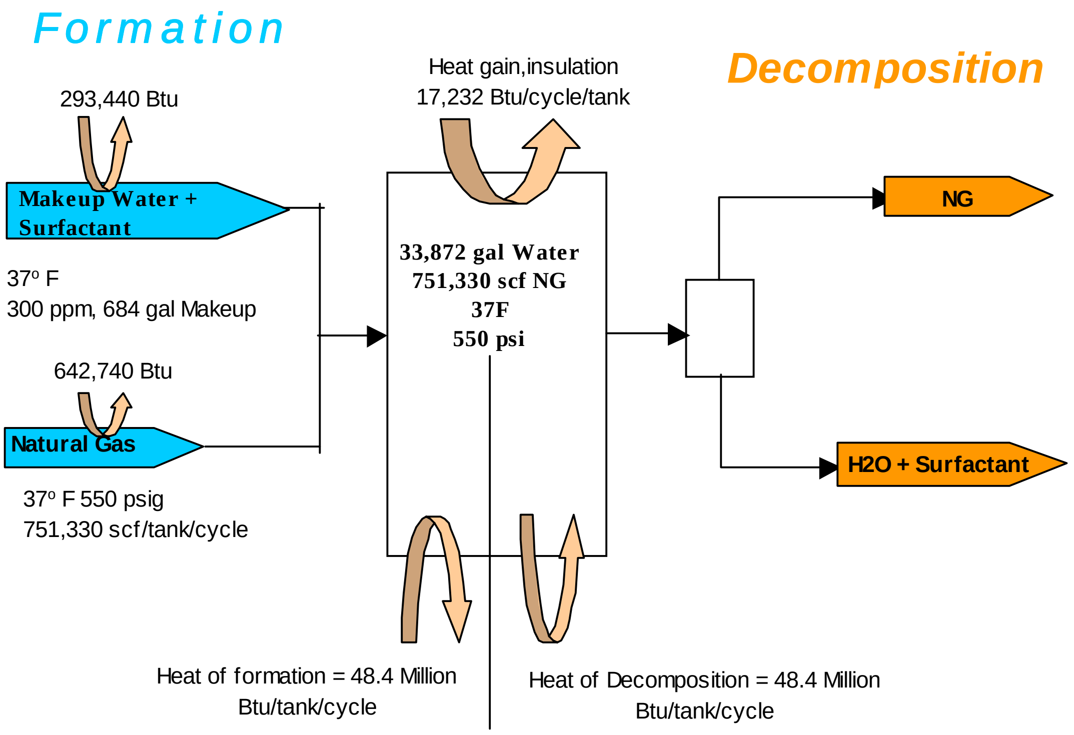

Fig. III.1. Mass and energy requirements, 1 storage tank
(Bounds, Montgomery, Pitman, Zhong, 1998)

Enough sensible heat of the entering makeup water and gas charge must be removed to bring them to 37°F. To assist in the sensible heat removal of these two streams, heat exchange with the cold exiting gas is made to lower the temperature of both entering streams to 53°F, the temperature at which hydrate nuclei began to form in the laboratory test cell, which prevents hydrates forming in any flow lines before the fluid reaches the formation tank. The major energy concern of the process is the latent heat of 49.3 million Btu that must be removed to form each tank of hydrates. The like amount of energy added to decompose is less demanding because the decomposition can be affected with a low-grade energy source at a reduced system pressure. The heat gain by the hydrates during storage can be kept to relatively low values with the super insulation commercially available for cryogenic storage. For one tank of a single cycle 738,700 scf of gas would be stored in the hydrates with an additional 12,600 scf compressed in free space of the tank; thus, for one cycle of 3 tanks 2,254,000 scf of gas would be stored.

The calculations to determine hydrate formation energy requirements are given in the Appendix. A basis was used of one formation/storage/decomposition tank of 10 ft diameter by 60 ft length. Any larger-scale process can be found then as an integer multiple of the base unit requirements. The following heat removal from one hydrate tank during formation and storage would be necessary: a. Latent heat of water, b. Gas sensible heat, c. Makeup water sensible heat, d. Initial water charge sensible heat, and e. Insulation losses. The initial water charge sensible heat would only be removed upon startup of the plant. These refrigeration needs could be partly offset by heat exchange with the exiting product gas and the Joules-Thomson effect of expanding feed gases.

TABLE III.B.1. Energy requirements to form hydrates, 1 tank.

Process Step	**Cooling, Btu/cycle/tank**
Latent Heat of Formation Water	48,372,800
Feed Gas Sensible Heat	642,700
Makeup Water Sensible Heat	39,502
Initial Water Charge Sensible Heat	253,900
Insulation Loss	17,237
Total	49,326,200

As expected, the latent heat extracted to form the hydrates is the overriding energy requirement. See Fig. III.B.1

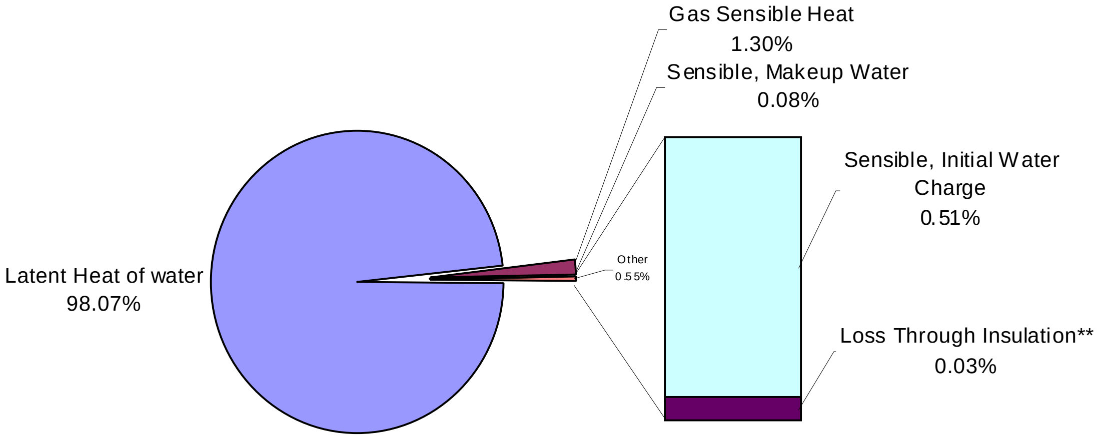

Fig. III.B.1. Cooling requirements for a cycle.

Some of the items in Table III.B.1 depend upon the number of cycles per year. The effect becomes less significant after about 10 cycles.

IV. ECONOMIC ANALYSIS

A. Equipment Costs

A tabulation is made for all equipment needed to conduct the process where 3 storage tanks operated in series comprise 1 cycle. That is, 3 storage tanks and the attendant processing equipment form a unit, and the entire unit would be involved in a single cycle of hydrate formation/storage/decomposition. Therefore, if a larger-scale process is desired, the costs and equipment listed in this report may be approximated from multiplication by an appropriate integer.

The listing and estimated pricing of equipment for the gas hydrate storage process is given in Table IV.A.1.

Table IV.A.1. Equipment list. (Bounds, Montgomery, Pitman, and Zhong)

Equipment Description	Quantity (1)	Size	Matl Construction	Unit Cost $	Cost 1 Tank, $	Total Cost 3 Tanks, $
Hydrate Formation, Storage, Decomposition Tank	1	10' D x 60' L	Carbon Steel, Lined	$300,000	$300,000	$900,000
Natural Gas Fired Refrig System	1	596 tons (2)	N/A	$682,744	$682,744	$682,744
Adsorption Plates	20	9,086 ft^2	Aluminum (4)	$1,357	$27,146	$81,439
Heat-Transfer Tubing	500	59' L x 3/4" o.d., 14 gauge	Aluminum (3)	$127	$63,720	$191,160
Surfactant Soln Storage Tank With Agitator	1	2734 gal Serves 3 Hyd Tanks	Carbon steel (6)	$9,702	$9,702	$9,702
Water Deionization Unit (7)	3	2,734 gal/60 min	n/a	$62	$62	$187
Insulation for Tank	3""	72"x50'x1" rolls	Cryogenic fiberglass	$4,970	$4,970	$14,910
Support System, Hydrate Tank	1	Aluminum	Construction of Support	$25,000	$25,000	$75,000
Feed Soln (makeup) Pump	1 (10)	205 gpm, P=50	Cast-Steel, Centrifugal	$7,546	$7,546	$7,546
Tempered Water Circulation Pump	1 (11)	2920 gpm, P=12	316 ss, Centrifugal	$12,600	$12,600	$37,800
Surfactant Soln Transfer Pump	1	273 gpm, P=20	Ductile Iron Casing, Cent.	$2,156	$2,156	$2,156
Insulation Vacuum Pump	3	0.75 hp	Cast Steel	$2,500	$2,500	$7,500
Brine Collection Tank (8)	1	1,014	Gallons, 304 ss	$8,948	$8,948	$8,948
Constant Pressure Regulator	1/tank	5"D	SS Flow Control	$8,624	$8,624	$25,872
Check Valves	2/tank (13)	8" D	Carbon Steel , Flanged	$485	$970	$2,910
Relief Valves	2/tank	5"D	SS Relief	$8,624	$17,248	$51,744
Heat Exchanger, Makeup H20	1/3 tanks	1000 ft^2	Carbon Steel	$30,000	$30,000	$30,000
Heat Exchanger, Feed Gas	1/three tanks	1000 ft^2	Carbon Steel	$30,000	$30,000	$30,000
Demister, Defoamer	1/tank	Vane-type (12)	6" Thick, Coalescing Type	$500	$500	$1,500
Foam, Mist Collection Vessel	1/three tanks (9)	8,117	Gallons, Carbon Steel	$19,404	$19,404	$19,404
Electrical-driven Refrigeration	1			$1,000	$1,000	$3,000
Hydrate Tank Supports	1	3"x3"x10'	Aluminum (5)	$3,222	$3,222	$9,667
Tank, to cool entering gas	1	2000 gal	carbon steel (14)	$9,000	$9,000	$9,000
			TOTAL =	$1,168,573	$1,267,063	$2,202,189

Notes:

1. Process is designed around equipment for a 24-hour cycle, with three tanks, 1 refrigeration unit, etc.
2. See Refrig section of calculations in Appendix.
3. Aluminum tubing cost = $2.16/linear ft.
4. Total wt of plates (Plates:h35 =n33) + fins * $1.70/lb alum.
5. Support cost = total no. supports of 18(Supports:b43)*Wt/bm*$1.70/lb alum
6. From Timmerhaus, 4th ed., See Tank, Appendix.
7. Water deionization for makeup water. Per personal conversation w/Hoppenjans, Ecolochem, Inc., $8,000/350,000 gals at 1000 gpm general surface supply water.
8. Brine collection tank used to collect brine used in hydrate formation phase. Tank holds brine during decomposition phase when cooling tower water flows thru tubing. 25% free space, for tubing in all 3 hydrate tanks; Timmerhaus, p.539.
9. 2% of hydrate tank water and surfactant removed from exiting gas. Size carbon steel vessel to collect 3 cycles of the solution from all 3 hydrate tanks.
10. Size for makeup water volumetric flow rate, p.527 Timmerhaus, all 3 tanks, to be filled in 10 minutes with a 50 psig pressure drop in lines, once per cycle.
11. Brine flow rate limiting. Tubing:d193 gives gpm/tube * Tubing:e197 no. tubes. Timmerhaus, p. 527, 1.8 factor for 316 ss, 12 psi drop through tubing.
12. Petroleum Engineer's Handbook; similar to gas-liquid separators. Use coalescing type, 6" thick vane-type. Effective for entrained liquid as well as foam removal. Centrifugal device on gas inlet.
13. Timmerhaus, p511. Flanged valves.
14. Carbon steel tank to store water for heat exchange, exiting gas and entering gas.

Therefore, $2,202,000 would be the purchased equipment cost for a gas hydrate storage facility that would form/store/decompose 2,254,000 scf of gas per cycle; the equipment would be amortized over a 20-year life. One cycle could be performed in a time as short as 24 hours; otherwise, the cycle duration would be determined by the time desired for storage.

The effect of equipment on gas-storage costs is given in Fig. IV.A.1.

