INVESTIGATION OF HIGH FREEZING TEMPERATURE, ZERO OZONE, AND ZERO GLOBAL WARMING POTENTIAL CLATHRATE FORMERS FOR DESALINATION

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Mission Statement

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interests of the American public.

U. S. Department of the Interior
Mission Statement

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned lands and natural resources. This includes fostering sound use of our land and water resources, protecting our fish, wildlife, and biological diversity, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U. S. administration.

Disclaimer

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GLOSSARY

Clathrate: A lattice-like structure in which molecules of one substance are enclosed within the crystal structure of another substance. In this application the clathrate, formed with R141b, is an ice-like structure with about seventeen water molecules surrounding a single molecule of R141b or other non-water molecule.

Clathrate Former: A hyrdocarbon or other non-water molecule that will form a clathrate with water crystals at elevated temperatures above the normal freezing point of ice; there are a multitude of clathrate formers that will form clathrate ice at various pressures and temperatures, in both liquid and gaseous form, both as inorganic or organic compounds, with various degrees of toxicity, flammability, and other characteristics. The clathrate former used in the demonstration plant and the experiments described in this report is dichloromonofluoroethane (CCl_2FCH_3) also known as Refrigerant 141b.

R141b: Dichloromonofluoroethane, a hydrochlorofluorocarbon (HCFC) clathrate former used as the primary agent in this research report that will form ice-like crystals in pure water at 8.5^{0}C (47.5^{0}F) and in seawater at approximately 7.5°C (45.5°F).

Latent Heat of Fusion: The heat energy absorbed or released, respectively, when a solid melts, or a liquid is solidified. In pure materials, the heat energy is absorbed or released at a constant temperature that is a property of the material.

Abbreviations/Acronyms

BTU	British Thermal Unit
°C	Degrees Centigrade
cm	Centimeter
m3	Cubic Meter
°F	Degrees Fahrenheit
kg	Kilogram
km	Kilometer
m	Meter
NELHA	Natural Energy Laboratory of Hawaii Authority
cm2	Square Centimeter
km2	Square Kilometer
m2	Square Meter
TDS	Total Dissolved Solids
ppm	Parts per Million
psig	Pounds per Square Inch Gauge
psia	Pounds per Square Inch Absolute
kPa	Kilopascals
lb/hr	Pounds per Hour
ODP	Ozone Depletion Potential
GWP	Global Warming Potential
Hp	Horsepower

1. EXECUTIVE SUMMARY

The work accomplished by Thermal Energy Storage, Inc (TESI) under Cooperative Agreement No. 99-FC-81-0110 with the Bureau of Reclamation included re-evaluation of the pilot plant, design and construction of a small-scale test rig, and experiments that demonstrated that the process can produce high quality fresh water. The results of experiments with the small scale test rig yielded water well within EPA potability limits. The survey of higher temperature clathrate formers yeilded several candidates with formation temperatures of 50°F or higher. TESI has concluded that additional development and testing on a pilot-scale should be done with the clathrate former selected from the candidates indentified here, and recommends the construction and testing of a pilot plant in the San Diego area.

The specific tasks included:

- a re-assessment of the performance of the pilot plant built and tested under a previous contract reported in Reference 1
- filtration tests that determined that crystals are filterable with standard metal screen materials shortly after formation, that were repeatable with consistent results
- a computational fluid dynamics analysis of the wash column to determine the design characteristics needed for successful operation
- design and construction of a modified wash column
- construction and modification as needed of a small-scale test rig
- experiments with the small-scale test rig
- a survey on alternative high temperature, zero ozone-depleting clathrage formers and selection of a higher temperature candidate
- reporting of the results

Experiments conducted with the small-scale test rig confirmed that clathrate cyrstals with a specific gravity greater than 1.0 can be transported up-slope at Pacific island sites or at other sites with similar undersea terrain. The horizontal crystallizer at the pilot plant constructed at the Natural Energy Laboratory of Hawaii Authority did not permit confirmation of this aspect of system operation.

The experiments were not without difficulities. Several times early shutdowns were caused by small crystal migration into seawater storage tanks, sequestering some crystal and R141b in those tanks. The migration of small crystals led to plugging of system components such as rotometers and filters, and to the termination of the test runs earlier than desired. These symptoms resulted primarily from the placement of filters in a location that protected the plate/frame heat exchanger from freezing but permitted the crystals to migrate to the seawater storage tanks. Relocation of the filters would have been the next step had experiments continued. Even with the difficulites, though, steady operation of the wash column was accomplished.

During these experiment, intermittent steady operation of the wash column as achieved, and displacement washing in the wash column effectively cleaned brine from the clathrate crystals. This was accomplished despite the relatively small size of the clathrate crystals. Other experimenters have reported great difficulty in washing small crystals. (Reference 2) The average (TDS) of four samples taken in 100 minutes of operation was 164 ppm. Two of the samples, the first and the last, were taken during the startup of the wash column and after an upset of the system. The average TDS of the two samples taken during the middle of the operating period, the most nearly equilibrium operation was significantly lower at 88 ppm.

The results of the work led TESI to conclude that clathrate freeze desalination can be made insensitive to crystal size through an ordinary filtration process; that filtration can substantially increase the crystal concentration in the slurry. In addition, the work demonstrated that clathrate freeze desalination is capable of producing excellent quality water. Finally, it has been determined that a higher formation temperature (-50°F) is possible with a commerically available material identified in the survey of alternative clathrate formers that have zero ozone-depletion potential. Higher formation temperatures are possible, aproaching 60°F, but selection of the calthrate former requires additional information about the characteristics of the crystals.

The experiments provided substantial valuable information for the design of a pilot-scale plant. A decanter, even with a low flow velocity, is inadequate for containing and concentrating small crystals. The specific gravity of the crystals is so close to that of water that the smallest crystals are carried out of a decanter, so filtration is essential to prevent the migration of crystals out of the decanter in the primary brine. It is essential to concentrate the slurry for two reasons. One is that the increased contact of crystals will tend to promote crystal growth by agglomeration. The second is that the greater concentration of crystals will reduce the water load on wash column. Test results indicate that the slurry concentration can be two to three times the prior design level and be pumpable. It is necessary to provide a design that minimizes the loss of clathrate former during the startup transient, and this may be as simple as relocating the filters in the flow stream. Finally, the higher temperature clathrate former requires a closed system design for the elements that contain it, and that the design must be capable of withstanding a pressure of approximately 100 psig.

TESI rcommends early completion of high temperature clathrate former characterization and has initiated this work. The company further recommends funding for the design and construction of a pilot-scale plant in San Diego at Scripps Institution of Oceanography, or at the City's Miramar water treatment and reclamation plant. TESI further recommends the preparation of a detailed capital and operating cost estimate for a demonstration-scale plant with higher temperature and pressure clathrate former.

2. BACKGROUND AND INTRODUCTION

In prior work TESI developed a process for the desalination of seawater by the injection of a hydrochlorofluorocarbon (HCFC) that would initiate the formation of clathrate crystals at temperatures well above the normal freezing point of water. The crystals are a cage-like structure with a clathrate former molecule surrounded by many water molecules. The clathrate freeze process is analogous to conventional freeze purification in that the solid crystal excludes the salt, permitting recovery of potable water.

In this instance, using R141b as the clathrate former resulted in a crystal with approximately 17 water molecules attached to an R141b molecule. With sufficiently cold seawater, such as that available at a depth of approximately 910 meters (2000 ft), mechanical refrigeration is not required to produce these crystals, resulting in less energy needed for a given quantity of potable water.

The process initially produces a slurry of seawater and crystals. The crystals must be separated from the seawater, and any surface film of seawater must be washed from the crystals. The crystals are then melted and the clathrate former is recovered for reuse.

In an earlier study TESI developed the criteria given in Reference 1 to define the desirable attributes of a clathrate former suitable for the desalination application. The attributes and criteria for clathrate former selection were modified somewhat during a subsequent experimental program (Reference 2) supported by the Bureau of Reclamation. The attributes and criteria for selection of a suitable clathrate former were sufficiently stringent that it was difficult to find a clathrate former which met all of the criteria. The clathrate former used in the experimental program was generally suitable, but a higher formation temperature would improve the economics of the process.

As part of the work under this agreement, TESI has re-examined the attributes and criteria for selection of a clathrate former for desalination and revised the selection criteria, ranking the attributes in terms of importance to a commerical desalination operation. In addition, the individual criteria have been revised as given in Table 2-1, to reflect lessons learned in prior work and consideration of the characteristics of candidate clathrate formers.

The primary change was the elimination of a non-flammability attribute with criteria specifying a high flash-point temperature and a self-extinguishing characteristic for the clathrate former. After an internal review, this attribute/criteria was deemed excessively restrictive. Many commerical processes make safe use of flammable materials, and several flammable materials are even used in home applications without extensive procedural and physical controls imposed on the user. The types of procedural and physical controls employed in other commercial processes that use flammable fluids are just as applicable to the safe use of a flammable clathrate former, providing assurance that flammable fluids can be used safely. The pressures in the system are relatively low so there is low potential for leakage or system rupture. Consequently, the criterion for non-flammability was eliminated as a go/no-go parameter, but will be considered as a desirable characteritic. The compatability criterion was amplified slightly to clarify it.

Table 2-1 Selection Criteria for Clathrate Former

Attribute	Criteria
Environmentally acceptable	Approved by the EPA for continued production and commercial use, zero-ozone depletion potential, and low global warming potential
Non-toxic	Low acute human and marine life toxicity, non-carcinogenic, and non-mutagenic
Stable	Slow decomposition or deterioration
Low cost	A Class II clathrate former, readily manufactured in commercial quantities, liquid in the operating pressure and temperature range
Suitable transition temperature	5.6 to 29.4°C (42 to 85°F)
Suitable operating pressure	One to seven atmospheres (100 to 710 kPa)
Compatible with standard materials	Chemically inactive and compatible with readily available and inexpensive construction and component materials

In addition to the earlier study, the set of experiments conducted at the NELHA pilot plant provided additional insights into practical aspects of the system and identified a key element of the system (the wash column) requiring further work. The wash column was designed to concentrate the slurry and to wash the surface seawater from the crystals. The design of the wash column was based on an expected crystal size of 300-400 microns. Subsequent to the experiments, the crystal size was estimated from a single experiment as being approximately 100 microns. The design of the wash column is quite sensitive to the permeability of the slurry, which in turn is driven primarily by the size (characteristic dimension) and shape of the crystals.

The smaller crystals resulted in a much lower drain flow from the wash column than was needed, and off-design operating conditions placed greater demands on it than anticipated in the design. The conditions for experiments at the pilot plant were off-design for several reasons discussed in this report so it was not possible to make a reasonable judgment regarding the feasibility of the wash column as the primary means of spearating and washing the crystals.

This work was undertaken as a means of finding a commercially suitable and environmentally acceptable higher-temperature clathrate former, which would improve the economics of the system, and extend its geographic applicability. In addition, it appeared likely that this work would also permit modification of the existing wash column and evaluation of the new clathrate former in the existing pilot plant at close to nominal operating conditions for the wash column.

Subsequent to the experiments under the prior support agreement and before this agreement was initiated, TESI carried out baseline experiments at the pilot plant. These experiments permitted a set of analyses that bounded the performance of the pilot plant, and indicated that the production capability of the plant was lower than thought because of greater environmental heat loads than expected, and possibly some internal bypass flows that reduced the effectiveness of the crystallizer heat exchangers.

After the award of this support agreement, Bureau of Reclamation technical and management personnel suggested that the key uncertainty was the performance of the wash column. It was suggested that an alternative might be to experiment with the clathrate former (R141b) used in the pilot plant for experiments to assure that information needed for a high-confidence design of the wash column was obtained.

The initial plan was to test with a new clathrate former at the pilot plant but this approach would permit testing a modified version of the wash column with R141b in parallel with the evaluation of higher temperature clathrate former candidates. TESI discussed a resumption of testing at the NELHA but uncertainties about the use of R141b there slowed the project.

During the prior study and pilot plant operation, a third-party adverse to NELHA made allegations of environmental insult, specifically a fish kill caused by the release of R141b into a tidepool. Trace quantities of R141b were detected in the dead fish and in flora samples from the area. Although the concentrations were orders of magnitude below the levels required to harm the aquaculture, the Hawaii Department of Health (DOH) intervened and required changes of NELHA. The NELHA reconfigured their outfall piping to eliminate a cooling water discharge to the tidepool, and re-routed it to a diposal pit. The disposal pit released the cooling water to the ocean through myriad passages in the lava below the surface.