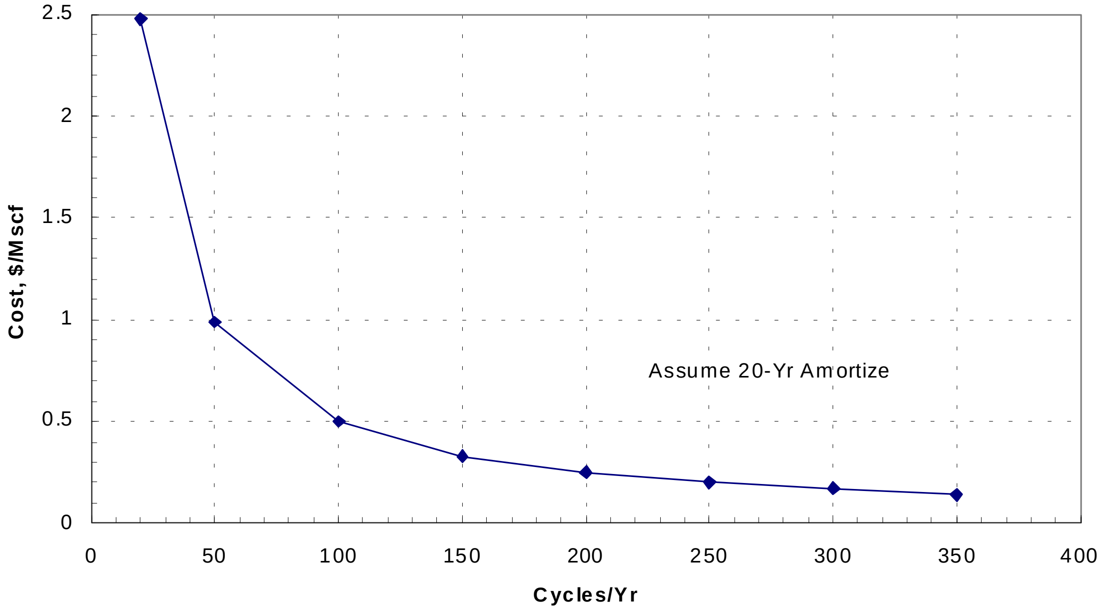

Fig. IV.A.1. Equipment impact on gas storage cost

B. Fixed Capital Investment

The fixed capital investment to install a gas hydrate storage process that could store 2,254,000 scf per cycle is presented in Table IV.B.1. The fixed capital investment is determined by the method of percentage of purchased equipment cost where factors found to be applicable in the chemical process industries for a solid/fluid plant cost are multiplied times the purchased equipment cost to give the other costs of the capital investment. That is, the equipment cost is first estimated, and then the factor in the second column of Table IV.B.1 is multiplied times that equipment cost to determine the capital cost item of the first column.

With a calculated equipment cost of $2,202,000 the fixed capital investment would be $6,893,000 to process the gas of three storage tanks over a 20-year life of the equipment.

TABLE IV.B.1. Fixed capital investment

Item	Factor	Cost
Direct Costs		
Purchased equipment, delivered	1	$2,202,189
Equipment installed	0.39	$858,854
Instrument., controls installed	0.13	$286,285
Piping installed	0.31	$682,679
Electrical installed	0.1	$220,219
Buildings	0.29	$638,635
Yard Improvements	0.1	$220,219
Total Direct Plant Cost		**$5,109,079**
Indirect Costs		
Engineering and supervision	0.1	$220,219
Construction expenses	0.17	$374,372
Total Direct and Indirect Costs		**$5,703,670**
Contractor's fee	0.18	$396,394
Contingency	0.36	$792,788
Fixed Capital Investments		$6,892,852

C. Labor Costs

The three largest costs of the hydrate storage process are refrigeration, equipment, and labor. One of the most important developments of the feasibility study was a simple, rapid formation process that could be performed in a quiescent system by just pressurizing the tank containing formation waters without mechanical stirring or circulating of processing fluids, and the hydrates would self-collect and self-pack in the container. As a consequence, labor requirements are reduced to a low value. The semi-continuous process operates with controls that admit feed gas to maintain a constant pressure in the forming stage. In a process where labor costs can make it economically unacceptable, the laboratory findings are pivotal in developing a practical process.

An estimate of labor requirement to operate the hydrate plant for a year was made by the method of Turton (Turton, 1998). It was assumed that the plant would be similar to a typical chemical plant and operate 24 hours per day with 3 shifts/day. The number of operators per shift was estimated on the basis of each major item of equipment. (See Appendix.) For this continuous operation, 5 operators would be necessary with an annual labor cost of $257,400.

D. Energy Costs

A fiber glass blanket insulation where the glass fibers are bonded with melamine resin is taken as representative of a super insulation that would be used on hydrate storage tanks. Such an insulation is used on cryogenic tanks. (John Manville, distributed by Lydall, Inc.)

As insulation thickness increases, its capital cost increases, but the heat gain of the cold hydrate tank decreases. These calculations are summarized in Table IV.D.1. Note the large decrease in heat gain to the tank from no insulation to 3 in. of insulation.

TABLE IV.D.1. Determining insulation thickness.

Ins. Thickness, in.	Heat Loss Btu/hr/tank	Heat Loss Btu/year/tank	20-Yr Loss, $ per tank	Insulation Cost, $ per tank	ROI, %
0	18,254,348	159,908,085,491	$74,986,207	0	11,303,600
0.2	10,550	92,419,318	$43,338	663	3,267
0.4	5,284	46,291,434	$21,708	1325	1,088
0.6	3,528	30,909,505	$14,494	1988	545
0.8	2,650	23,217,392	$10,887	2650	326
1	2,123	18,601,740	$8,723	3313	218
1.2	1,772	15,524,465	$7,280	3976	156
1.4	1,521	13,326,318	$6,249	4638	117
1.6	1,333	11,677,650	$5,476	5301	91
1.8	1,187	10,395,313	$4,875	5963	73
2	1,070	9,369,413	$4,394	6626	59
2.2	974	8,530,018	$4,000	7289	50
2.4	894	7,830,504	$3,672	7951	42
2.6	826	7,238,591	$3,394	8614	36
2.8	768	6,731,223	$3,156	9276	31
3	718	6,291,493	$2,950	9939	

ROI = Incremental Return on Investment
Assume a return on investment of 25% is required.

ROI = Incremental increase in energy savings/incremental cost of insulation * 100

By taking an incremental Return on Investment (ROI) as the incremental energy savings divided by the incremental cost of insulation as insulation thickness is increased, it is determined that an insulation thickness of 3 in. would be desirable. See Fig. IV.D.1.

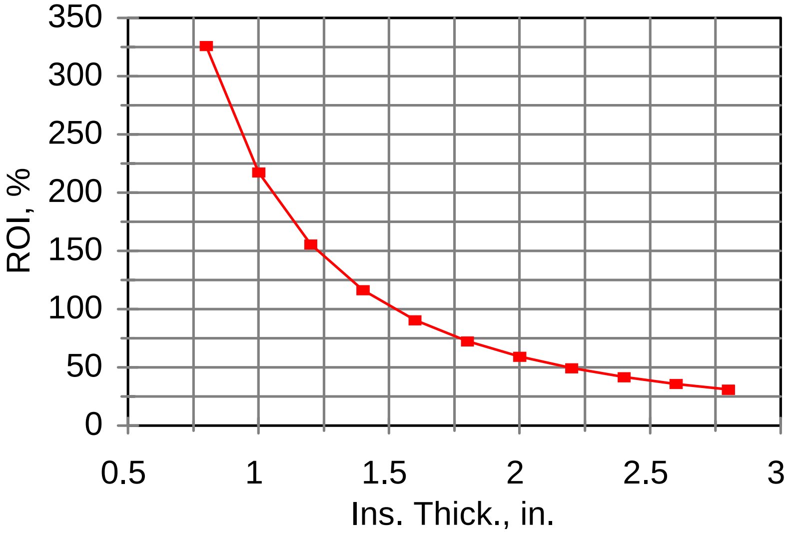

Fig. IV.D.1. Choosing insulation based on Return on Investment.

Because of the low heat gains through the insulation, storage temperatures of the gas hydrates can be maintained with a household-size electrical refrigeration unit on each storage tank. Overwhelmingly, the primary refrigeration demand comes from removing the latent heat of hydrate formation. A large gas-fired refrigeration unit would add the costs per 1000 scf of natural gas stored as given in Fig. IV.D.2.

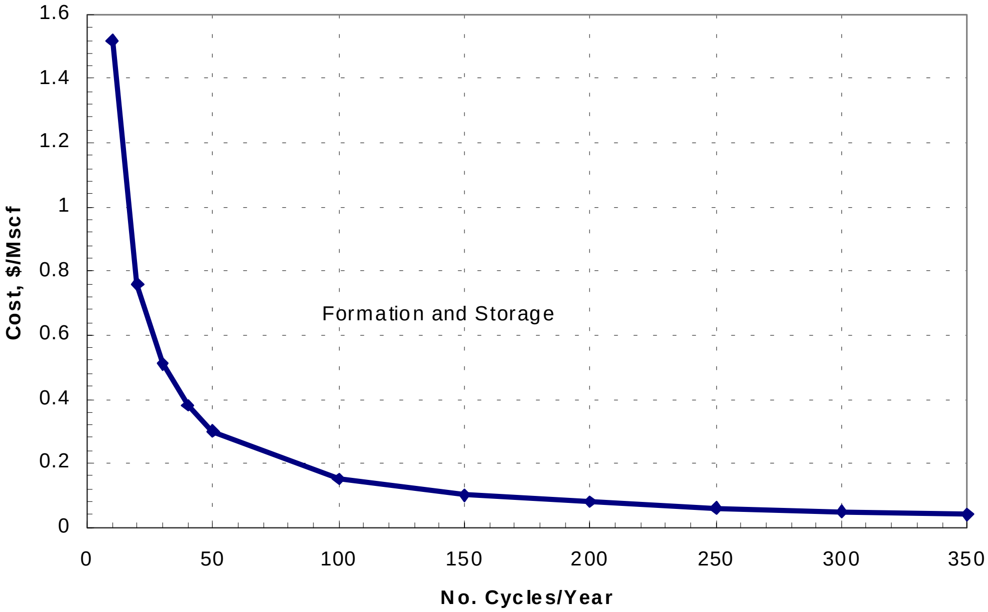

Fig. IV.D.2. Refrigeration costs

E. Cycling Effects

The fixed capital investment to process 2,254,000 scf of natural gas in one cycle was estimated to be $6,893,000. One cycle covering formation to decomposition can be achieved in 24 hours. A larger-scale operation would involve integer multiples of these costs and storage capacities. In other words, the equipment and facilities would be repeated with this unit cost if larger operations were wanted.

(1) Development costs

The fixed capital investment, which includes direct and indirect costs, represents the development costs for a gas hydrate storage facility. Based on a 20-year life of the facility and the fixed capital investment being amortized over the 20-year life, the development cost per 1000 scf of gas was determined. See Fig. IV.E.1

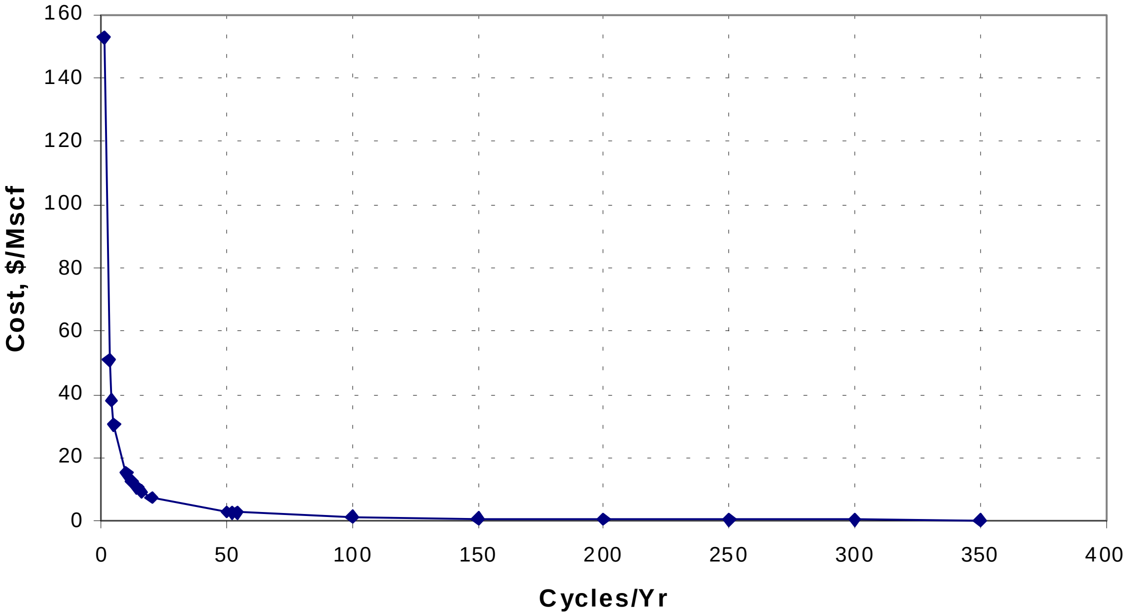

Fig. IV.E.1. Development costs of gas-hydrate storage facility

It is evident that the development cost is prohibitive for one cycle per year. However, the cost drops precipitously as the number of cycles increases. Since the shortest achievable cycle time in the design is 24 hours, it is possible to have 300 cycle per year, if an 18% downtime is assumed.

Therefore, the process becomes attractive for meeting frequent demands for stored gas but it is economically not attractive for bulk storage in 1 or 2 cycles per year.

(2) User Costs

The operating costs to store natural gas in hydrates are summarized in Table IV.E.1. See the Appendix for the calculations.

TABLE IV.E.1. Product or user costs (Timmerhaus, 1990)

ITEM	DETERMINED BY	COST	BASIS
Raw Matls	Calculate	$181	per cycle
Operating Labor	Calculate	$257,400	per year
Utilities	Calculate	$1,888	per cycle
Supervisory Labor	15% Operating Labor	$38,610	per year
Maintenance and Repair	6% Fixed Capital Investment	$20,679	per year
Operating Supplies	15% Maintenance and Repairs	$3,102	per year
Laboratory Charges	15% Operating Labor	$38,610	per year
Depreciation	Calculate	$110,109	per year
Property Taxes	4% Fixed Capital Investment	$27,571	per year
Insurance	1% Fixed Capital Investment	$3,446	per year
Plant Overhead	70% Operating Labor+Supervision+ Maintenance	$221,682	per year
Administrative	25% Operating Labor	$64,350	per year
Contingency	1% Total Product Cost	$7,876	per year

Labor is minimized in the process because of forming the hydrates from a quiescent system. That is, no mechanical stirring and no processing steps to collect/pack the hydrate particles; the action of the surfactant accomplishes these functions. Nevertheless, labor is still the largest user cost. In one regard, the results in the table emphasize that the process could not be competitive if labor costs were not kept low by use of surfactant and adsorption plates.

If one takes the approach that the storage facility is operated as a chemical plant in which 24-hour shifts operate 300 days per year (65 days downtime), then operating costs per 1000 scf of gas decline precipitously with the number of cycles per year. Then, the operating costs decrease as given in Fig. IV.E.2.

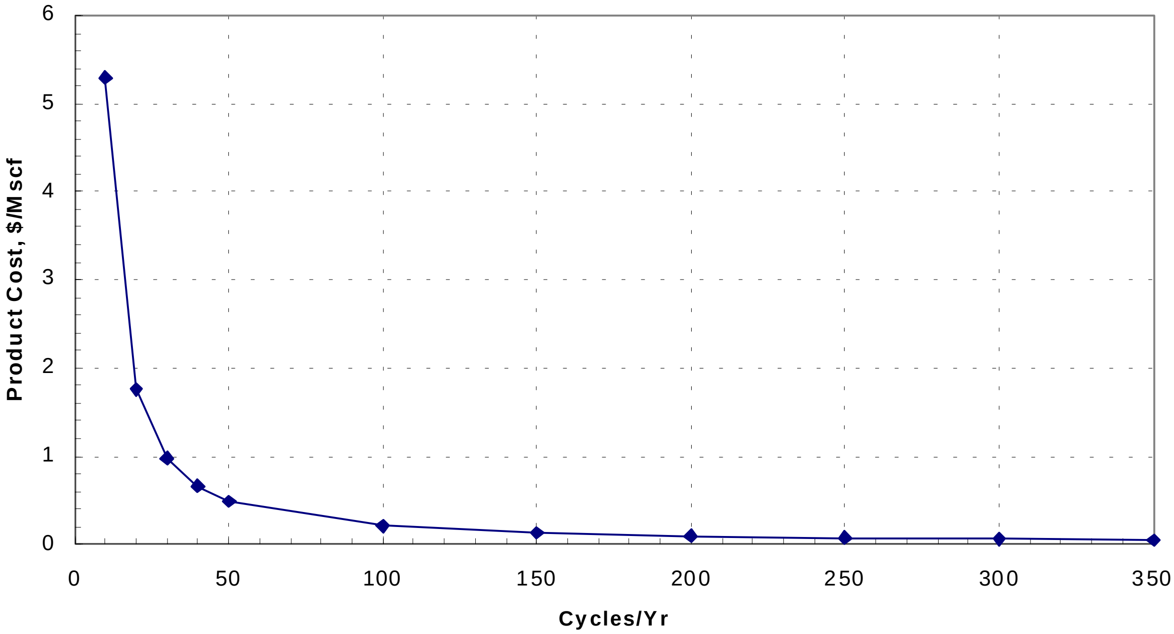

Fig. IV.E.2. Product (user) costs of stored hydrate gas

F. Economic Comparison Hydrate Storage with Conventional Storage Means

Estimates of development and user costs are reported for conventional methods of storing natural gas. Here, these two costs are calculated for hydrate storage and compared to conventional methods.

(1) Development Costs

The development costs per 1000 scf of gas were compared to conventional storage development costs. Conventional storage costs are given in Table IV.F.1.

TABLE IV.F.1. Approximate costs of natural gas storage by conventional means. (Beckman, 1997)

Type Storage	Development Cost, $/Mcf	User Cost, Single-cycle, $/Mcf
Depleted Reservoir	2- 3.50	0.20- 1.50
Salt Cavern	7- 14.00	0.80- 4.50
Aquifer	2- 4	0.60- 1.75
LNG	25- 40	10+

The comparison is best made by viewing Fig. IV.G.1.

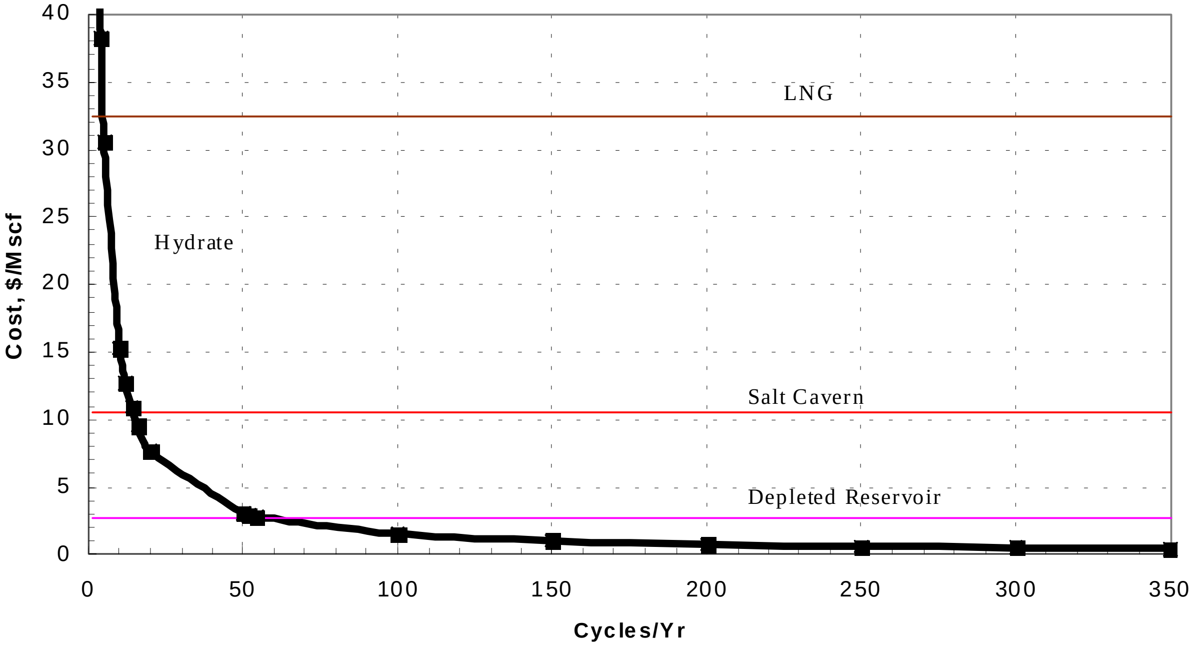

Fig. IV.G.1. Comparison of development costs

Note that the gas-hydrate process becomes competitive with LNG when 4 cycles or more per year are made. From the standpoint of development costs, the hydrate process becomes competitive with salt cavern and depleted reservoir storage for cycling above 14 and 54 cycles/year, respectively.

(2) User costs

The cost of storing the natural gas in hydrates, i.e., the user cost that must be charged the customer, was determined, and the calculations are included in the Appendix. Also, see Table IV.E.1. How these user costs compare to conventional storage user costs is shown in Fig. IV.G.2.

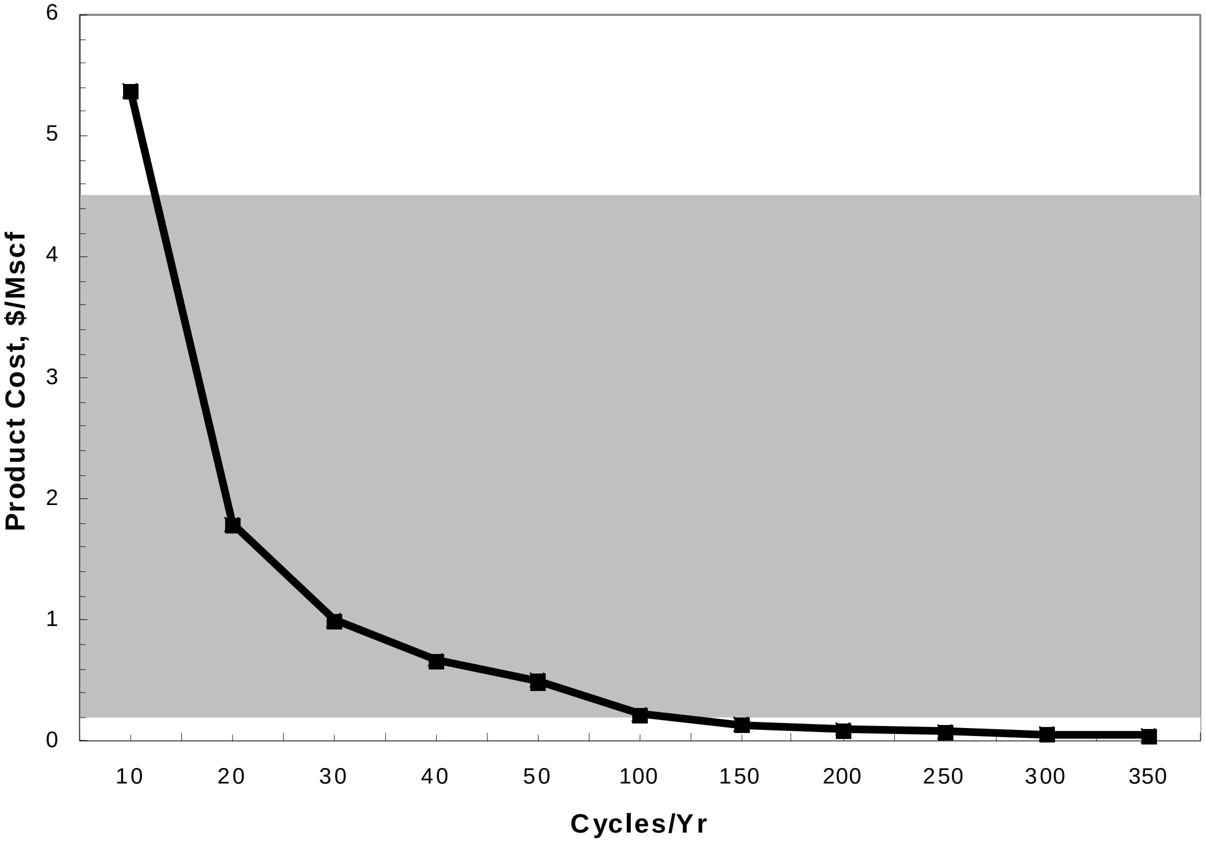

Fig. IV.G.2. Comparison of hydrate user costs with conventional storage

It is observed in Fig. IV.G.2 that less than 13 cycles of hydrate storage per year would not be economically competitive with conventional storage from the standpoint of user costs. In the range of 13 to 125 cycles per year, the hydrate storage is competitive. Above 125 cycles per year, the hydrate storage user costs become less than conventional storage.