The DOH eventually established requirements on the effluent and set the maximum concentation of R141b at discharge at the detection limit for the material. TESI considered this requirement to be unreasonable and NELHA's technical staff was supportive of this position, but the support from NELHA's Board and executive management was at best nominal. Consequently, the decision was made to conduct tests on a smaller scale in San Diego and remove the pilot plant from the NELHA site and cease experiments there until the environment was more conducive to research and experimentation.

Although it was a disappintment to be unable to continue testing at NELHA, there were some benefits obtained in testing on a smaller scale. One of the remaining drums of R141b was shipped to San Diego for experiments here. By using a chiller to lower the temperature of the seawater, its use would permit simulation of a higher temperature clathrate former. The greater temperature difference for heat absorption would be accomplished by reducing the inlet temperature to the crystallizer rather than by increasing the clathrate formation temperature.

The project proceeded on that basis and Innovative Engineering Services was selected as a subcontractor to construct a small-scale test rig and to conduct the experiments. In parallel, Dr. John Ripmeester was engaged to assist with the identification and initial characterization of zero ozone-depletion factor clathrate formers.

3. CONCLUSIONS AND RECOMMENDATIONS

General conclusions drawn from the work under this Agreement are that the clathrate desalination process is capable of producing high quality water and that only detailed engineering work is necessary to complete the design of a desalination plant. New clathrate formers have been identified with higher formation temperatures and zero ozone-depletion potential which has the potential to make the process more economical but this requires further evaluation. Because the new clathrate formers operate at higher pressures which make it possible to substantially reduce primary seawater cooling flowrates, the economics of the process should be re-evaluated based on a more detailed design of a demonstration-scale plant.

The general recommendations to the Bureau of Reclamation are to provide funding for construction of a pilot-scale demonstration plant in the San Diego area. In addition, it is recommended that the detailed design of the demonstration plant and the preparation of a detailed capital and operating cost estimate be prepared in the next phase of the deveopment effort.

3-1 Specific Conclusions

- the Pilot Plant Re-assessment showed that a lower quantity production of crystals gave lower slurry concentration and smaller crystals gave lower drain rates, which resulted in the wash column being overloaded with seawater
- filtration tests determined that crystals are filterable with standard metal screen materials and that filtration was repeatable with consistent results
- analysis showed that displacement washing of crystals is required for an effective desalination process
- a simple decanter, even with a low flow velocity, is inadequate for containing and concentrating small crystals
- the slurry must be concentrated to promote crystal growth and to reduce water load on the wash column
- the slurry concentration can be two to three times the design level and be pumpable
- the small-scale test rig confirmed that clathrate crystals can be transported up-slope at NELHA or any other site with similar undersea terrain

- without filtration, small crystal migration resulted in plugging system components such as rotometers

- clathrate freeze desalination can be made insensitive to crystal size by filtration with standard filter screens

- filtration can be used to increase the crystal concentration in the slurry

- increased slurry concentration will enhance crystal growth

- displacement washing in the wash column effectively cleaned brine from small clathrate crystals:

Sample 1:	139 mg/l (139 ppm)
Sample 2:	85 mg/l (85 ppm)
Sample 3:	90 mg/l (90 ppm)
Sample 4:	340 mg/l (340 ppm)

- higher clathrate formation temperatures (50°F) are possible with the commercially available material identified

- clathrate freeze desalination is capable of producing high quality water at competitive or lower cost

3.2 Specific Recommendations

- early completion of characterization of higher-temperature clathrate formers (work authorized by TESI)

- incorporate cyclic back-pulsed filters as the primary method for concentrating the slurry (or secondary to a decanter) to promote crystal growth and reduce the seawater load on the wash column

- incorporate cyclic back-pulsed filters on the wash column drain to recapture any crystals that escape through the drain

- retain a wash column in the plant design but modify the wash column design to use porous media with a porosity of approximately 20% in the drain section of the wash column

- increase the slurry concentration to 50-75% by weight of the slurry

- incorporate an auger pump to transfer concentrated slurry to the wash column

- examine the potential benefits of using direct contact heat exchange at the surface rather than below the surface of the sea

- determine the design modifications necessary for higher clathrate formation temperatures (>50°F)

- design and construct a pilot-scale plant in San Diego at the
    - Scripps Institution of Oceanography,
    - City of San Diego Miramar Reclamation Plant, or
    - Rented space near TESI office

- prepare a detailed design and detailed capital and operating cost estimate for a demonstration-scale plant with the selected higher-temperature and higher-pressure clathrate former

4. DESIGN PERFORMANCE EVALUATION

Early in the project, the work focused on understanding the capabilities of the pilot plant, the function of the wash column, and the characteristics of the clathrate crystals as they affect the wash column design. A set of benchmark tests of the pilot plant was planned, but TESI was unable to reach agreement with the NELHA about how to accomplish experiments required for this program. This resulted in having to modify the project to make use of the heat transfer data available from earlier clathrate testing to learn why the wash column had performed poorly. In addition, tests were done with R141b, the clathrate former selected for the pilot plant, to estimate crystal size and growth rate under typical conditions. The wash column was also subjected to a computational fluid dynamics analysis to determine the configuration needed for various parameters such as crystal pack permeability, wash column porosity, and slurry inflow and rinse flowrates. Finally, alternatives to the wash column were explored, including some small scale testing with filter media to evaluate conventional filters as the means of separating the crystals for washing.

4.1 Pilot Plant Thermal Performance Re-evaluation

One of the potential causes of the unexpectedly poor performance of the wash column in the experiments at the pilot plant could have been lower production of clathrate crystals. If the production rate were lower, the slurry entering the wash column would be more dilute, making the accumulation of crystals in the column occurs more slowly. In addition, modifications in the system from time to time as experiments were done led to an increased flow of seawater into the wash column, thereby decreasing the solids concentration in the slurry.

A more detailed heat balance model was prepared and used to evaluate the performance of the crystallizer heat exchangers (CHXs). The crystallizers were modeled as 40 short segments; the remainder of the plant was modeled with three components that represented the heat gain in the decanters, wash column, startup tank and piping.

The amount of heat added by pumps was assumed to be minimal. With all of the system pumps operating, their added heat load would be on the order of 10,000 BTU/hr, as compared with a nominal heat load on the crystallizers of 550,000 BTU/hr. At the pilot plant the heat added by pumps is a small fraction of the cooling available if the plant is relatively well insulated. It can be significant if the ambient heat load is large and the margin for clathrate production is small.

Two CHX configurations were modeled and analyzed. One model represented a parallel flow configuration, and the other was for a counterflow configuration. Although additional detail could be added to either model, the models are considered adequate for determining which configuration should be used. The heat transfer models assume a product side flowrate of 60 gpm and a shell side cooling flow of 850 gpm. The cooling water inlet temperature was assumed to be 42.8°F. These assumptions closely match the conditions observed during experiments with the pilot plant. Several cases for each configuration were analyzed, and the results follow.

4.1.1 Thermal Conductance. The thermal conductances for ambient heat load were based on heat transfer tests done at the site after the January 1998 experiments reported in Reference 1. The tube-to-shell conductance was based on an updated calculation specific to the flows observed. After the experiment to determine the tube-to-shell conductance was done it was discovered that the end baffles were partially detached and , therefore, permitting an unknown amount of flow to bypass the tubes. It was not possible to determine exactly when the damage occurred. For this reason, the results to tube-to-shell heat transfer testing done at the pilot plant were somewhat ambiguous. If no bypass was assumed, the tube-to-shell conductance would be less than half of the value calculated for the design of the CHXs.

4.1.2 Parallel Flow Configuration – No R141b Injection (Base Case). In this instance, the shells were assumed to be in parallel flow configuration without external insulation. The performance without addition of R141b, shown in Figure 4-1, indicates that the CHXs reduce the temperature of the product side stream in the second CHX to the cooling water temperature at about the half-way point in the second CHX. From this point, because the ambient heat load causes the cooling water temperature to increase, the product side stream is heated slightly by the cooling water. The temperature differences from the point of temperature inversion are small and the product stream temperature tracks the cooling water temperature. The temperature difference is small and it would be difficult to observe with the plant control system instrumentation.

4.1.3 Parallel Flow – R141b Injection. When R141b is introduced, the formation of clathrate crystals releases the heat of fusion. The product stream temperature is increased as shown in Figure 4-2, because the heat of fusion is released throughout the length of the CHXs. The temperatures were calculated assuming that R141b would be available to react along the entire length of the CHX tubes. This is an idealization that should be a reasonable approximation given that any increase in temperature by formation of clathrate limits the conversion of unreacted R141b in the product side stream, forcing the reaction to be distributed along the length of the crystallizer.

Crystal formation and growth occurring along the entire length of the crystallizer requires maintaining a high enough flowrate in the crystallizer tubes to keep R141b droplets in suspension. R141b droplet size was not measured but visual examination of the seawater

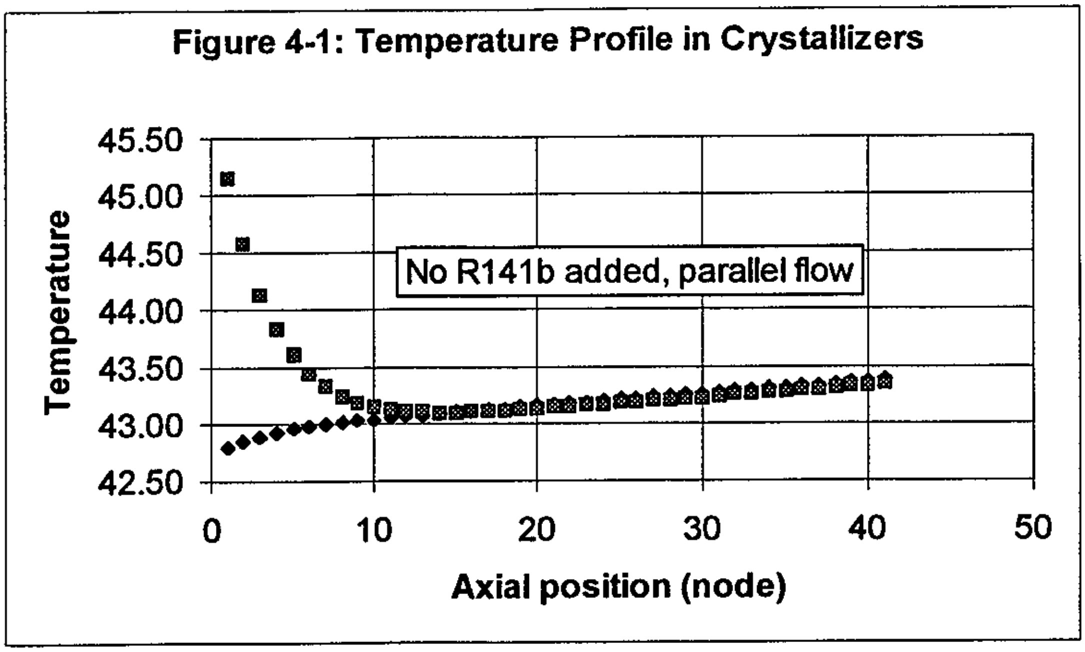

Figure 4-1: Temperature Profile in Crystallizers

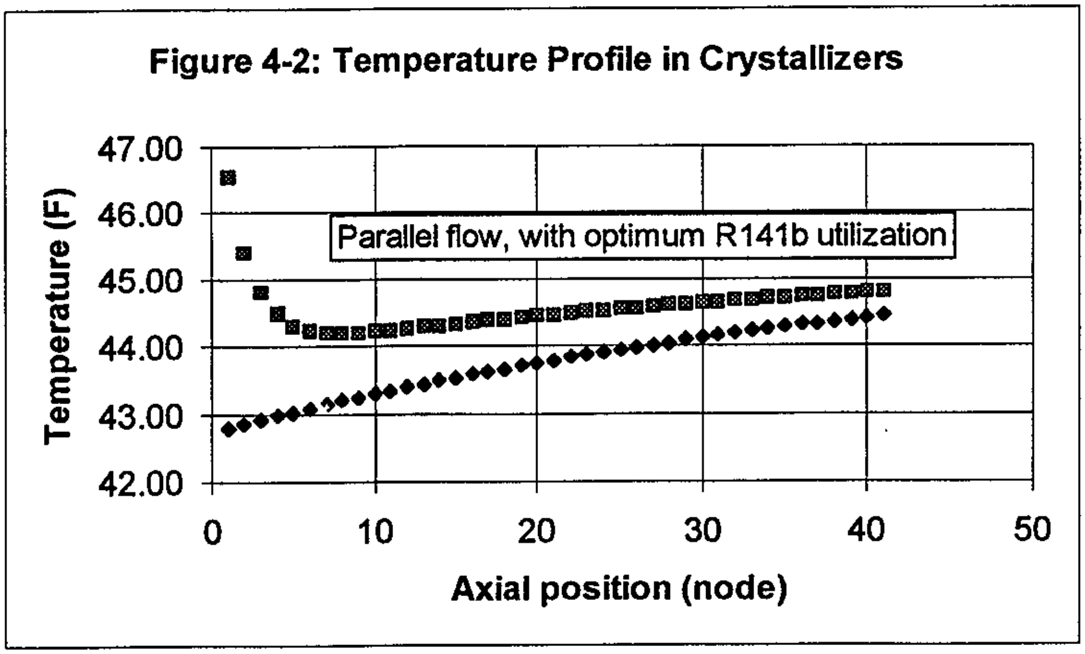

Figure 4-2: Temperature Profile in Crystallizers

with R141b in it indicated that the droplets were smaller than the clathrate crystals.