V. Extensions and Limitations of Proposed Design

Gas-Fired Refrigeration-- The design includes gas-fired refrigeration to remove the latent heat of hydrate formation. The natural gas refrigeration unit is important for two reasons: economy of fuel usage and utilization of methane-rich gas that accumulates in the process. The two reasons are very much related because the hydrates as they form occlude gas leaner in methane than the free gas from which they form; the free gas in the formation tank above the forming hydrates, therefore, becomes richer in methane as the process develops. While gas-fired refrigeration would use this accumulating methane-richer gas to supply cheaper cooling to the process, reducing methane-rich gas above the hydrates would also result in lower operating and storage pressures for the process. (The benefits of lower pressures from rich methane use were not included in the design.)

Some background information on the refrigeration unit may be obtained in the final report entitled “Development of a Gas Fired Absorption Chiller for the United States Market” by Carrier Corporation for the Gas Research Institute (Decker, 1992).

Larger or Smaller Scales-- The concept submitted in this report is for a design that is modular in the sense that a scale larger than the 2,254,000 scf of gas stored per cycle could be approximated by integer multiples of the given equipment and cost. Of course, a larger-size operation would be somewhat cheaper per unit of gas stored because of the “0.6 rule-of-thumb” in scaleup of some equipment without purchasing duplicate equipment and because labor costs per Mscf would be lower.

Also, the conceptual process would be versatile enough to serve on a smaller scale or in remote areas for other applications. For example, cost savings could result from its location near a gas source of higher pressure where the gas expansion would reduce refrigeration costs.

Basic design of the process would remain the same for larger- or smaller- scale versions in applications other than a power plant.

Rate of Hydrate Decomposition-- Any low-grade heat source at ambient or higher temperatures could be used to decompose the hydrates. In the proposed process 110^o F water from the power plant, ordinarily going to a cooling tower, would be used to decompose hydrates. (The minor cost savings to the hydrate process by circumventing the cooling tower was not included in the economic calculations.) In another setting the process could use surface water, or even ambient air, to circulate through the heat transfer tubing and decompose the hydrates. With reduced pressures and a relatively low equilibrium temperature, the hydrate decomposition rate is high.

The proposed process involves decomposing the hydrate contents of the three parallel storage tanks, and calculations show that the decomposition could be done in one hour. However, removing the gas in that time frame could cause excessive foaming problems and excessive gas velocities. In such case the cycle time could be extended above 24 hours, an arbitrary choice, or the formation time could be lowered by several means to allow more time for decomposition while maintaining a 24-hour cycle.

A pilot-plant scale would be particularly useful in verifying the practical decomposition time.

Hydrate Formation Time-- In a micellar solution, hydrate formation rate in the large-scale process is not limited by reaction rate. Heat transfer to remove the latent formation heat limits. In the calculations, enough tubes were inserted (500) to give the necessary heat transfer in 7 2/3 hours to fill each tank with hydrates, there being three tanks to fill in series per cycle. Since there is sufficient tank space for more heat-transfer tubes, the cycle time could be shortened by adding more tubes at the expense of more tons of refrigeration.

Gas Purity-- No methyl alcohol must be in the entering gas stream because of its retardation of hydrate formation.

V. CONCLUSIONS

The project established the feasibility of a new natural gas storage method for either large-scale commercial applications or smaller applications in remote areas. This is significant because of the limited number of methods that are available. A breakthrough occurred in Phase I that overcame some seemingly insurmountable technical and economic problems involving hydrate storage of natural gas. Namely, surfactant micellar solution was found to form hydrates rapidly in a quiescent system, self-pack crystals by adsorption as the hydrates form, and convert interstitial water of packed particles to hydrates. By this simplification, manual labor is minimized and equipment maintenance is minimized in a hydrate-storage process. For example, the lack of mechanically moving parts (quiescent system, no mechanical stirring) and the lack of a hydrate-particle separation step from the slurry (particles adsorb and build on metal surfaces) reduce maintenance and labor.

A conceptual design and an economic analysis were made. The economic analysis showed the major contributor to user cost to be refrigeration to remove latent heat of hydrate formation. High gas-supply pressure, gas-fired refrigeration unit, super insulation, and energy exchange of process streams in a large-scale facility would reduce refrigeration costs. The major contributor to development cost is the equipment capital investment, namely, the formation/storage/decomposition tank. When all of the costs are considered, hydrate storage becomes competitive for multiple cycles.

Therein is a distinct advantage of the hydrate storage process as designed: a formation/decomposition cycle can be accomplished within a 24-hour period and numerous storage cycles can be performed in a year. Advantages of the proposed hydrate storage process are the following:

1. Safety of storage. Gas is essentially encased in ice with a slow release if the tank ruptures. (Conceivably, the hydrates could be stabilized indefinitely by pressurizing with an inert gas or water to enhance safety. Crystal stability depends upon the total pressure and not partial pressure of the occluded gas. This step was not proposed in the conceptual design.)
2. Low-pressure storage. A pressure of 550 psig was used as the basis of the design to optimize gas capacity with costs. (Conceivably, the hydrates could be formed at 550 psig but stored near atmospheric pressure if a storage temperature of -20°C to 0°C were maintained. But the conceptual design is based on a 550 psig formation/storage pressure and a storage temperature of 37°F.)
3. Aboveground storage.
4. Attractiveness of economy increases as the number of storage cycles is increased.
5. Size of storage facility can be any multiple or fraction of the size of the conceptual unit presented in this report.
6. Application versatility. Size, location, safety, simplicity make possible a wide variety of applications ranging from large power plants to remote units of a small-scale application.

VI. RECOMMENDATIONS

Demonstrate a small pilot plant of the process. For the process to be available for industrial use, a demonstration of the conceptual design beyond the laboratory would be needed. The pilot would necessarily be an outside unit, possibly on the grounds of a power plant.

Secondarily, concurrent with the pilot plant, further laboratory evaluations could assist in evaluation of data for the pilot plant, as needed.

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APPENDIX

(Calculations)

III.Economic Analysis of an Industrial-Size Gas Hydrate Storage Process

F. Insulation

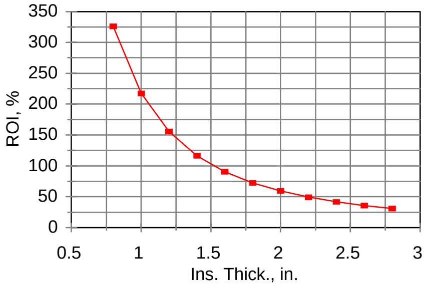
Calculations:

TABLE III.F.1. Determining insulation thickness

Ins. Thickness, in.	Heat Loss Btu/hr/tank	Heat Loss Btu/year/tank	20-Yr Loss, $ per tank	Insulation Cost, $ per tank	ROI, %
0	18,254,348	159,908,085,491	$74,986,207	0	11,303,600
0.2	10,550	92,419,318	$43,338	663	3,267
0.4	5,284	46,291,434	$21,708	1325	1,088
0.6	3,528	30,909,505	$14,494	1988	545
0.8	2,650	23,217,392	$10,887	2650	326
1	2,123	18,601,740	$8,723	3313	218
1.2	1,772	15,524,465	$7,280	3976	156
1.4	1,521	13,326,318	$6,249	4638	117
1.6	1,333	11,677,650	$5,476	5301	91
1.8	1,187	10,395,313	$4,875	5963	73
2	1,070	9,369,413	$4,394	6626	59
2.2	974	8,530,018	$4,000	7289	50
2.4	894	7,830,504	$3,672	7951	42
2.6	826	7,238,591	$3,394	8614	36
2.8	768	6,731,223	$3,156	9276	31
3	718	6,291,493	$2,950	9939	

ROI = Incremental Return on Investment

Assume a return on investment of 25% is required.
ROI = Incremental increase in energy savings/incremental cost of insulation * 100



Cryo-Lite cryogenic insulation fibler glass blanket marketed by Lydall, Inc.

Reference: Personal conversation D.A. Armstrong of Lydall, Inc. It has

low thermal conductivity (0.0192 Btu/hr-ft-R) at 1 atm and 80F. Under

vacuum (p<0.001 mm Hg) its thermal conductivity can go as low as 0.0021 Btu/hr-ft-R.

It is made of high quality fine fibers bonded with a melamine resin.

Properties:

Light weight (1 lb/ft^3)
Flexibility   (easy to cut and fit)
Fast pumpdown times
Flame resistant
Stable
Oxygen compatibility

If 3 inches (3 layers) of insulation is wrapped around the storage tank (total surface area is 1991 ft^2/tank)

Price = $249.60 per roll of 72" x 50' x 1" = $0.83 per ft^2 per inch thickness

Total price for insulating 1 tank = $4,970 per tank

Total price for insulating 3 tanks = $14,909 per 3 tanks

Plate Design

II.B.2. Plate Volumes and Weights

Plate Vol = L*W*T/12

where
L= length, ft.
W = Width, ft
T = Thickness, in.

Wt. Plate = W = Plate Vol*(specific gravity)*(density water)
W = V*SG*D

Adsorp Surface = L*W*2
Specific Grav, Al = 2.7

Note: Fins add to weight, area, volume of plates.

Table II.B.1. Plate and fins sizes, weights, volumes

	Plates							Fins					
Thick, in.	No.	Length, ft.	Width, ft.	No. of Plates	Adsorp Surf ft**2/plate	Volume, cu ft/plate	Weight, lb/plate	No./plate	Length, ft.	Width, in.	Volume, cu ft	Weight, lb/plate	Adsorp Surface, ft**2/fin
0.25	1	59	2.451	4	289.22	3.01	507.58	1	59	6.25	0.32	4	61.46
0.25	2	59	3.528	4	416.30	4.34	730.61	1	59	6.25	0.32	4	61.46
0.25	3	59	4.151	4	489.82	5.10	859.63	1	59	6.25	0.32	4	61.46
0.25	4	59	4.497	4	530.65	5.53	931.28	1	59	6.25	0.32	4	61.46
0.25	5	59	4.623	4	545.51	5.68	957.38	1	59	6.25	0.32	4	61.46
			Total =	20	9,086	94.65	15,946	20			1.60	22	1,229

Vol, Plates + Fins = 96 cu ft

Wt, Plates + Fins = 15,968 lbs
Adsorp Surf, Plates + Fins = 10,315 ft**2

Note: The thickness of the support beams is 3 in.
The distance between the edge of the adsorption plate and the tank wall is 3 in. all the way around.

Scale Factors for Test Cell to Plant Scale

Surf area lab cell/Volume lab cell = 4/D Note: No plates present.

To achieve at least the rate of hydrate formation in the large-scale tank as in the lab test cell, one must have at least a surface area/volume ratio equal to the test cell

Diameter of large-scale tank= 10 ft
To make the large-scale equivalent to the laboratory cell:
Surf area large tank = 4*vol large tank/dia large tank
Surf area large scale tank = 1,884 ft^2 Note: If equivalent to test cell.

Calculated Surface Area of plates of large tank = 10,315 ft^2 Note: Not counting inside surface of tank or supports.

Therefore, Large tank surface area is over-designed by a factor = 5.48

II.B.1. Tank Design

Hydrate Tank Volume & Weight

Vol tank = 3.14*D**2*L/4
D = 10 ft
L = 60 ft
Vol tank = 4710 cu ft
Vol tank = 35,231 gal

Water in Hydrate Tank, Volume & Weight

Vol Water = Vol Tank - Vol Tubing - Vol Plates - Vol Fins - Vol supports

Vol Tank = c8 ft^3
Vol Tubing = Tubing:C18 ft^3
Vol Plates = Plates:H34 ft^3
Vol Fins = Plates:m33 ft^3
Vol supports = ft^3

Vwater = 4,522 ft^3 = 33,822 gals

Weight water = Ww = Volume water*62.4 lbf

Wwater = 282,154 lbf

Makeup Water Soln Storage Tank

Estimate the required volume of water and surfactant to store enough makeup water for 3 tanks of 1 cycle.

Assume: 2% of water in tanks entrained with gas when hydrates are decomposed.

Volume of Water in 1 tank = 33,822 gals Hydrate tank
Vol Makeup Water, 1 tank = 676 gals

Assume 300 ppm SDS surfactant , 0.3 g/l
Wt surfactant per makeup vol, 1 tank = 1.69 lbs
Wt surfactant makeup, 3 tanks = 5.08 lbs
Vol makeup H20, 1 tank = 902 gals (with 25% free space)
Vol makeup H20, 3 tanks = 2,706 gals (with 25% free space)

$9,702 Cost of carbon steel tank corrected to 1998 prices. Tank agitated.
From Timmerhaus, 4th ed. p. 539.

II.B. Tubing for Heat Transfer

Calculate Volumes and Weights

Assume: Tubing would be placed side by side on supports and inside surface of tank.
Tubing would enter one end of tank and exit at the head of the other end.
Each tube would extend the length of the tank. Tubing made of aluminum.

No. tubes= n	500
o.d, in.	0.75
Length, ft.	59
i.d., in.	0.459
Thick, in.	0.083
Sp. Gv.	2.7

outside	Vol 1 Tubing =	0.18	ft^3	Vol = Pi/4*o.d.^2*L/144	
outside	Vol all tubing =	90.46	ft^3	Vtot = vol*n	
	Wt 1 Tubing =	63.08	lbf	Wt(tub) = Length*Pi*(o.d.-i.d.)*thickness*sp.gv.*62.4/144	lbf
	Wt all tubing =	31,538	lbf		

Calculate Velocities in Cylindrical Aluminum Tubing --1st approximation.

Aluminum alloys have unusual ability to maintain strength and shock resistance at temperatures as low as -250C (-425F). Good corrosion resistance and relatively low cost make these alloys very popular for low-temperature equipment. For most welded construction the 5000-series aluminum alloys are widely used.

Perry's ChE Handbook, 1984, p. 23-58.

Modulus of Elalsticity of Aluminum Alloys 5052 and 5454 = 10,500,000 psi at about 32F

Specification Minimum Tensile Strength, 5052 Al plate = 25,000 psi
Specification Minimum Yield Strength, 5052 alloy plates = 9,500 psi

Reference: ASME Boiler and Pressure Vessel Code, an American National Standard,
Section VIII, Rules for Construction of Pressure Vessels, 1986 ed., p. 128.

Specification Minimum Tensile Strength, 5454 alloy, seamless extruded tube = 31,000
Specification Minimum Yield Strength, 5454 alloy, seamless extruded tube = 12,000

Aluminum heat exchanger tube dimensions given in Perry's.

o.d., in.	i.d., in.	Wall, in.	BWG	Velocity @ 1 ft/s, Capacity, gal/min
0.125	0.084	0.083	14	0.0175
0.125	0.206	0.022	24	0.1037
0.375	0.209	0.083	14	0.1068
0.375	0.331	0.022	24	0.2679
0.5	0.334	0.083	14	0.273
0.5	0.43	0.035	20	0.4528
0.625	0.459	0.083	14	0.5161
0.75	0.584	0.083	14	0.8348

Rule of Thumb: Limit velocity of liquids (water) in metal pipes to less than 5 ft/sec

to prevent erosion and water hammer.

Acceptable range of pressure drops in a heat exchanger: for a

system pressure >10 psig, pressure drop range can be 5 psi up

to 50% of system gauge pressure.

A tube-side velocity of 1-10 ft/s is selected, with a typical value of 4 ft/s for heat exchangers>'

Process Design Principles, Seider, 1999, p307

Practical Process Engineering, Sandler, Luckiewicz, 1987.

tube o.d., in.	tube i.d., in.	Velocity, ft/sec	No. Tubes	Vol Flow, gal/min	Inlet Press, psia	Reynolds No.,	f	Press drop, psia	Stress, psi	Safety Factor
0.125	0.084	2	20	8.22	50	761	0.01	10	2,006	5
0.375	0.209	3	20	30.68	50	2,840	0.007	6	1,596	6
0.5	0.334	5	20	81.72	50	7,563	0.0062	9	1,986	5
0.625	0.459	6	20	134.76	50	12,473	0.0059	9	2,388	4
0.75	0.584	7	20	200.03	50	18,514	0.0055	9	2,794	3

Vol flow, gpm = No. tubes*pi/4*(id)^2/144*velocity*60*7.48

Press Drop = [2*2fLV^2/Dgc] per tube

where f = Fanning friction factor

L = 2*length of the tank

Reynolds No. = DV*density/viscosity

Note: Velocities in table above kept below 10 ft/s and pressure drop below 10 psi.

Stress = P*2b^2/(b^2-a^2)

This stress is that from a pressure external to the tubing.

P= 550 psi which is max pressure when inside p=1 atm.

b = in. which is od of tubing

a = in. which is i.d. of tubing

Note the safety factors in the above table are conservative since only atmospheric

pressure was assumed to exist on the inside of the tubing.

Calculate No. Tubes Needed for Heat Transfer, Hydrate Formation --1st Approximation

q = U*A*(Change in temp of cooling water)

where,

U = 200 Btu/(h*ft^2*F) An approximation. See Sandler, p. 508.

A = ft^2 inside area of tubing.

A = (no. tubes)*2*L*Pi*id/12

T2 = temp brine in tubes = 28F (corresponds to lab test cell)

T1 = temp of water in tank forming hydrates = 37F

T2-T1 = 9 F degree temp between hydrate tank and brine

tube i.d., in.	Vol Flow, gal/min	U, Btu/ft^2hrF	A, ft^2	Q Btu/hr	Req. Time, hrs
0.084	8.22	200	51.87	93,371	526
0.209	30.68	200	129.06	232,316	211
0.334	81.72	200	206.26	371,261	132
0.459	134.76	200	283.45	510,206	96
0.584	200.03	200	360.64	649,151	76

Heat to Remove from Tank During Hydrate Formation = (Latent heat of water forming hydrates)
and + (sensible heat of makeup water) + (heat gained from outside during form)
and + (sensible heat of gas)

Latent Heat = 48,372,778 Btu/cycle
Sens. Makeup= 39,502 Btu/cycle
Sens. Gas = 642,740 Btu/cycle
Insulation = 17,237 Btu/cycle

Total = 49,072,256 Btu/cycle

To meet this requirement, a cycle must be the time given in the above table.
As seen in the table the cycle time is not practical, so more tubes needed.

What flow rate of water necessary to absorb the the heat of c136?
Q = mCp(T2 brine - T1 brine)
m = Q/(Cp*deltaT*8.33)
m = 841,575 gal/cycle

Assume the formation part of the cycle is 4 hours.
From the above table, it is evident that the flow rate must be much larger than supplied by 20 tubes.
The flow rate must be about 47 times greater than supplied by 20 of the 1/2" tubing.
i.e., about 1000 of the 1/2" tubes would be needed.

Assuming a 4 hour cycle time, the following number of tubes are approximated:

	with 20 tubes		4-hr cycle	
o.d., in.	Vol flow, gal/min	Vol flow, gal/hr	Vol Flow, gal	No. tubes needed
0.125	8.22	493	1,973	8,532
0.375	30.68	1,841	7,363	2,286
0.5	81.72	4,903	19,613	858
0.625	134.76	8,086	32,342	520
0.75	200.03	12,002	48,007	351

Therefore, the 3/4" o.d. tubes are needed to supply the needed flow rate, pressure drop,
velocity, and stress safety factor with enought room to place them in the tank.

Finally, is the assumed value of 200 Btu/ft^2-hr-F valid?

hi = 0.023*k/D*(DG/viscosity)^.8 *(Cp*viscosity/k)^.333
hi = 0.023 *k/D*(Re)^.8 * (Pr)^.333
Where,
G = mass velocity lb/ft^2-sec
Cp = 1 Btu/lb-F
k = 0.32 Btu/ft/hr/F at 32F
Viscosity = 0.001205568 lb/ft-sec at 32F
Re = 18,514 from i84
Pr = 13.56

hi = 934.82 Btu/ft^2-hr-F

Ui = overall coefficient = 1 / [(1/hi) + (xw/km * id/avg d)]

xw = 0.01383333333 ft. from d84 and c84
km = 12.46 Btu/ft-hr-F for Aluminum 5052 alloy
ln mean d = 0.66
Ui = 488.55 Btu/ft^2-hr-F

Final Interation -- Calculation of Cycle Time, Hydrate Formation

Given:
1. 3/4" o.d. tubing, Aluminum 14 BWG
2. Velocity cooling brine = 7 ft/sec
3. Pressure drop in tubing = 12 psi
4. Reynolds No. in tubing = 17,633
5. Maximum stress on tubing = 2,794 psi a safety factor of 3.
6. Volumetric flow rate/tube= 5.84 gpm/tube
7. Heat to remove in hydrate formation = 53,719,256 Btu/cycle

Find:
1. Maximum # tubes from tank geometry.
   Max Allowable 3/4" o.d. tubing = 500
2. Find gpm flow rate satisfying tubing size and velocity.
   GPM = No. tubes*pi/4*(i.d.)^2/144*velocity*60*7.48 = 2,920 gal/min

3. hi = 899.03 Btu/ft^2-hr-F

4. Ui = 478.60 Btu/ft^2-hr-F

5. Pressure Drop in Tubing = 12 psi 2fLV^2/(D/12*gc)*density

Time/Cycle, hrs	Total gals all tubes	Hydrate Energy Req	Cum Heat Transfer	H20 temp rise, F
1	175,229	49,072,256	1.94e+07	33.62
2	350,457	49,072,256	3.88e+07	16.81
3	525,686	49,072,256	5.82e+07	11.21
4	700,914	49,072,256	7.76e+07	8.40
5	876,143	49,072,256	9.70e+07	6.72
6	1,051,372	49,072,256	1.16e+08	5.60
7	1,226,600	49,072,256	1.36e+08	4.80
8	1,401,829	49,072,256	1.55e+08	4.20

Therefore, from the table above, 7 hours would be the needed cycle time in order to raise the temperature of the cooling brine from only 28-33 F. Note that the mass flow rate of cooling brine is set by tube size and no. The amount of heat transferred is set by the hydrate formation demand. The rate of heat transferred is set by the heat transfer coefficient , surf area, and temperature difference driving force. The pressure drop inside the tubing would be 12 psi.

Calculation of Heat Transfer for Hydrate Decomposition

Assume use water from turbine of power plant at 110 F to decompose hydrates.

Avg Hot Water Temp = 80 F Using a conservative avg temp in line.
Hydrate Temperature = 37 F
Velocity water = 7 ft/sec
Pressure Drop of Water = 10 psi
Density heating water = 62.3 lbm/ft^3
Viscosity heating water = 0.982 cp
k m = 12.46 Btu/(ft-hr-F)

Reynolds No. = DV*Dens/Visc = 32,162
Prandtl No. = 7.30

hi = 0.023*k/D*(Re)^0.8*(Pr)^0.333 = 1,183 Btu/ft^2-hr-F

Ui = 549 Btu/ft^2-hr-F

Q = Ui*A*(t2-t1)*time

Flow Time	Btu Q required	Btu Q transferred
1	48,372,778	136,601,420

Therefore, heat can be transferred to decompose the hydrates in less than 1 hour.

Hydrates: volumes, weights, gas content

Sp Gv Hydrates = 0.92

Thick, hyd on plates = 0.5 ft

Adsorp surf, plates = Plates:g33

Vol fins Plates:m33 ft^3

Gas content, hydrates = 155 vol/vol

Total vol hyd on plates = Vhp = [Total adsorp surf area of plates*thick hydrates on plates - vol fins]/sp.gv.*0.95 (95% coverage)

Vhp = 4,689 ft^3

Vhp = 33,324 gal

Note: This gives a 95% coverage of the plates.