The suspension velocity in horizontal flow for a 400-micron droplet of R141b in seawater, at the concentrations used in the pilot plant, is approximately 0.95 ft/sec, or some 46 gpm. The nominal flowrate of 60 gpm through the dual pass heat exchangers gave a flow velocity of about 2.4 ft/sec, a substantial margin.

After the crystallizers were modified to single pass, with 60 gpm through the product side of the CHXs the flow velocity was decreased to about 1.23 ft/sec, decreasing the margin to approximately 30%, but maintaining the ability to keep relatively large droplets of R141b in suspension. The suspension velocity for clathrate crystals is approximately 0.42 ft/sec for 400-micron crystals. The margin for 400-micron crystals is greater because of their lower density than pure R141b. The margin for both R141b and for crystals is even greater for smaller diameter droplets and crystals.[1]

4.1.4 Parallel Flow – R141b Injection – Reduced Tube-to-Shell Conductance. The lower tube-to-shell side conductance estimated from heat transfer test results is a possibility but is thought to be unlikely. The apparent lower conductance probably resulted from bypass flow around the damaged end baffles. The lower conductance value was used, though, for a sensitivity study to determine the effect on clathrate production. The temperature profiles for this case are shown in Figure 4-3. As would be expected, the product side temperatures are higher, and the clathrate production rate is some 28% lower than the comparable case with higher conductance.

4.1.5 Counterflow – No R141b Injection. A counterflow configuration of the crystallizers was thought to provide the potential for improved heat transfer and clathrate production. As in the parallel flow configuration one base-case analysis was done with no R141b added. With no R141b injection, and no clathrate formation, the temperature of the product stream is reduced throughout the length of the CHXs as shown in Figure 4-4. The exit temperature is slightly greater than the cooling water inlet temperature.

4.1.6 Counterflow – R141b Injection. In counterflow, with the introduction of R141b the heat of fusion increases the product side temperatures as shown in Figure 4-5, and the heat transfer is correspondingly greater. The counterflow arrangement has greater heat transfer and a 4% higher rate of clathrate production than parallel flow. Because the reconfiguration to counterflow would require minimal effort the change should be worthwhile.

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[1] The term "diameter" as used here to describe crystals size is synonymous with the characteristic dimension, i.e., the dimension for which 80% by size weight of the crystals are smaller.

Figure 4-3: Temperature Profile in Crystallizers

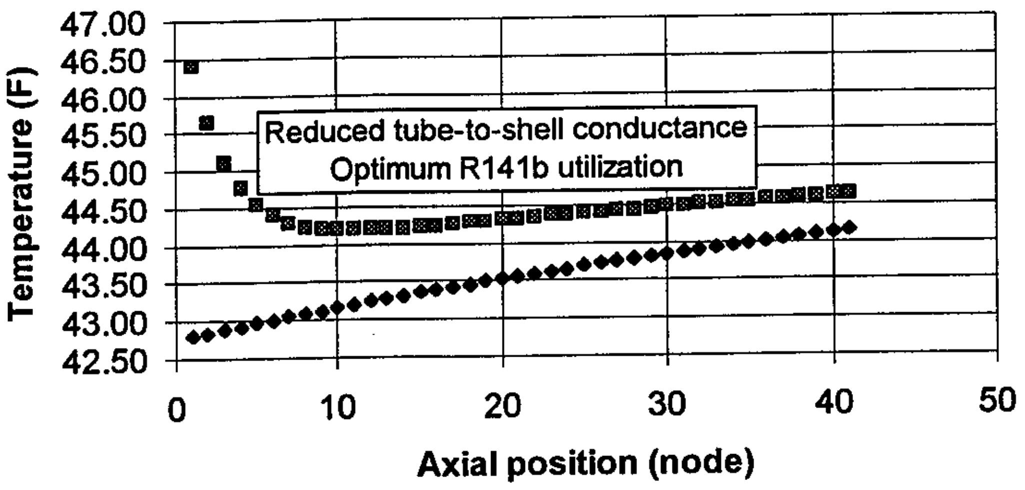
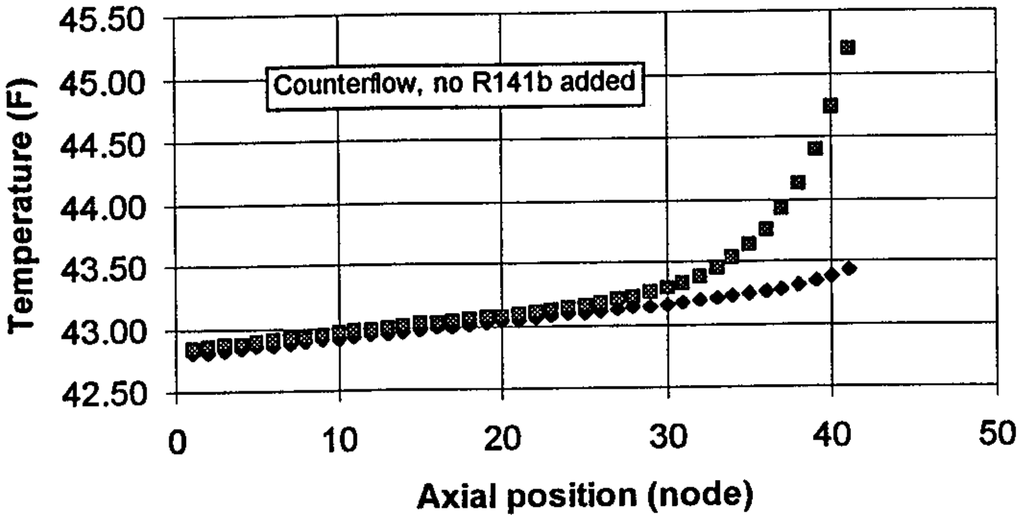


Figure 4-4: Temperature Profile in Crystallizers



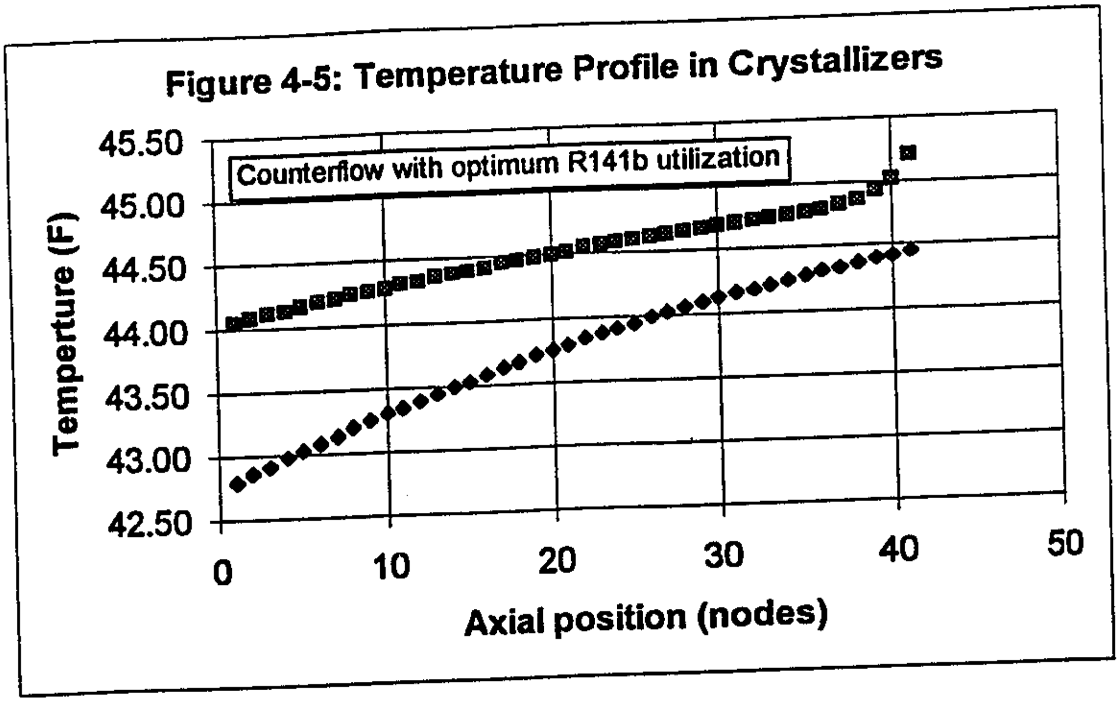


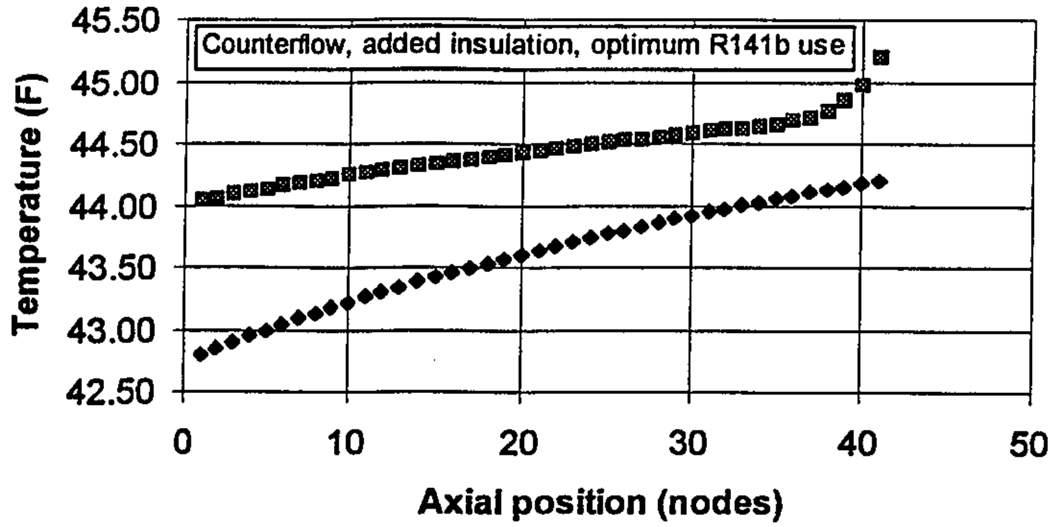
Figure 4-5: Temperature Profile in Crystallizers

4.1.7 Counterflow – R141b Injection – Insulation Added. Insulation of the CHXs and the balance of plant have a greater effect on production than reconfiguring the CHXs. The temperature profiles for counterflow with insulation, given in Figure 4-6, correspond with an increase in production of about 15% over the existing configuration.

4.1.8 Counterflow/Series/Parallel-R141b Injection – Insulation Added. The NELHA reconfigured the cooling drain, eliminating an outfall to a tide pool and making a longer run from the CHXs to a discharge pit that drained into the lava under the Laboratory. One other change may be necessary if the new drain produces a much higher pressure drop and a significant reduction in cooling seawater flow. Making this change would be a significant effort and cost, so it would be done to prevent a loss of capacity if the cooling flow is reduced substantially by the new drain. An increase in flowrate to 1000 gpm by making the change results in an insignificant increase in production capacity.

The production rate for each of the above cases is summarized in Table 4-1. Note that the original design called for a clathrate production rate of approximately 3440 lb/hr. The more detailed plant heat balance indicates that the production capacity of the plant was significantly lower than expected, in the range of 35 to 50% of the design level.

Figure 4-6: Temperature Profile in Crystallizers



the difference is attributable to lower heat transfer stemming from the lower clathrate formation temperature, from ambient heat load, and perhaps from lower heat transfer conductance in CHXs.