Hydrates on Each Plate, Summary

Plates					Adsorp	4-Plate	4_plate	Hydrate	Hydrate	Gas	Gas
Thick, in.	No.	Length, ft.	Width, ft.	No. of Plates	Surf ft**2/plate	Vol Hyd ft^3	Wt Hyd lbf	Vol/plate ft^3/plate	Wt/plate lbf/plate	content/ plate, scf	Content/ 4 plates, scf
0.125	1	59	2.451	4	289.22	590.69	33,173	147.67	8,293	22,889	91,557
0.125	2	59	3.528	4	416.30	859.76	48,284	214.94	12,071	33,316	133,263
0.125	3	59	4.151	4	489.82	1011.58	56,810	252.90	14,203	39,199	156,795
0.125	4	59	4.497	4	530.65	1095.90	61,546	273.97	15,386	42,466	169,864
0.125	5	59	4.623	4	545.51	1126.60	63,270	281.65	15,818	43,656	174,624
			Total =	**20**	**9,086**	4684.53	263,083	1171.13	65,771	181,526	**738,716**

Calculate Free Gas Compressed in Void Space of Tank

Given:

1. Plates 95% covered to leave 5% void space.
2. Plates 59 ft length, leaving 1 ft free space on ends
3. Pressure in tank = 550 psig.

Volume of tank = 4710 ft^3 from C8 of tank section.

Free Vol of tank = 235.5 ft^3 which is 5% of tank volume uncovered plates

Free Vol, end tank = 78.5 ft^ 3 which is the 1 ft of length of tank free.

Total Free Vol, tank= **314** ft^3 tank vol occupied by compressed gas.

scf compress gas = 12,614 scf to be added to that stored in hydrates

Calculations for Plate Support Network

Reference:
Flinn, Trojan, Engineering Materials and Their Applications, 3rd ed.
p.433

Deflection of a Beam = WL^3/(4Ebh^3)
where,
W= concentrated load at center
L = lenght of span
E = molulus of elasticity
I = moment of inertia, bh^3/12

W = weight of hydrates on 10 ft of 10 plates + wt plates + wt tubing, all for 1 quadrant
b = 3 in. (width of the support beam.)
E = 10500000 psi (for aluminum alloy, page 71 Flinn)
L = 10 ft. (Length of beam = diameter of the tank)
h = 3 in. (thickness of 3"x3" Al support beam.)

Table I. Vary beam width and thickness for imposed weight.

Deflection in.	Weight, lbf	Length, L, ft.	Width, b, in.	Thick,h, in.
0.492999011683	7,765	5	3	3
2.49580749664	7,765	5	2	2
39.9329199463	7,765	5	1	1

Note: The cross beam supports are located every 6 ft down the length of the tank.
The vertical supports anchor the cross beam supports every 6 ft in the center of tank.
The sides of the tank anchor the cross beam supports on each end.
Therefore, 5 ft of beam supported on both ends supports the plate weight and hydrate weight of 6 ft of each quadrant.

No. Beams	Beam Volume ft^3	Beam Wt lb/beam	Total Beam Weight, lb
18	0.625	105.3	1,895

Note: Beams are each 3" x 3" x 10' and a total of 9 horiz + 9 vertical
Specific gravity aluminum = 2.7

Wt Beam = 2.7*62.4* beam volume

IV.D.2. Latent heat

Note: Heats of hydrate formation is taken from Handa for individual gases.
Heat of formation of the typical gaseous mixture is calculated with mole fraction as weighting factor.
9.486E-4 Btu = 1 J
Handa, Y.P., "Compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of methane, ethane, and propane, and enthalpy of dissociation of isobutane hydrate, as determined by a heat-flow calorimeter",
J. Chemical Thermodynamics, 1986, vol 18, 915-921.

TABLE EN#1. Calculate latent heat hydrate formation

Gas Component	mole fraction	Heat of Formation, kJ/mol gas	Gas mix, kJ/mol gas	Gas mix, Btu/mol gas	Gas mix, Btu/lb-mol gas	Gas mix, Btu/scf gas	Gas mix, Btu/lb-mol H20	Gas mix, Btu/lb H20
methane	0.894	54.2	48.45	45.96	20,868	55.06	3,478	193.22
ethane	0.063	71.8	4.52	4.29	1,948	5.14	325	18.04
propane	0.035	129.2	4.52	4.29	1,947	5.14	325	18.03
isobutane	0.008	133.2	1.07	1.01	459	1.21	76	4.25
	1		58.57	55.56	25,222	66.55	4,204	233.54

Example calc of table:
48.7 kJ/mol gas * (0.9486 Btu/1 KJ) = 46.20 Btu/mol-gas
46.2 Btu/moles-gas * (454 g-mol gas/lb-mol gas) = Btu/lb-mol gas=
20,975 Btu/lb-mol gas
Putting on a basis of Btu/scf gas
20,975 Btu/lb-mol gas / 379 scf/lbmol = 55.3 Btu/scf
Putting on a basis of Btu/lb-mol H20,
20,975 Btu/lb-mol gas/(5.7 l-mol H20/lb-mol gas)= 3680 Btu/lb-mol H20
Putting on a basis of Btu/lb-H20,
3680 Btu/lb-mol H20/18 lb H20/lb-mol H20 = 143 Btu/lb H20
As a comparison from Chem & Physics Handbook, Heat fusion ice = 6.01 kJ/mol water = 143 btu/lb-H20
On a hydrate basis: 6.01kJ/mol water *6 mol water/mol gas = 34.7 kJ/mol gas

lculation of Latent Energy to Form 1 Tank of Hydrates Ca

Assume volume of gas occluded in hydrates is 155 scf gas/ft^3 hydrates

Vol hydrates on plates = [Total adsorpt surf area of plates* thick hydrates on plate - vol fins]/sp. gv.
See Hydrates, D13
Latent Heat To Fill 1 Tank= (Btu/scf gas)*(ft^3 hydrates on plates)*155 scf/cuft

Latent Heat to Fill 1 Tank = **48,372,778** Btu
Gas Occluded in 1 Tank = **738,716** scf (includes compressed gas in tank)

Calculation of Sensible Heat to Cool Gas from Ambient to 37F.

Assume: Gas enters at 60F.
Assume: Cool gas to 37F.

Energy to cool= (cp of gas)*(60-37 F)*(Gas occluded in 1 tank + compressed gas)
Note: Heat capacities from Himmelblau, D.M., Basic Principles and Calculations in Chemical Engineering, 3rd ed., 1974, Prentice-Hall.
cp = a+bt+ct^2+dt^3 J/mol-C
Note: Calculate the mean heat capacity at the mean temperature and use mole fraction as weighting factor.

Gas mol fract.		a	b	c	d	Cp @ 45F J/mol-C	Cp@ 45F Btu/lb-F	Cp mix @ 45F Btu/lb-F	Avg Mol Wt., lb/lbmol
0.894	methane	34.31	0.05469	0.000003661	-0.000000011	34.71	0.52	0.46	30.67
0.063	ethane	49.37	0.1392	-0.00005816	0.0000000073	50.37	0.75	0.05	3.11
0.035	propane	68.032	0.2259	-0.0001311	0.0000000317	69.66	1.04	0.04	2.38
0.008	i-butane	89.46	0.3013	-0.0001891	0.0000000499	91.63	1.37	0.01	0.72
1								**0.56**	**36.88**

Enthalpy of cooling by removal of sensible heat of occluded gas =
Cp*(53-37F)*(Molec Wt)*scf/379 Note: leaving decomposed gas cools entering gas to 53F, just above hydrate condition.)

Enthalpy = **642,740** Btu (to fill 1 tank with the gas to be occluded.
Also includes sensible heat for
compressed gas in tank not occluded.)

Calculation of Sensible Heat to Remove in Cooling Water Charge Initially

Water Charged to Tank = 282,154 lbf (See Tank page, c25)

Cp = 1 Btu/lb/F (Water)

Q = mCp(60F-37F)

Sensible Heat to Cool Initial Water Charge = 6,489,536 Btu

Calculation of Sensible Heat to Remove in Makeup Water

Assume: 2 mass% of initial water is entrained with the gas upon withdrawal.

Makeup Water = 5,643 lbm

Heat exchange between produced cold gas and entering warm water cools H20 to 53F

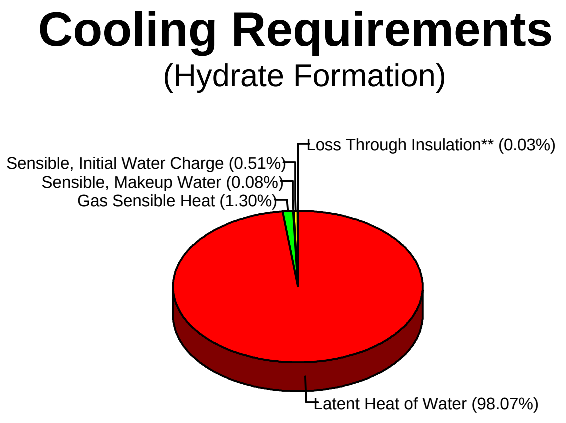
Just above hydrate forming temperature.

Sensible Heat to Cool Makeup Water = 39,502 Btu

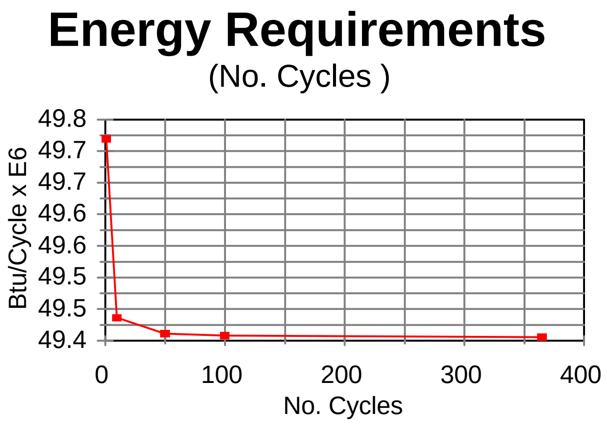
Summary of Energy Requirements

Item	Refrig. Require., Btu/cycle/ 1 tank	
Latent Heat of Water	48,372,778	
Gas Sensible Heat	642,740	
Sensible, Makeup Water	39,502	
Sensible, Initial Water Charge	253,938	90% of initial charge water cooled down from 38 to 37F
Loss Through Insulation**	17,237	
Total Energy =	**49,326,195**	**Btu/cycle/tank**

Assume** : The heat gain through the insulation must be removed by refrigeration.
Each cycle will be 24 hours of formation/decomposition. Therefore,
this heat gain applied to a 24 hour span of
1 cycle/tank.



Item	Refrig. Require., Btu/cycle				
No. of Cycles ---------->	1	10	50	100	365
Latent Heat of Water	48,372,778				
Gas Sensible Heat	738,716				
Sensible, Makeup Water	39,502				
Sensible, Initial Water Charge*	253,938	253,938	253,938	253,938	253,938
Loss Through Insulation**	314,575	31,457	6,291	3,146	862
Total =	49,719,509	49,436,391	49,411,225	49,408,080	49,405,796
Total MM =	49.72	49.44	49.41	49.41	49.41



Refrigeration Costs

A. Formation of Hydrates

TABLE I. Costs based on 1 cycle of stated duration and 1 tank.

		Time Duration of one cycle, hours										
Item		1	2	3	4	5	6	7	8	9	10	24
		BTU/min for the given cycle										
Latent Heat, Water	48,372,778	806,213	403,106	268,738	201,553	161,243	134,369	115,173	100,777	89,579	80,621	33,592
Sensible Heat, Gas	738,716	12,312	6,156	4,104	3,078	2,462	2,052	1,759	1,539	1,368	1,231	513
Sensible Makeup Water	39,502	658	329	219	165	132	110	94	82	73	66	27
Sensible, Initial H20 Charge	253,938	4,232	2,116	1,411	1,058	846	705	605	529	470	423	176
Insulation Loss	314,575	5,243	2,621	1,748	1,311	1,049	874	749	655	583	524	218
Total =	49,719,509	828,658	414,329	276,219	207,165	165,732	138,110	118,380	103,582	92,073	82,866	34,527

Cengel and Boles, Thermodynamics, An Engineering Approach, 2nd ed., p. 585:
Cooling capacity of a refrigeration system is often expressed as tons of refrigeration.
It is the capacity that can freeze 2000 lbs of water at 32F in 24 hours.
1 ton refrigeration = 200 Btu/min.
The cooling load of a typical 200-m^2 residence is in the 3-ton (10-kW) range.

		Time Duration of one cycle, hours										
		1	2	3	4	5	6	7	8	9	10	24
Item		**Tons of Refrigeration**										
Latent Heat, Water	48,372,778	4031.06	2015.53	1343.69	1007.77	806.21	671.84	575.87	503.88	447.90	403.11	167.96
Sensible Heat, Gas	738,716	61.56	30.78	20.52	15.39	12.31	10.26	8.79	7.70	6.84	6.16	2.57
Sensible Makeup Water	39,502	3.29	1.65	1.10	0.82	0.66	0.55	0.47	0.41	0.37	0.33	0.14
Sensible, Initial H20 Charge	253,938	21.16	10.58	7.05	5.29	4.23	3.53	3.02	2.65	2.35	2.12	0.88
Insulation Loss	314,575	26.21	13.11	8.74	6.55	5.24	4.37	3.74	3.28	2.91	2.62	1.09
Total ----->	49,719,509	4,143	2,072	1,381	1,036	829	691	592	518	460	414	173

Note: 1. Assume each cycle is 24 hours.
2. Assume that 3 tanks could be filled (7 hrs set by heat transfer rate) and 7 2/3/hrs tank on refrigeration.
3. Assume 1 hour for decomposition of all 3 tanks.
4. Therefore, filling/decomposition of 3 tanks could be done in a 24-hour period.
5. Refrigeration would be selected to fill 1 tank in 7 2/3 hours.

To refrigerate 3 tanks in a cycle would require = 543 tons

B. Refrigeration to replace heat gain through insulation.

Heat gain, 3" insulation = 718 Btu/hr/tank
Heat gain, 3" insulation = 12 Btu/min/tank
Heat gain, 3" insulation = 35.9 Btu/min/3 tanks
Tons Refrig for ins. loss = 0.18 tons refrig.

Note this would need to be a separate small unit that would run during storage only.

C. Capital Cost of Refrigeration Equip. for Formation
Gas Powered

50-ton unit cost = $149,000 (1989 pric)
Reference: Decker, GRI-92/0334
Assuming six-tenths rule for cost of other sizes,

Cost larger unit = (596/50)^.6 * $149,000
Cost larger unit = $622,971
Using the Ch.E. Plant Cost Index to correct for inflation of CPI equipment:
1989 Index = 355.4
1998 Index = 389.5

Current Cap. Cost Refrig = **$682,744** for refrig of 543 tons of refrig for formation.
which will service 3 tanks in one 24-hr cycle

D. Capital Cost for Refrigeration Unit for Insulation Gains
Electrical Power-Driven
Refrig for unit for ins gains of 0.18 tons refrig/24 hours storage period in 3 tanks for 1 cycle .

Cost Refrig for Ins Gain = **$1,000** Cap Cost for refrig equip.

E. Fuel Costs for Refrigeration
1. Refrig Unit for Hydrate Formation

Full-load demand for 50-ton gas-fired refrig unit =1.35 MM Btu/hr (GRI report).
Required for size calcd for storage (See Refrig Costs:d44)
Example: (596 tons/50 tons)*1.35 MM Btu/hr = 16.1 MM Btu/hr
Btu content of natural gas = 1,000 Btu/scf = 1 MM Btu/Mscf
16.1 MM Btu/hr * scf/1000 Btu = 16.1 Mscf/hr
Assume 44% efficiency of the conversion; 16.1/.44= 36.6 Mscf/hr
Use gas price of $2.70/Mscf,
NG cost = $2.70*36.6= $98.82 /hr

ng cost for refrig = $90 per hr for ng to drive refrig.

Plots of Costs of Hydrate Storage Process

$682,744 is the cost of a gas-powered refrig unit that will remove the heat
to fill 3 tanks with hydrates in a 24-hr cycle.

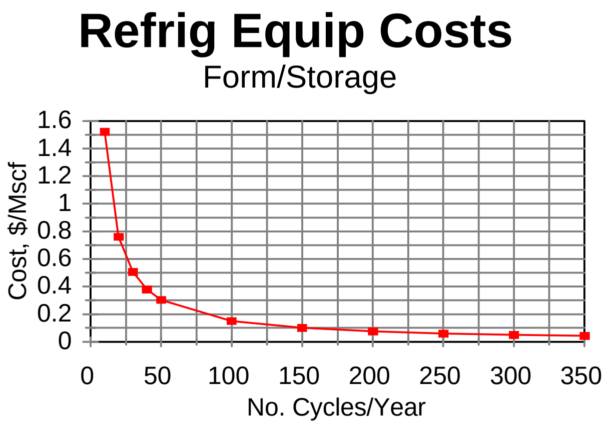
Assume the life of the refrigeration unit is 20 years.
$1,000 is the cost of a small refrig unit to replace heat gain through the
insulation during the storage phase of each cycle.
Assume life of the small unit is 5 years.

is the cost of the natural gas to drive the refrigeration unit each cycle.
Assumes an efficiency of 44% of the conversion.

738,716 is the scf of gas to be stored in each tank in hydrates.
2,216,148 is the scf of gas to be stored per cycle (i.e. 3 tanks)
12,614 is the scf of gas stored in each tank, compressed in void space.
37,841 is the scf of gas stored in each tank, compressed in 3 tanks
2,253,990 is the total scf of gas stored per cycle in the 3 tanks

Table I. Refrig equp cost per cycle to form 3 tanks of hydrates

No. cycles per year	Cost/cycle Refrig Equip	Cost/cycle Small unit	scf/cycle	Refrig. Cost/ Mscf
1	$34,137	$200	2,253,990	15.23
2	$17,069	$100	2,253,990	7.62
3	$11,379	$67	2,253,990	5.08
4	$8,534	$50	2,253,990	3.81
5	$6,827	$40	2,253,990	3.05
10	$3,414	$20	2,253,990	1.52
20	$1,707	$10	2,253,990	0.76
30	$1,138	$7	2,253,990	0.51
40	$853	$5	2,253,990	0.38
50	$683	$4	2,253,990	0.30
100	$341	$2	2,253,990	0.15
150	$228	$1	2,253,990	0.10
200	$171	$1	2,253,990	0.08
250	$137	$1	2,253,990	0.06
300	$114	$1	2,253,990	0.05
350	$98	$1	2,253,990	0.04



Fuel Costs for Refrigeration Units

Gas-Powered Unit

Full-load gas demand for a 50-ton gas-powered refrigeration unit would be about
1.35 MM Btu/hr = 22,500 Btu/min. Ref.: Report on gas-powered refrig units.

The above statement would indicate a 44% efficiency of energy conversion.

Assume: 7 2/3 hrs/tank each cycle. Refrigeration required = 596 tons to process
3 tanks in series for a 24-hour cycle.

Refrig. Required = 596 tons * 200 Btu/min = 108,510 Btu/min

Assume: Btu value of methane = 1000 Btu/scf
Then, Btu value of 1000 scf = 1,000,000 Btu/Mscf where the natural gas used
would be the methane-rich portion that grows as hydrates form.

scf natural gas required = 0.108509868009 Mscf/min
scf natural gas required = 6.51059208055 Mscf/hr

Assume: cost of natural gas = $2.75 per Mscf

Natural Gas Fuel Cost= $17.90 per hr

Length of one cycle = 24 hours (3 tanks in series, each filled in 7 2/3 hours)
Fuel Costs per tank = $137.32
Fuel Cost/Mscf stored = $0.19

Electrical-Powered Small Units

Note: One small refrigeration unit would be needed for each tank to remove
heat gained through the insulation.

718 Btu/hr/tank heat gained thru ins. (see Costs:c48)
16,521 Btu/tank/cycle = B103*7.67 hr/tank *3

scf stored/tank/cycle = 738,716 scf per Hydrates:o31

22.36 Btu/Mscf the energy loss by each tank per gas stored in it over a 24-hr cycle.

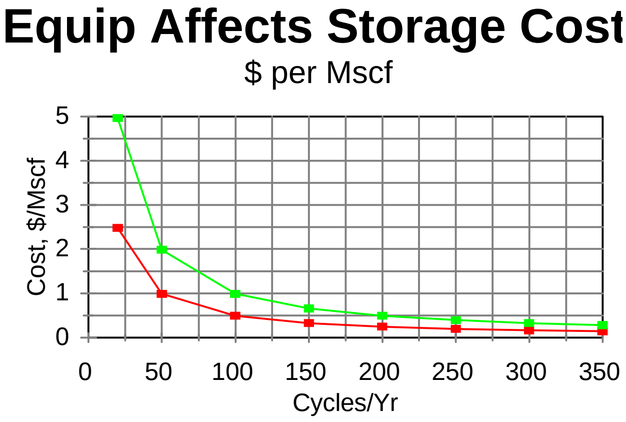
Assume: Cost of electricity = $0.08/ kW-hr
9.486 Btu = 2.778 E-3 kW-hr

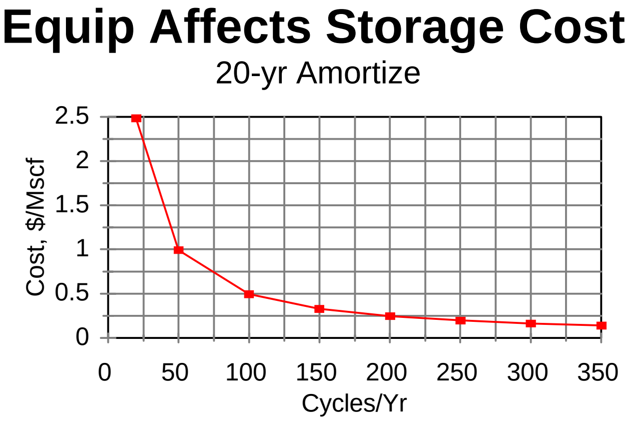
Assume: 40% efficiency.
0.0013099 dollars/Mscf of gas stored in a single tank over a 24 hr cycle
$0.97 per tank per 24 hour cycle to remove heat gained thru insulation

Equipment Costs as a Function of Life and Cycles/Yr

Gas Stored/Cycle = 2,216,148 scf for 3 tanks
Equipment Cost = $2,202,189 for 3 tanks and supporting equipment
Assume either a 10-year life of the equipment or a 20-year life.

No. Cycles Per Year	Equip Cost, 10-Yr Life	Equip Cost, 20-Yr Life	Cost, $/MSCF 10-Yr Life	Cost, $/MSCF 20-Yr Life
1	$220,219	$110,109	99.37	49.69
5	$44,044	$22,022	19.87	9.94
10	$22,022	$11,011	9.94	4.97
20	$11,011	$5,505	4.97	2.48
50	$4,404	$2,202	1.99	0.99
100	$2,202	$1,101	0.99	0.50
150	$1,468	$734	0.66	0.33
200	$1,101	$551	0.50	0.25
250	$881	$440	0.40	0.20
300	$734	$367	0.33	0.17
350	$629	$315	0.28	0.14

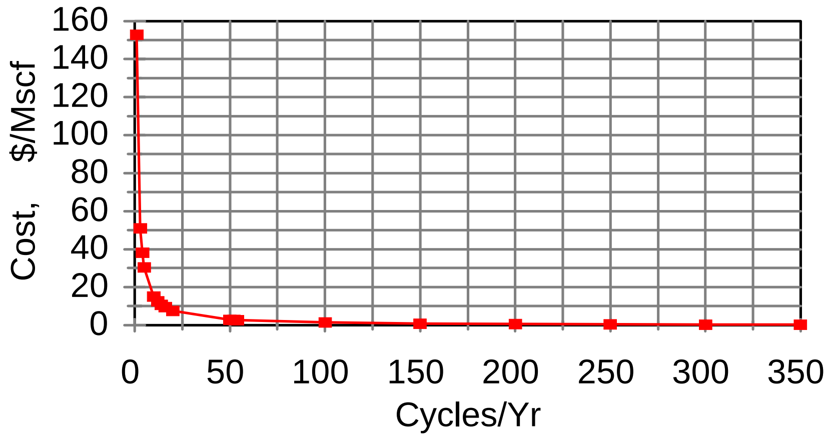




Development Costs as a Function of Cycles

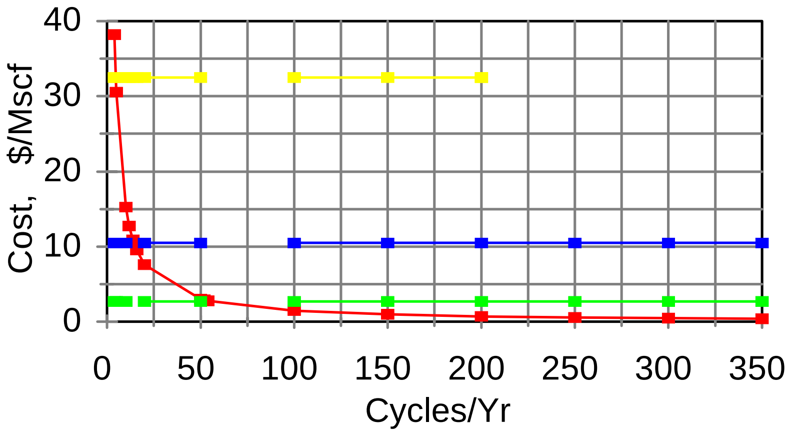
Assume: Development costs is the fixed capital investment.
Life of plant would be 20 years and FCI amortized over 20 years.