Table 4-1: Clathrate Production Rate

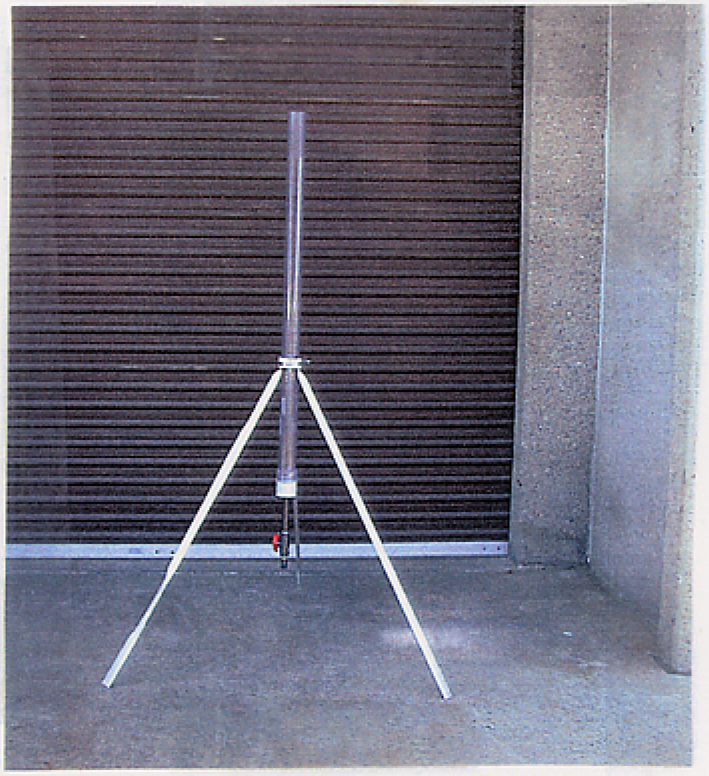
Configuration	**Clathrate Production Capacity (lb/hr)**
Existing configuration – nominal tube-to-shell Conductance	1714
Existing configuration – low tube-to-shell conductance	1232
Modified for counterflow in CHXs	1782
Modified for counterflow – insulation added	1962
Modified for series-parallel counterflow-insulation added	1965

4.2 Clathrate Crystal Size

During the pilot plant experiments, a catch test reported in Reference 1 provided information sufficient for an approximate calculation of the permeability of the clathrate crystal "ice bed" in the wash column. The calculation, using the method of Wilfred Hahn, the wash column designer, yielded a crystal size of 110 microns. The design of the column anticipated a crystal size of 300 microns. A difference of actual, from design assumption that large, would have a substantial effect on the performance of the column.

4.2.1 Permeability Experiments and Crystal Size. The small-scale permeability experiments conducted by TESI indicate that the clathrate crystals grow fairly quickly to approximately 100 microns and then continue to grow rather slowly from that size. The TESI experiments made use of a simple permeability tester (Figure 4-7) that consisted of a clear PVC pipe with a screen and ball valve at the bottom. The pipe was two inches diameter and extended four feet above a screen made of nominally 100-micron polypropylene mesh. The screen had little resistance to flow and served to hold back the crystals and build a particle bed. Absent crystals the test article drained in about six seconds.

Figure 4-7: Permeability Tester



Three batches of crystals made with filtered seawater from Scripps Pier were used for the experiment. One batch was made immediately prior to the experiment with the permeability test article; one 17 hours prior to the experiment; and the other 38 hours prior to the experiment. The slurry was formed at 32°F and stored at 39°F during the crystal growth phase. The slurry was not agitated during storage. In each instance, after the test article was cooled down (to prevent melting the clathrate), the pipe above the filter was filled with one of the batches (stirred) of clathrate crystals. The clathrate slurry was allowed to settle for approximately 30 seconds. Then the ball valve was opened and the pipe was drained into graduate cylinders. The amount drained and the corresponding time was recorded at fixed increments of cumulative amount drained. After the experiment was terminated the height of the particle bed was measured. These data permitted calculation of flowrate and head for the measured thickness of particle bed, and that permitted calculation of permeability and particle size.

The calculation of particle size requires an assumption of the free volume fraction and the shape of the particles. The particle size reported here used the design assumptions of Wil Hahn, a free volume fraction of 0.5, and uniform-size spherical particles. Hahn's paper on the design of wash columns noted that a value of 0.5 was consistent with experience.

The Hahn method for calculating crystal size was checked by calculating the crystal size using methods given in Perry's Handbook. This method is more detailed and requires an assumption about a shape factor for the crystals. Based on microscope observations of crystals a shape factor of 0.83 (rounded sand grains) was assumed. The Perry's method calculations gave larger crystal sizes for each experiment than Hahn's method, but it should be noted that the results are sensitive to the shape factor assumption. For the assumed shape factor, the differences were 30% or less in each instance, as indicated in Table 4-2 below.

Table 4-2: Inferred Crystal Size (microns)

Storage/growth time	**0.1 hours**	**17 hours**	**38 hours**
Hahn Method	87 microns	210 microns	201 Microns
Perry's Handbook method	111 microns	271 microns	244 microns
Difference	28%	29%	21%

These data indicate a relatively slow growth rate for the clathrate crystals. Surprisingly, the batch aged the longest in the TESI experiments did not have the largest crystals, indicating considerable uncertainty in the growth rate. The two aged-batches were stored at 39°F with no stirring, so the subcooling was only slightly greater than that which would be experienced at the pilot plant.

4.2.2 Crystal Measurement. A long-term measurement was provided by Dr. Ripmeester for a batch of crystals that were aged for 4 to 5 days. Because Ripmeester made direct measurements of the crystal size, he provided a histogram of crystal size rather than a single characteristic value as inferred from the flow tests. Perry's indicates that the characteristic dimension to be used for non-uniform particles is that for which 80 to 85% of the particles by weight are larger. It was assumed for comparison with Ripmeester's measurements that the characteristic dimension inferred from flow tests corresponds with that rule. The histogram, shown in Figure 4-8 as a cumulative frequency chart yielded the characteristic particle size of 700 microns (size for which 80% are larger).

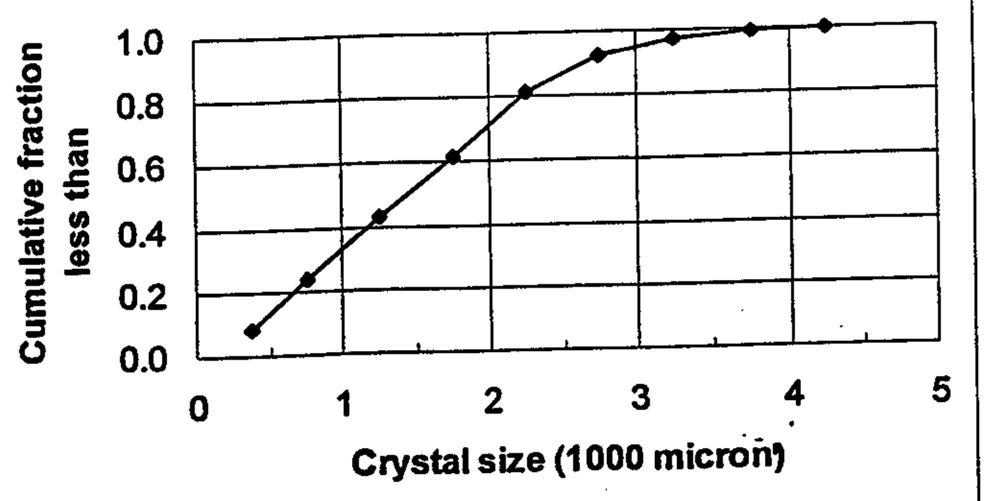


Figure 4-8: Crystal size measurements

Permeability tests done within minutes of clathrate formation, and also many hours later, combined with direct measurements taken after 4-5 days for growth are shown with the single point representation of Ripmeester's data in Figure 4-9. These data indicate that it would take 38 hours (1.6 days) for the particles to grow to a characteristic dimension as large as 300 microns. The data for crystal growth are limited but do permit drawing a general conclusion that the crystals grow fairly quickly to the 100 micron range, and more slowly after that.

There are several characteristics of the clathrate crystals that have a substantial effect on the permeability of the crystal "ice bed" that forms in the wash column. The characteristic dimension of the crystals, an equivalent diameter, and the porosity of the "ice bed" most strongly affect the rate at which brine drains from the column,. In general, the drain flow rate is proportional to the square of the characteristic dimension of the crystals.

When the conditions are such that small crystals are formed, the permeability of the

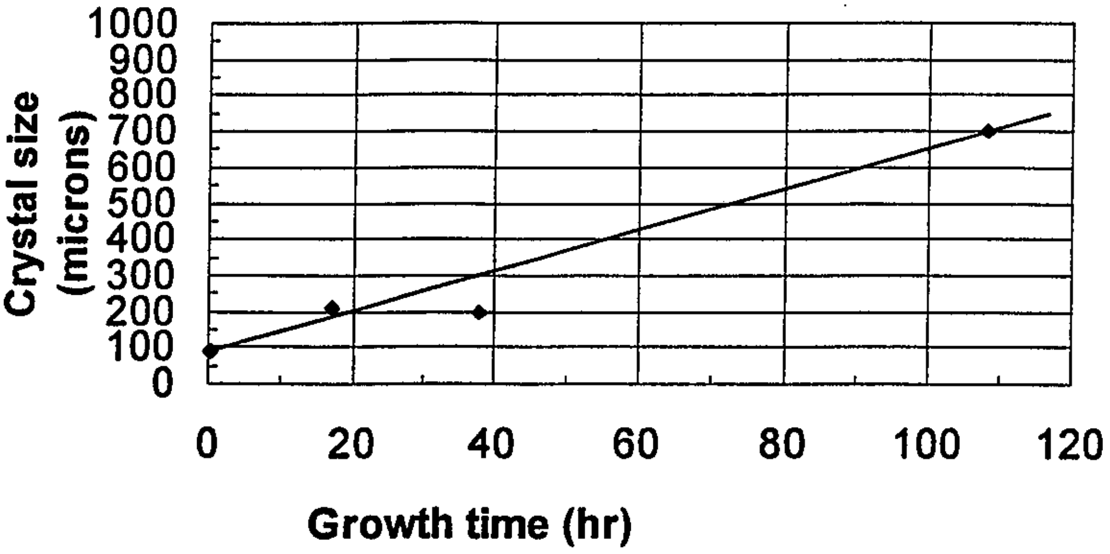


Figure 4-9: Crystal Growth

clathrate crystal is much lower and the drain rate for the wash column is substantially lower. If the drain rate is insufficient the clathrate column will remain filled with brine, and any wash water added will spill over the top. If the crystals are larger, the permeability is greater and the drain rate is then controlled by the drain hole cross-section.

The crystal size appears to depend on the amount of R141b injected, the injection method, and the degree of subcooling available to initiate crystallization. As the temperature approaches the formation temperature it appears that the crystals formed are significantly larger, perhaps because fewer crystals are initiated and more water is available to react with the clathrate former.

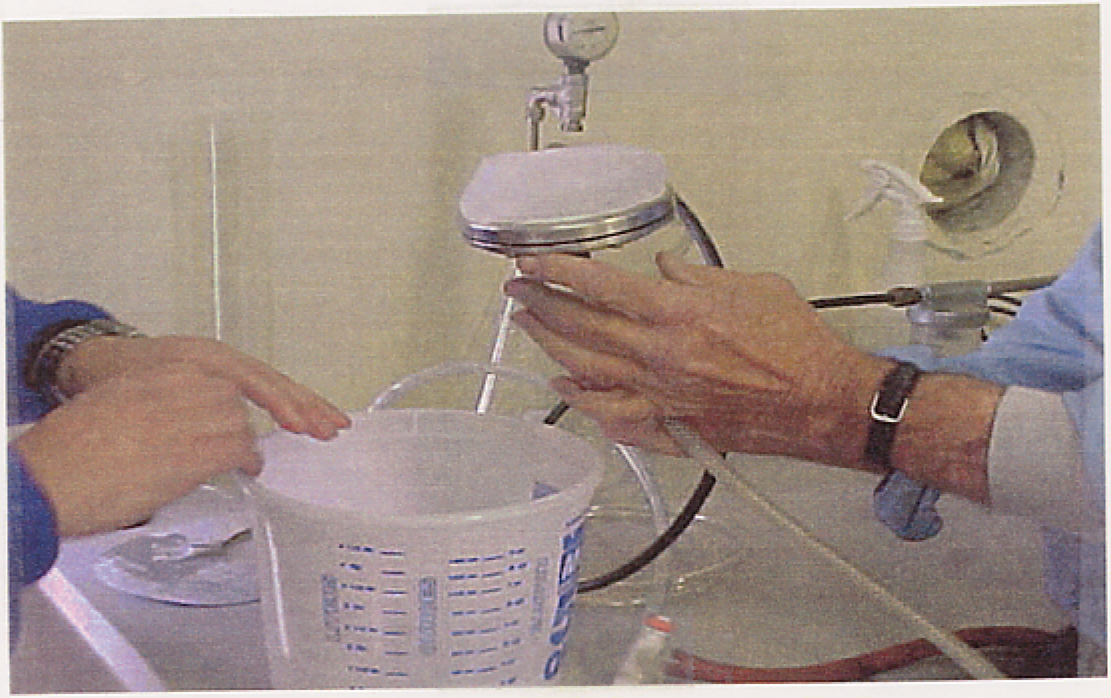
It would be useful to examine this more closely since it implies a trade-off. Although larger size crystals improve wash column performance, the power required for removing the heat of formation is increased. This is because the heat of fusion is absorbed as a sensible temperature increase in the cooling water flow. If the crystal initiation temperature is higher, because formation is limited to the phase transition temperature, the mass flow of cooling water must be increased, with a proportional increase in pumping power.

4.3 Separation/Filtration Evaluation

Experiments to determine the filterability of the clathrate slurry were accomplished at US Filter/Whittier on March 30 and April 1, 1999. The experiments were helpful both to obtain typical design data and to familiarize the US Filter engineering people with the behavior of the clathrate slurry. Multiple experiments were completed using what US Filter engineers refer to as their "bomb test" to produce the data necessary to design their standard filtration equipment.

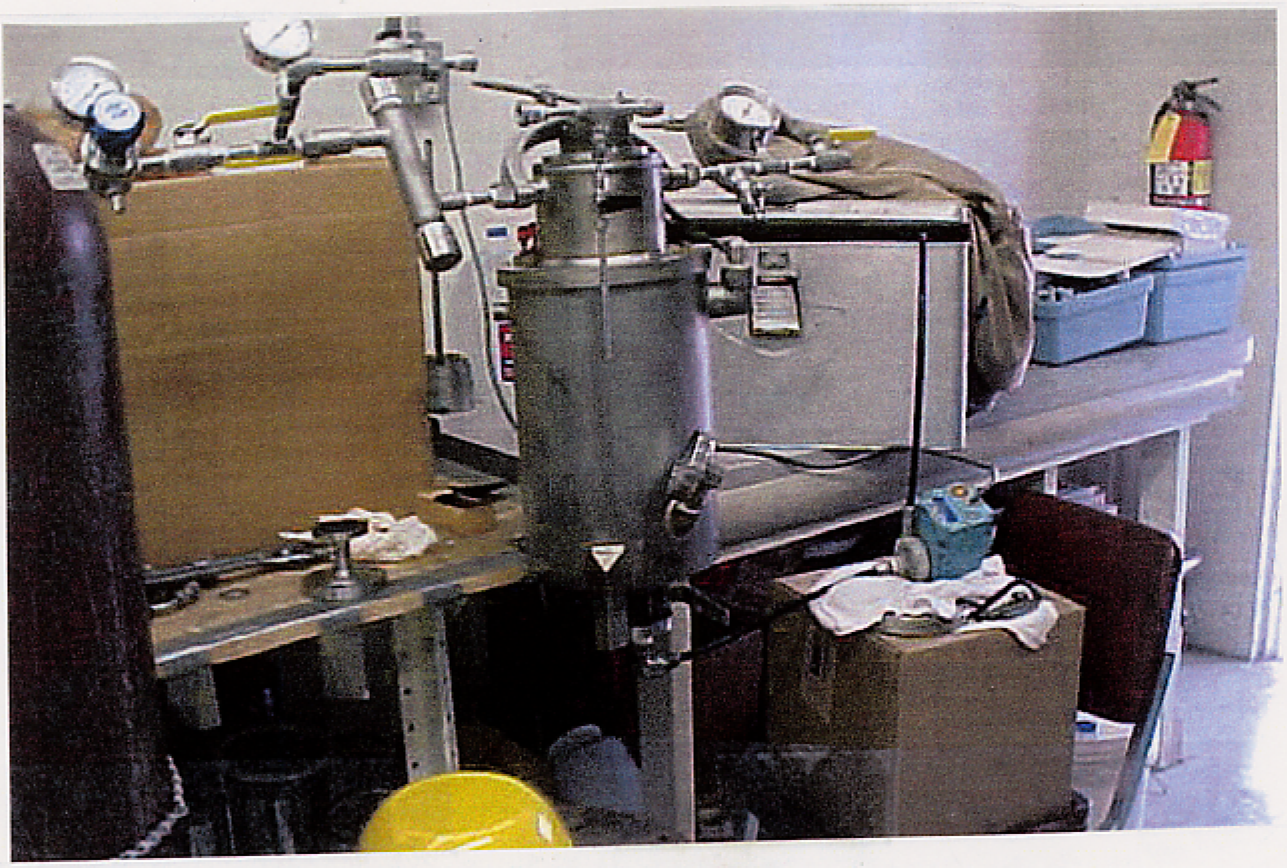
Some of the tests were done with a ½-inch diameter screen, and some with a larger screen about 2 inches in diameter. In addition to the quantitative tests a simple evaluation with a 60 micron screen connected to a vacuum system showed that the slurry would develop a thick "cake" on the filter, as shown in Figure 4-10

Figure 4-10: Preliminary Filtration Evaluation



The "bomb test" apparatus, shown in Figure 4-11, permits testing with nitrogen pressurizing the filter to provide motive force. The "bomb" tests were done with a 60-micron rated stainless steel screen generally at a pressure of 10 psig. A few were done at 2 psig. The most useful results were obtained in test series 3, 6, and 7 and best illustrate the results obtained. In these tests two configurations of the bomb were used.

Figure 4-11: "Bomb Test" Apparatus



Test 3 was done using a filter leaf in a spool piece below and outside of the test bomb. This configuration yielded typical results until heat transfer into the filter housing and a loss of temperature control on the bomb resulted in melting of the filter cake in the filter assembly and very high flowrates. The high flowrates effectively terminated the test run.

Lower flowrates were measured in Test 3 relative to Tests 6 and 7 and probably resulted from settling of the clathrate into roughly 6 inches of ½-inch diameter pipe above the filter leaf prior to pressurizing the bomb to start the test. The depth of filter cake was thus much greater than in Tests 6 and 7 throughout the duration of the test.

Tests 6 and 7 were done with the ½-inch filter leaf at the bottom of a tube extending from the top of the bomb down into the slurry, as shown in Figure 4-12. Test 6 was done with a minimal amount of time for crystals to grow, on the order of five minutes. The slurry for Test 7 was prepared as Test 6 progressed and allowed to sit in an ice chest for approximately 40 minutes to permit crystal growth before the test was initiated. In both

Figure 4-12: Internal Filter Leaf Configuration

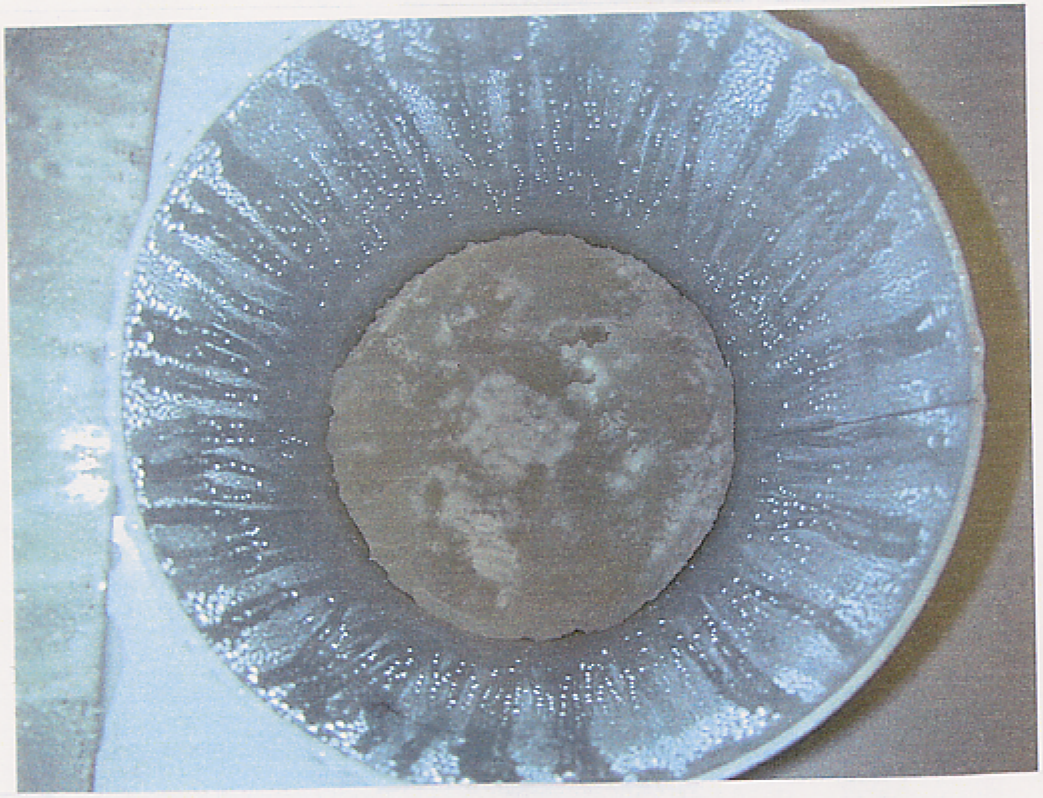
of these tests there was no opportunity for the clathrate to settle into a piping segment above the filter, nor onto the filter prior to starting the test run.

During the initial moments of Test 6, very small clathrate crystals were observed in the graduate cylinder used to collect the filtrate. The crystals had an appearance similar to wisps of a low concentration of smoke. The small crystals settled more slowly than larger crystals. As the test proceeded, the small crystals apparently began to be retained on the filter because they stopped appearing in the graduate cylinder. After the test the "cake" on the filter was examined and found to be relatively hard, like packed snow, and somewhat difficult to dislodge. It was removed before the initiation of Test 7.

During the initial moments of Test 7, no small clathrate crystals were observed in the graduate cylinder. Evidently enough growth occurred so that no small crystals passed through the screen. After the test most of the "cake" on the filter fell off as the bomb was disassembled, and what remained was soft and easily dislodged. The lower initial flowrates probably resulted from a cake forming quickly on the filter screen.