No. Cycles per Year	FCI Amortiz 20 Years	Cost, $/Mscf 20-Yr Life	Development $ Depleted Res.	Development $ Salt Cavern	Development $ LNG
1	$344,643	$152.90	2.72	10.5	32.5
3	$114,881	$50.97	2.72	10.5	32.5
4	$86,161	$38.23	2.72	10.5	32.5
5	$68,929	$30.58	2.72	10.5	32.5
10	$34,464	$15.29	2.72	10.5	32.5
12	$28,720	$12.74			32.5
14	$24,617	$10.92			32.5
16	$21,540	$9.56			32.5
20	$17,232	$7.65	2.72	10.5	32.5
50	$6,893	$3.06	2.72	10.5	32.5
52	$6,628	$2.94			
54	$6,382	$2.83			
100	$3,446	$1.53	2.72	10.5	32.5
150	$2,298	$1.02	2.72	10.5	32.5
200	$1,723	$0.76	2.72	10.5	32.5
250	$1,379	$0.61	2.72	10.5	
300	$1,149	$0.51	2.72	10.5	
350	$985	$0.44	2.72	10.5	



Development Costs

Fixed Capital Investment



Development Costs

Hydrate Storage Process

Product Costs

What would be the user cost for storing the natural gas in hydrates?

The product cost (user cost) will be comprised of the following:

TABLE I. Product Costs

		Cost/Cycle		
Raw Matls	Calculate	$181	per cycle	
Operating Labor	Calculate	$257,400	per year	
Utilities	Calculate	$1,888	cycle	
Supervisory Labor	15% Operating Labor	$38,610	per year	
Maintenance and Repair	6% Fixed Capital Investment	$20,679	per year	
Operating Supplies	15% Maintenance and Repairs	$3,102	per year	
Laboratory Charges	15% Operating Labor	$38,610	per year	
Depreciation	Calculate	$110,109	per year	
Property Taxes	4% Fixed Capital Investment	$27,571	per year	
Insurance	1% Fixed Capital Investment	$3,446	per year	
Plant Overhead	70% Operating Labor+Supervision+Maintenance	$221,682	per year	
Administrative	25% Operating Labor	$64,350	per year	
Contingency	1% Total Product Cost	$7,876	per year	
	Total =	$793,436	per yr	(Divide by no. cycles and add+Raw matls +Utili*21 hrs*no. cycles

Notes for calculation of Table I:

Raw Matls: Makeup water + initial water/20 yrs + surfactant

			Cost
Initial water =	33,822	gals/1 tank	$778
Initial water =	101,467	gals/3 tank	$2,334
Makeup W=	676	gals/1 tank	$16
Makeup W =	2,029	gals/3 tank	$47
Initial surf =	85	lbs/1 tank @300 ppm	$85
Initial surf =	254	lbs/3 tank @300 ppm	$254
Makeup Surf=	1.69	lb/1 tank @ 300 ppm	$2
Makeup Surf=	5.08	lb/3 tank @ 300 ppm	$5

Total Raw Matl Cost per Cycle (3 tanks) = $181 Assumes initial spread over 20 year life of plant

Unit Cost H20, deionized =	$0.02	per gal deionize
Unit Cost SDS Surfactant =	$1.00	per lb
Unit Cost H20, not deionized =	$0.10	per 1000 gal (Timmerhaus, p. 200)

Operating Labor:

Reference: Turton, et al., Analysis, Synthesis, and Design of Chemical Processes, Printice-Hall, 1998, p. 84.
Labor requirements broken down into how many operators typically needed to run specific items of equipment.

Item	Operators/ shift/ equip	No. Equip Items, Hydrate Process/cycle	Operators/ shift
Refrig Unit	0.5	1	0.5
Reactors	0.5	1	0.5
Ht Exchangers	0.1	2	0.2
		Total =	1.2

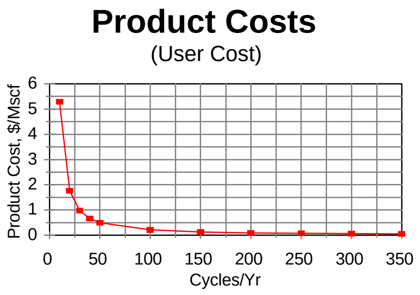
Note: A single operator works 49 wks/yr; 5 8-hr shifts/wk = 245 shifts/op/yr
Plant operates 24-hrs/day = 365 days/yr * 3 shifts/day = 1095 operator shifts/yr
4.5 operators are hired for each operator needed in plant at any time (1095/245)
Typical chem. plant operator makes $21/hr = 46,800/yr in 1996 = $51,480 currently.

Operating Labor = 5.4 That is, 4.5*no. operators
5 Operators

Labor Costs, current = **$257,400** for entire year

Table II. Product costs per Mscf as a function of no. cycles/yr

No. cycles	Prod Costs/ Year	Gas stored Mscf/yr	Prod cost/Mscf
1	$833,261	2,254	$369.68
2	$436,543	4,508	$96.84
3	$304,304	6,762	$45.00
4	$238,184	9,016	$26.42
5	$198,513	11,270	$17.61
10	$119,169	22,540	$5.29
20	$79,497	45,080	$1.76
30	$66,273	67,620	$0.98
40	$59,661	90,160	$0.66
50	$55,694	112,699	$0.49
100	$47,760	225,399	$0.21
150	$45,115	338,098	$0.13
200	$43,793	450,798	$0.10
250	$42,999	563,497	$0.08
300	$42,470	676,197	$0.06
350	$42,092	788,896	$0.05



Purchased Equipment Cost

Table III. Equipment list. (Bounds, Montgomery, Pitman, and Zhong)

Equipment Description	Quantity (1)	Size	Matl Construction	Unit Cost $	Cost 1 Tank, $	Total Cost 3 Tanks, $
Hydrate Formation, Storage, Decomposition Tank	1	10' D x 60' L	Carbon Steel, Lined	$300,000	$300,000	$900,000
Natural Gas Fired Refrig System	1	596 tons (2)	N/A	$682,744	$682,744	$682,744
Adsorption Plates	20	9,086 ft^2	Aluminum (4)	$1,357	$27,146	$81,439
Heat-Transfer Tubing	500	59' L x 3/4" o.d., 14 gauge	Aluminum (3)	$127	$63,720	$191,160
Surfactant Soln Storage Tank With Agitator	1	2734 gal Serves 3 Hyd Tanks	Carbon steel (6)	$9,702	$9,702	$9,702
Water Deionization Unit (7)	1	2,734 gal/60 min	n/a	$62	$62	$187
Insulation for Tank	3"	72"x50'x1" rolls	Cryogenic fiberglass	$4,970	$4,970	$14,910
Support System, Hydrate Tank	1	Aluminum	Construction of Support	$25,000	$25,000	$75,000
Feed Soln (makeup) Pump	1 (10)	205 gpm, P=50	Cast-Steel, Centrifugal	$7,546	$7,546	$7,546
Tempered Water Circulation Pump	1 (11)	2920 gpm, P=12	316 ss, Centrifugal	$12,600	$12,600	$37,800
Surfactant Soln Transfer Pump	1	273 gpm, P=20	Ductile Iron Casing, Cent.	$2,156	$2,156	$2,156
Insulation Vacuum Pump	3	0.75 hp	Cast Steel	$2,500	$2,500	$7,500
Brine Collection Tank (8)	1	1,014	Gallons, 304 ss	$8,948	$8,948	$8,948
Constant Pressure Regulator	1/tank	5"D	SS Flow Control	$8,624	$8,624	$25,872
Check Valves	2/tank (13)	8" D	Carbon Steel , Flanged	$485	$970	$2,910
Relief Valves	2/tank	5"D	SS Relief	$8,624	$17,248	$51,744
Heat Exchanger, Makeup H20	1/3 tanks	1000 ft^2	Carbon Steel	$30,000	$30,000	$30,000
Heat Exchanger, Feed Gas	1/three tanks	1000 ft^2	Carbon Steel	$30,000	$30,000	$30,000
Demister, Defoamer	1/tank	Vane-type (12)	6" Thick, Coalescing Type	$500	$500	$1,500
Foam, Mist Collection Vessel	1/three tanks (9)	8,117	Gallons, Carbon Steel	$19,404	$19,404	$19,404
Electrical-driven Refrigeration	1			$1,000	$1,000	$3,000
Hydrate Tank Supports	1	3"x3"x10'	Aluminum (5)	$3,222	$3,222	$9,667
Tank, to cool entering gas	1	2000 gal	carbon steel (14)	$9,000	$9,000	$9,000
			TOTAL =	$1,168,573	$1,267,063	$2,202,189

Notes:

1. Process is designed around equipment for a 24-hour cycle, with three tanks, 1 refrigeration unit, etc.
2. See Refrig section of calculations in Appendix.
3. Aluminum tubing cost = $2.16/linear ft.
4. Total wt of plates (Plates:h35 =n33) + fins * $1.70/lb alum.
5. Support cost = total no. supports of 18(Supports:b43)*Wt/bm*$1.70/lb alum
6. From Timmerhaus, 4th ed., See Tank, Appendix.
7. Water deionization for makeup water. Per personal conversation w/Hoppenjans, Ecolochem, Inc., $8,000/350,000 gals at 1000 gpm general surface supply water.
8. Brine collection tank used to collect brine used in hydrate formation phase. Tank holds brine during decomposition phase when cooling tower water flows thru tubing. 25% free space, for tubing in all 3 hydrate tanks; Timmerhaus, p.539.
9. 2% of hydrate tank water and surfactant removed from exiting gas. Size carbon steel vessel to collect 3 cycles of the solution from all 3 hydrate tanks.
10. Size for makeup water volumetric flow rate, p.527 Timmerhaus, all 3 tanks, to be filled in 10 minutes with a 50 psig pressure drop in lines, once per cycle.
11. Brine flow rate limiting. Tubing:d193 gives gpm/tube * Tubing:e197 no. tubes. Timmerhaus, p. 527, 1.8 factor for 316 ss, 12 psi drop through tubing.
12. Petroleum Engineer's Handbook; similar to gas-liquid separators. Use coalescing type, 6" thick vane-type. Effective for entrained liquid as well as foam removal. Centrifugal device on gas inlet.
13. Timmerhaus, p511. Flanged valves.
14. Carbon steel tank to store water for heat exchange, exiting gas and entering gas.

Fixed Capital Investment

Use typical ratios found to be applicable for estimating capital investment items based on delivered-equipment cost for a solid-fluid processing plant. Ref: Timmerhaus, p. 183.

Table 2. Fixed capital investment

Item	Factor	Cost
Direct Costs		
Purchased equipment, delivered	1	$2,202,189
Equipment installed	0.39	$858,854
Instrument., controls installed	0.13	$286,285
Piping installed	0.31	$682,679
Electrical installed	0.1	$220,219
Buildings	0.29	$638,635
Yard Improvements	0.1	$220,219
Total Direct Plant Cost		**$5,109,079**
Indirect Costs		
Engineering and supervision	0.1	$220,219
Construction expenses	0.17	$374,372
Total Direct and Indirect Costs		**$5,703,670**
Contractor's fee	0.18	$396,394
Contingency	0.36	$792,788
Fixed Capital Investments		$6,892,852