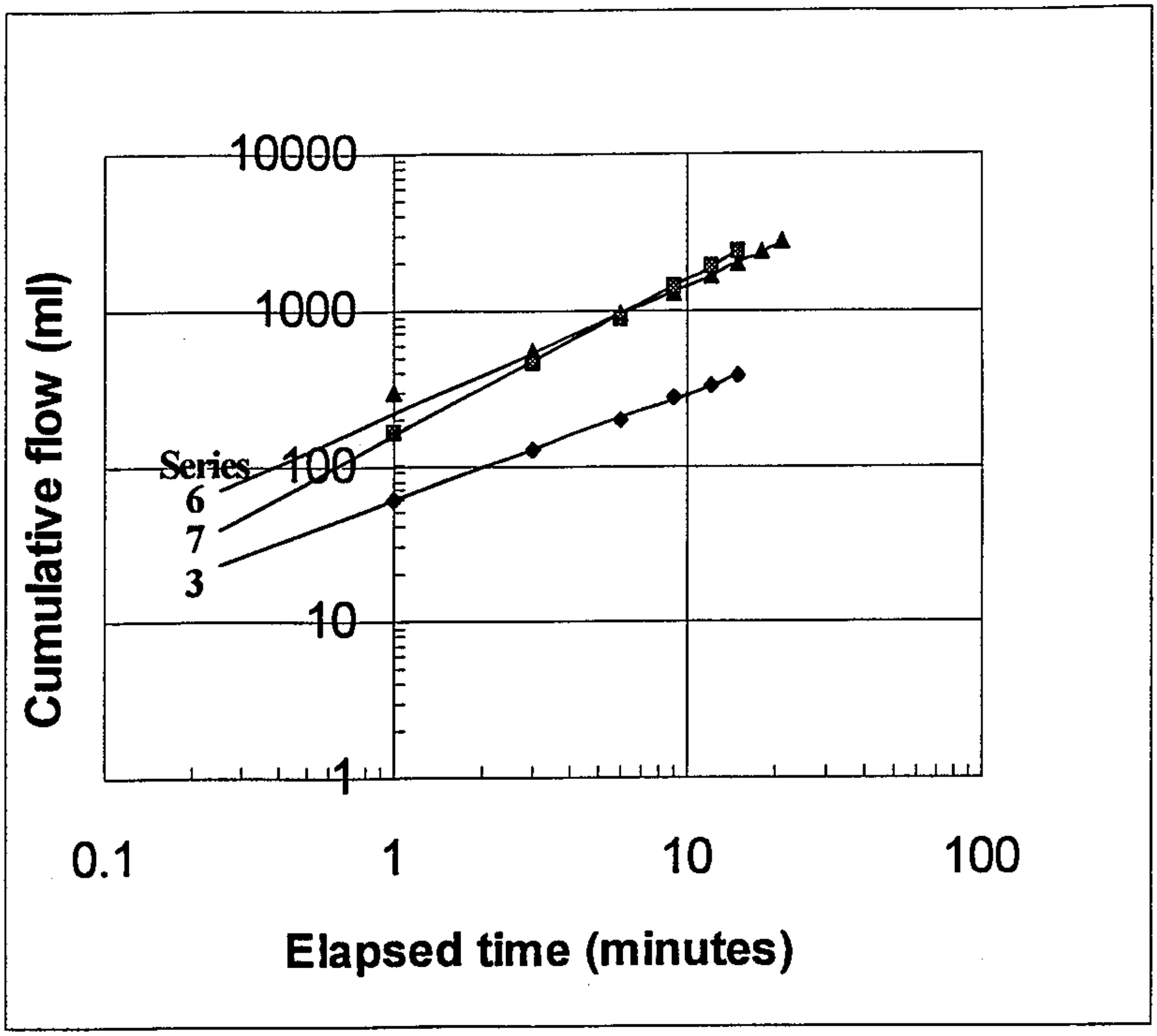
The clathrate remaining in the bomb after Tests 6 and 7 was relatively dry on top, as indicated by the white appearance of the clathrate in the photo taken after Test 7 (Figure 4-13). This relatively dry condition had been observed in the wash column but only after permitting the column to drain for an extended period.

Figure 4-13: Clathrate Crystals Remaining in "Bomb"



The cumulative total unit flow is shown for each of the three tests in Figure 4-14. Of these, Test 3 is representative of a filter at the bottom of a settling tank. Tests 6 and 7 are more representative of the performance of a filter that is oriented vertically, or horizontally with upflow through the filter. The flowrates calculated from the data in Figure 4-14 decrease exponentially throughout the test. At the end of the 12-minute test the flowrates are decreasing slowly and the results would correspond with flowrates of 0.5 to 4.7 gpm from the wash column, after adjusting for the head and flow cross-section differences. We measured approximately 1.9 gpm from the wash column in a catch test done during the project reported in Reference 1, so these results bracket the wash column

Figure 4-14: Cumulative Flow Data – Series 3, 6, and 7



data and provide further confirmation that the permeability of the agglomerated clathrate crystals is lower than the values used in the design of the wash column.

4-4 Wash Column

After the decision to take the parallel approach and investigate clathrate formers at the same time as the wash column was being evaluated, no further effort was expended on the analysis of the pilot plant. In part, the difficulty in establishing acceptable criteria for continuing experiments at the NELHA with R141b influenced this decision. Because of the difficulty in making the wash column work properly, consideration was given to using a simple filtration process, and the premise for using the wash column was re-examined.

4.4.1 Crystal and Brine Separation Requirements. The physical requirement for separation of the crystals and the brine are imposing. The development of the wash column was a response to these requirements so they were considered again. The physical considerations discussed here indicate the nature of challenge the separation poses.

The concentration of salt in the deep seawater at NELHA is about 34,500 ppm. The target for the water from clathrate crystals is 100 ppm or less, a reduction in salinity of 99.7%. The reduction in salinity is accomplished in the TESI process by formation of clathrate crystals but they initially form in the seawater, making a slurry of crystals and slightly more concentrated brine. As was discussed previously the crystals can be filtered from a brine slurry to exclude much of the seawater. It is not easy, though, because the large salinity reduction required means that very little seawater can be left remaining in the slurry.

The amount of brine allowed in the slurry after filtration can be estimated from the shape and size of the crystals. Although the shape of the crystals is not known exactly when they are small, from observation of larger crystals it seems likely that they are roughly spheroidal. If we make the assumption that they are spheres and that they pack efficiently, in either a face-centered or hexagonally-centered close packed configuration, the volume fraction of seawater filling the interstitial space will be about 26 percent.

If we assume a volume of 1 cubic foot of slurry that has been packed efficiently with crystals, the volume of clathrate would be 0.74 cubic feet, and the volume of brine would be 0.26 cubic feet. The clathrate has a density of 65.7 lb/cu ft so this gives a weight of clathrate of 48.6 pounds. The seawater has a density of 64.2 lb/ct ft assuming no increase in salinity during crystal formation, giving a weight of brine of 16.7 lb. Each pound of clathrate yields 0.726 pounds of water so we would have 35.3 pounds of water. With these quantities of water and brine, the salinity of the product resulting from interstitial brine with no drainage would be about 11,000 ppm.

As the amount of brine remaining in the interstitial space is reduced, the salinity of the end product is reduced. The approximate relationship is shown in Figure 4-15, assuming that fresh water is used in a rinse process such as is employed in a wash column. If a simple draining/filtration process is used, to get to the product salinity target the amount of brine remaining in the interstitial space among the crystals must be reduced to less than 1 percent of the original amount.

The difficulty of simply draining the brine from the crystals is illustrated by the effect of crystal size on the total surface area of crystals in the clathrate ice bed and the surface tension of the water. Small crystals result in a large surface area as shown in Figure 4-16 and small interstitial spaces among the crystals. The large surface area means that only a very small film of brine can be permitted to remain. For example, to achieve a reduction

Figure 4-15: Interstitial Brine Fraction

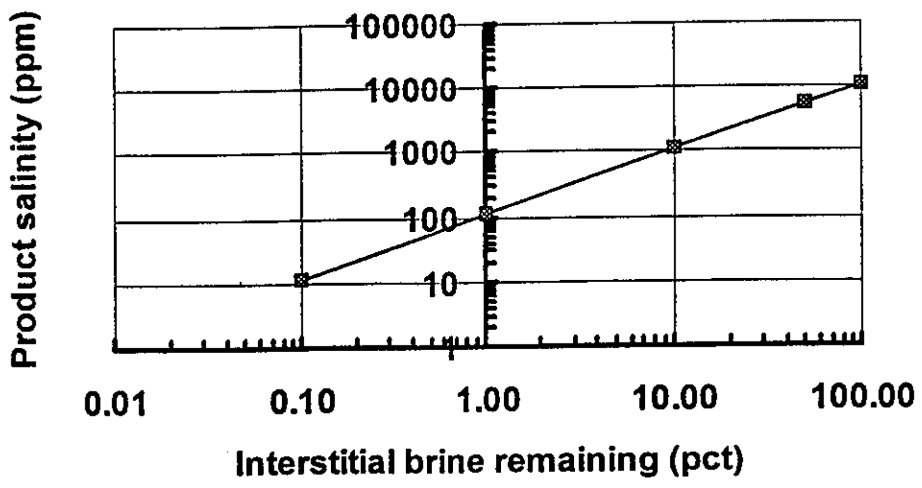
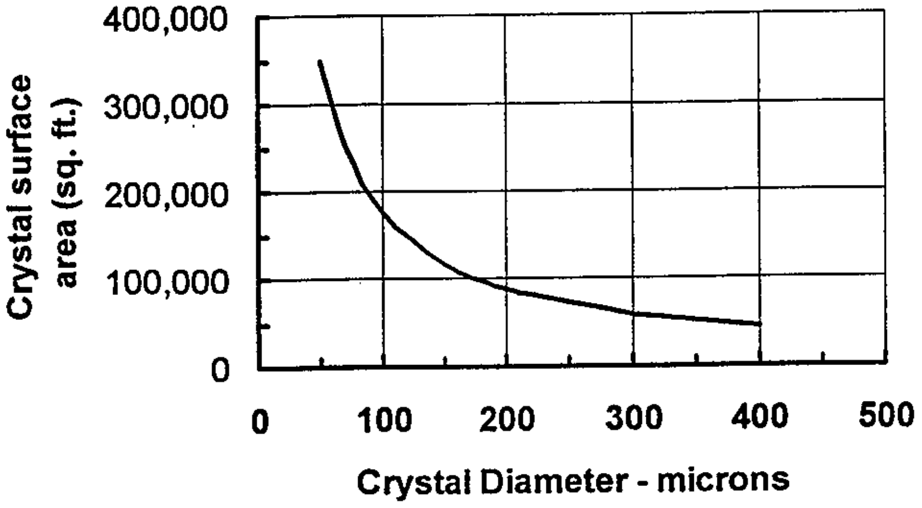


Figure 4-16 Crystal Surface Area in Pilot Plant Wash Column

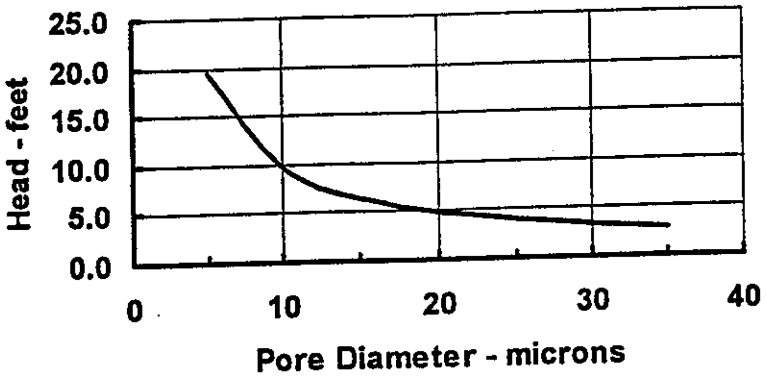


to 1% of the interstitial space with 50-micron crystals the average film thickness of brine on the surface of the crystals can be only 0.03 microns thick.

Draining the crystals is problematic because surface tension effects can keep water in the interstices even though it can drain from the larger gaps between the crystals. If the crystals are simply drained, quite a bit of brine will be retained in the interstitial spaces. The brine retained will probably not amount to 26 percent of the volume but will nevertheless be a significant quantity. Simple tests of drained samples indicated a product salinity of 5000-7000 ppm.

The effect of surface tension in small interstitial spaces can easily support a head equivalent to the height of the wash column. The head that can be supported by this phenomenon is shown as a function of the pore diameter in Figure 4-17.

Figure 4-17: Head Supported by Surface Tension



In actuality, the varying size of crystals will probably result in a different crystal packing fraction, probably a bit less efficient than 74 percent. That would mean that achieving the target salinity in the product by simple filtration would be more difficult than the calculation given here. It is likely that even the use of a centrifuge would leave an excessive amount of seawater in the interstitial space.

The advantage of counterflow displacement washing obtained in a wash column is that there is no air/water interface that permits relatively large quantities of brine to remain in the interstitial space. The freshwater is lower density and naturally remains on top of the brine with limited mixing occurring by diffusion. As long as the hydrostatic pressure is sufficient, the fresh water continues to drive the brine from the clathrate crystal bed, with very little remaining to affect the salinity of the product water. The operating difficulty is that the clathrate crystals are denser than the brine and thus tend to sink rather than rise and accumulate at the bottom of the "ice" bed.

4.4.2 Literature Review. Several articles on clathrates and on crystal separation and washing were reviewed and the literature includes a mix of successes and failures. The failures tended to be in those systems which produced "small" crystals. In most instances there was little quantitative definition of "small." The smaller crystals proved more difficult to wash, and also presented greater difficulty in the mechanics of moving the clathrate ice bed upward in the wash column. The smaller crystals tend to bridge into the drain holes and "gear" into the wash column, indicating a need for some positive mechanical system to lift the clathrate ice bed.

Wiegandt, in an article on separation and washing, said the following: "Landis and Wiegandt found no examples (emphasis added) of beds composed of solids having a specific gravity>1.0 which were easily moved upward by water in co-current flow, even in upward expanding conical columns; the ability to float seems important."

It seems that the wash column as designed is in one sense upside-down in that the crystals have a specific gravity greater than 1.0 so the crystals tend to sink. The articles mention filter arrangements that were used with counter-flow washing. It is clear from the US Filter experiments that a filter system that can increase the slurry concentration can be made up of their standard filter elements.

These could be used in conjunction with a different design concept for the wash column. Given the ability to control the slurry concentration, it should be possible to have the wash column upside-down in a hydraulic sense and still make it insensitive to crystal size. This will require increasing the concentration of the slurry via decanters, filtration, or some combination so that mechanical interaction among the crystals carries them upward to the bottom of the crystal bed in the wash column.

4.4.3 Computational Fluid Dynamics (CFD) Modeling, To examine the prospect of making the existing wash column work, TESI hired Innovative Engineering Solutions Inc. (IES) to analyze the wash columns for varying conditions using Flow3D, a computational fluid dynamics flow simulation program. That work was completed using a crystal size of approximately 100 microns, estimated from the drain test done at the pilot plant and confirmed in permeability TESI experiments. The CFD model permitted parametric variations on crystal size, drain area porosity, crystal void fraction, and inflow rate, rinse flowrate, and slurry concentration.

The results were not greatly different than those obtained analytically by Wil Hahn except that the analysis was done for a crystal with a characteristic dimension about one-third the size used in Hahn's final design calculations. The model permitted examination of the importance of various parameters, and a determination of the drain area requirements. The results also yielded a linear model for estimating the design parameters of a wash column given the crystal size.

The initial model of the wash column produced lower flowrates than the IES engineers expected. To validate the wash column model, a model of the permeability test rig shown in Figure 4-7 was also developed and used to simulate the permeability test. The results of that work were intended to ensure that the coefficients in the model were of the right magnitude and that there were no gross errors in the model. The results compared favorably with the analysis used to estimate crystal size, indicating that the coefficients used in the model were comparable in quality with the other data and reasonably approximated actual conditions.

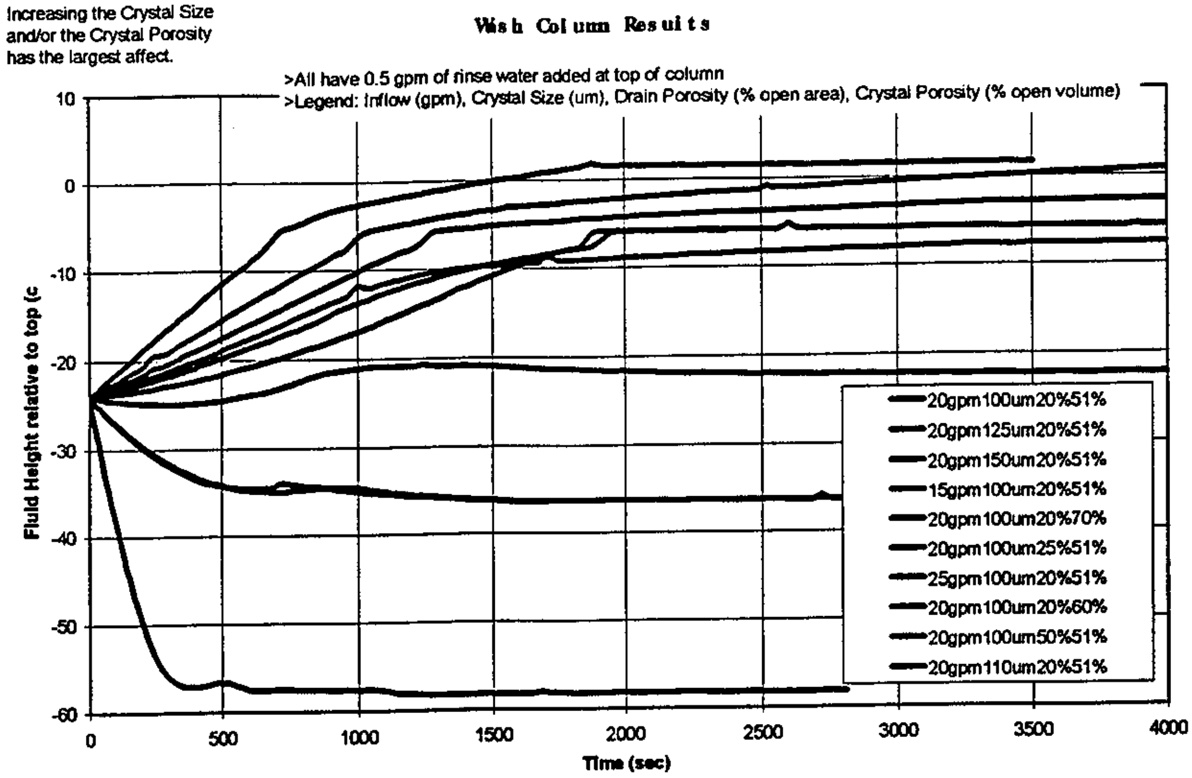
The results of the simulation were presented in several graphics. One of the presentations, given in Figure 4-18, shows the liquid level in the wash column from the time that inflow is initiated, assuming the initial condition of a partially full clathrate ice bed. In some conditions the drain rate was quite high and increased fairly quickly. The results indicate that the wash column should work with smaller crystals if the drain area were substantially increased (a factor of 15) and the brine inflow were reduced by using a more concentrated slurry. These changes would be relatively simple, and calculations of the stress levels in the porous region indicates that even at a 20% porosity the stresses should be far below the strength of high density polyethylene.

The other graphics show pressure and concentration profiles, as typified in Figure 4-19. They look much like Wil Hahn's sketches and graphs of what he termed the "brine crown," which was a concentration boundary profile developed from less detailed calculation. Figure 4-19 corresponds with one of the parametric cases that assume 20 gpm of seawater in the slurry, 0.5 gpm of rinse water, 100-micron crystal size, and a sidewall porosity of 20%. The chart on the left maps the pressure distribution in the crystal bed; on the right the concentration is displayed (Figure 4-19).

4.3 Implications for Plant Design

4.3.1 Pilot Plant Capacity. The pilot plant as-built capacity was 35 to 50% of the design capacity, because the CHXs were not as effective as the original design calculations indicated. The lower heat transfer capability resulted from ambient and solar

Figure 4-18: Transient Response of Wash Column

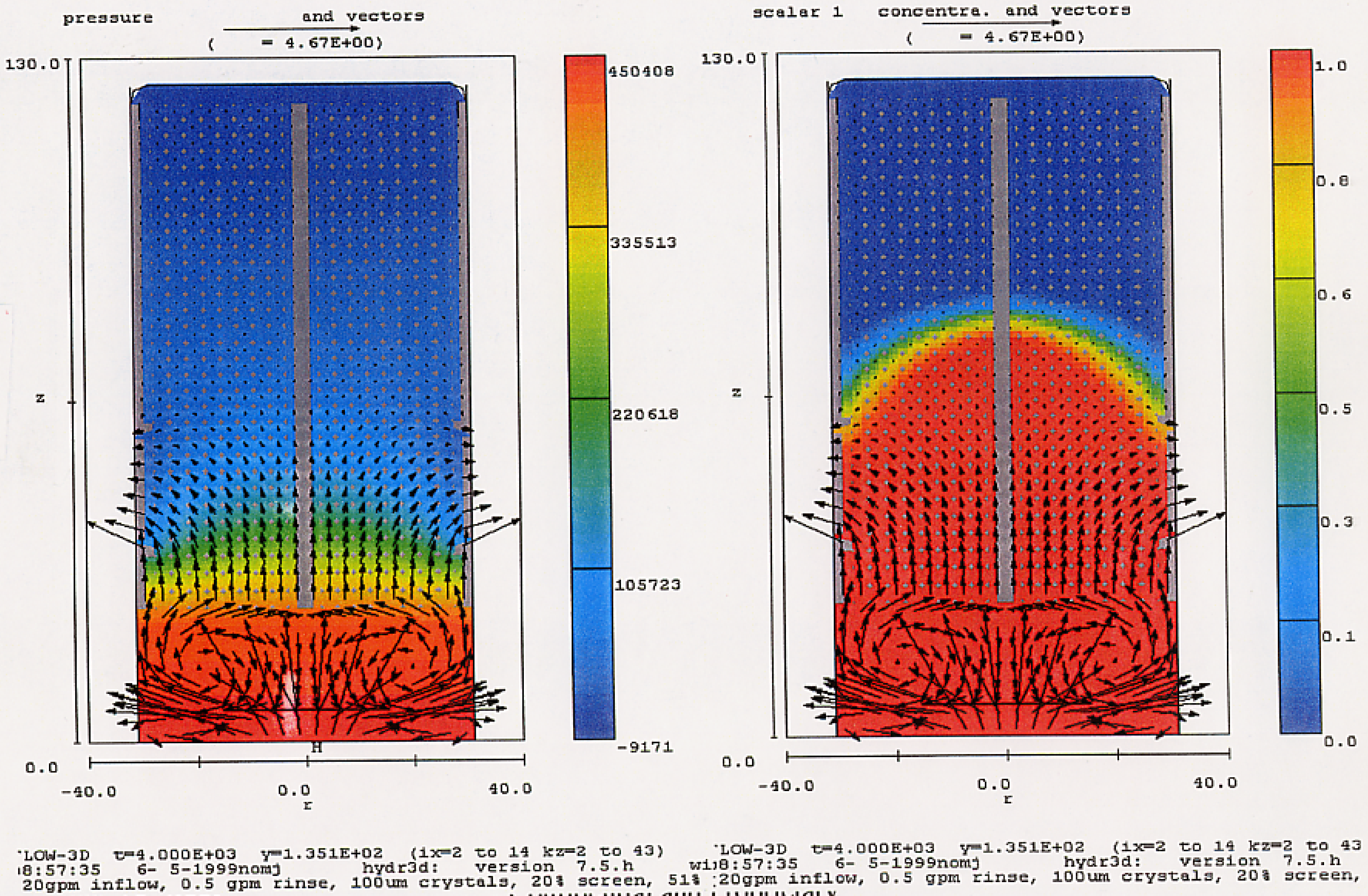


heat load, a smaller temperature difference because the formation temperature was approximately 1°F lower than the design value assumed, and because the crystallizer heat exchangers had a lower overall conductance.

Nevertheless, these results indicate that the wash column could work, given somewhat different operating conditions, e.g., a slurry concentration of about 25% and an increase in the drain area. Regarding the latter, this increase would be substantial, from 900 drain holes to nearly 14,000. The number of drain holes increases the potential for "gearing" the clathrate ice bed into the drain holes and preventing proper operation. If the force required to lift the ice bed is excessive, either the ice bed will be fractured and flow through the fissure will overflow the top, or the pump backpressure will cause it to stall or overload and trip off-line. If the pilot plant at NELHA were to be used for further experimentation, the performance could be improved with some simple and low cost modifications, including:

1) Replumbing the crystallizers in counterflow. The increase in capacity is about 4% but this is a minor modification.

Figure 4-19: Wash Column Pressure and Concentration Profiles



2) Insulating the crystallizers, and better insulating the balance of plant tanks. The increase in capacity is about 11 percent, and with counterflow yields an increase of about 15%.

Had experimentation continued at NELHA, to provide operational flexibility a vertical auger would have been designed, constructed, and installed in the wash column inner tank. The auger would serve primarily to keep the drain holes clear but would also provide a lifting force to maintain a coherent ice bed above the drain region. These modifications should be sufficient to make the wash column operate properly.

The reassessment indicates that the pilot plant could have served for further experiments to confirm that the changes in the wash column were effective. The production would have been somewhat lower (65 to 70%) than the initial design but certainly sufficient for an assessment of the modified wash column.

5. EXPERIMENTS WITH SMALL SCALE TEST FACILITY

A small scale test facility was constructed in the laboratories of Innovative Engineering Solutions, Inc. (IES). The facility or "test rig" was used for a series of experiments that evaluated three configurations of a redesigned wash column and also simulated the effect of a higher temperature clathrate former.

The system was approximately a 10% scale model of the pilot plant, having a nominal capacity of 0.5 gpm. The chiller used at the pilot plant was shipped to IES for use in the new facility. Because the chiller capacity is strongly dependent upon the operating temperature the capacity was significantly less than the nominal capacity.

Filtered seawater was obtained from Scripps Pier for the experiments, and R141b was used as the clathrate former. The seawater was stored in six polyethylene drums, two of which were connected to the system. When additional seawater was needed it was pumped from the storage drums into the system seawater storage drums via flexible tubing with a small portable pump.

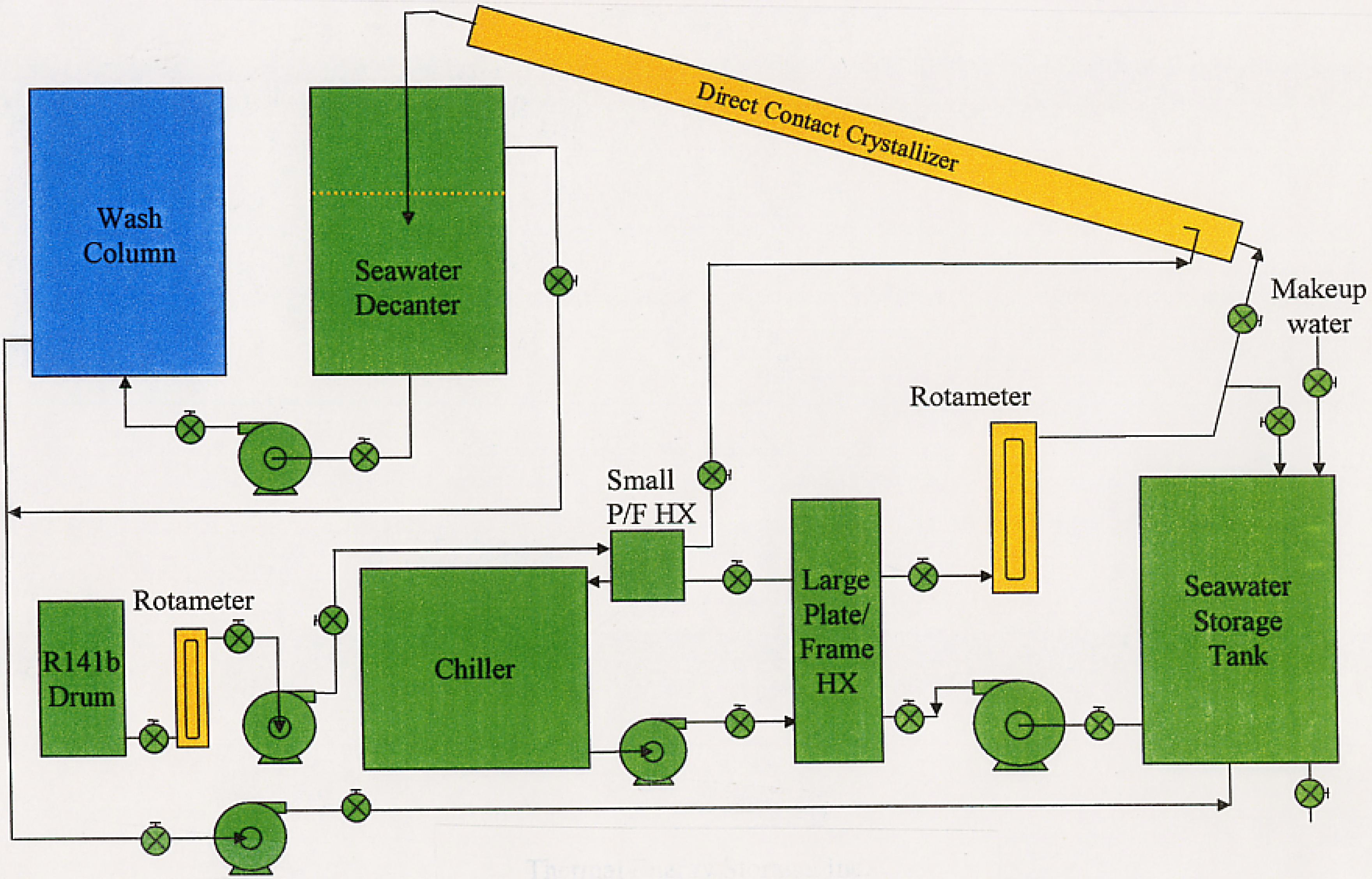
To obtain a larger temperature difference for heat absorption, the chiller cooled the seawater to temperatures below those available at the pilot plant. The chiller provided cooling to 35-40°F in the test facility versus 43°F for the cooling water at the pilot plant. The lower temperature gave the small test rig the potential for higher weight concentration of clathrate crystals in the slurry. Production capability was proportionately higher because of the proportionately higher heat removal capacity.

The test facility is shown schematically in Figure 5-1 as it was first constructed, with a crystallizer configuration intended to simulate the slope of the ocean floor near the NELHA facilities. The facility was in this configuration for the first four experimental test runs. The test loop was modified for the last experiment to incorporate an auger in the wash column and to eliminate the up-sloping piping segment.

The operation of the test facility, referring to Figure 5-1, was as follows: The chiller provided cooling via circulation of water mixed with an automotive antifreeze through a plate frame heat exchanger. Circulation of about 30 gpm was provided by a 1-hp pump and the temperature of the primary circulating water was controlled by the chiller thermostat to the set point +1.5°F.

Water drawn from seawater storage tanks was pumped through the plate frame heat exchanger and cooled to approximately the temperature of the cooling water. It flowed from the plate frame through a rotometer to the direct contact crystallizer heat exchanger installed on the roof of the lab facility. The rotometer was used to measure the flowrate

Figure 5-1: Small Scale Test Facility Schematic



into the crystallizer. The crystallizer installation on the roof of the lab is shown in Figure 5-2.

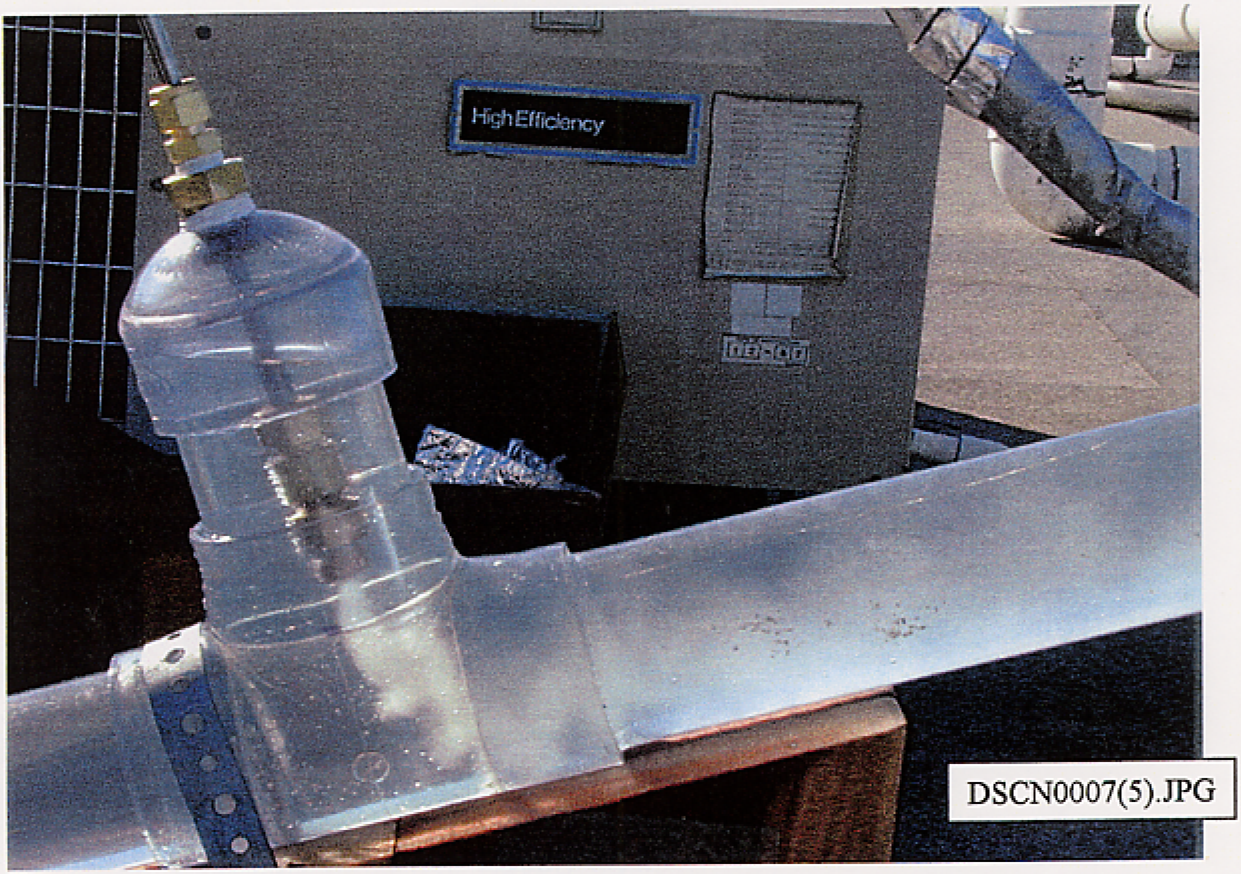
Figure 5-2: Direct Contact Crystallizer Heat Exchanger

The piping was insulated with Rubatex foam with the crystallizer over-wrapped with aluminized polyethylene bubble laminate. The clathrate former (R141b) was injected at the lower end of the crystallizer.

The initial injector configuration mounted the injector in the wall of the tube that formed the crystallizer. In this configuration, the injector extended past the center of the tube, and it appeared that the R141b was hitting the opposite side of the tube and coalescing into large droplets ("marble") of liquid. The liquid marbles remained in the lower part of the crystallizer and drained into the seawater tanks when the system was shut down.

The injector configuration was modified to the one shown in Figure 5-3 using clear PVC, and that eliminated the problem. The injector pump pressure was maintained at about 80 psig, and the flow was controlled by bypassing some of the flow through the small (R141b) plate frame heat exchanger and returning it to the storage drum.

Figure 5-3 Primary R141b Injector



DSCN0007(5).JPG

The slurry that formed in the crystallizer then flowed into the seawater decanter. The decanter was intended as the collection point for the crystals. The decanter cross-section reduced the flow rate so that crystals would settle to the bottom of the decanter. The decanter had a conical bottom so that the crystals would settle into a central drain for transfer into the wash column. A variable speed positive displacement pump transferred the slurry from the decanter into the bottom of the wash column. The overflow from the decanter drained into the seawater tanks.

The product crystals from the wash column were transferred into an R141b decanter (not shown on Figure 5-1) that contained an electrical heating element. The crystals were melted, releasing the R141b which settled to the bottom of the decanter for reuse. The water released when the clathrate was melted was returned to the system to prevent the salinity in the closed loop from increasing continuously as crystals were produced.

Several experiments were performed with the small test rig. One was done to characterize the environmental heat load on the system, and the remainder were experiments with either tap water or seawater to evaluate the system. These experiments are briefly described in the remainder of this section.

5.1 Ambient Heat Load/Chiller Capacity. An initial experiment was done on January 5, 2000 to establish the ambient heat load on the system and the chiller capacity at lower than rated temperatures. These two factors determined the clathrate production capacity of the test facility.

The test loop was filled with tap water, and the heat removal rate was estimated from the temperature changes while operating with a constant flow rate. The result of the experiment gave an ambient heat load on the system of approximately 3500 BTU/hr and a chiller capacity of 35,000 BTU/hr at the temperatures expected during the experiments. The chiller was rated at 5-ton (60,000 BTU/hr) nominal capacity at 59°F but it was significantly less at the lower temperatures needed for the experiments. The combination of chiller capacity reduction and ambient heat load gave a net heat removal capacity of approximately 31,500 BTU/hr for producing clathrate crystals. The basis for these estimates is given in Appendix A.

Because the transient effects on the heat transfer measurement the calculation of ambient heat load may have been overstated somewhat and may have been as low as 1000 BTU/hr giving a net heat removal capacity of 34,000 BTU/hr. These results correspond with a potable water production rate of 0.33 – 0.36 gpm with a sensible temperature rise of 7°F, and 0.45 – 0.5 gpm with a 10°F temperature rise.

5.2 Tap Water Experiment. The ambient heat load test was followed by an experiment on January 7, 2000 that was intended as a shakedown operation of the system using tap water. The system produced an abundant amount of clathrate crystals which collected in the piping, and substantial quantities of crystals that floated to the surface as small "rafts" buoyed to the surface by contained bubbles. These tended to exit the decanter through the sidewall drain near the top of the decanter. During the test run the R141b injection pump main shaft seal began leaking badly, and the R141b flow rate decreased to zero.

The bubbles were thought to be either air or R141b. Because the vapor pressure of R141b is low at the test loop temperatures, the more likely explanation was air and subsequently it was found that air remained in the vertical leg of the return from the crystallizer to the decanter. The flow rate was not sufficient to fill this leg with water and was the likely source of the bubbles.

The test was terminated when the R141b leakage was noted. Inspection of the pump revealed that the shaft seal O-ring had failed, and it was subsequently found that a Buna-NO-ring had been mistakenly installed at the factory. The pump had been ordered with a Viton O-ring and the Buna-N part lasted only about two hours.

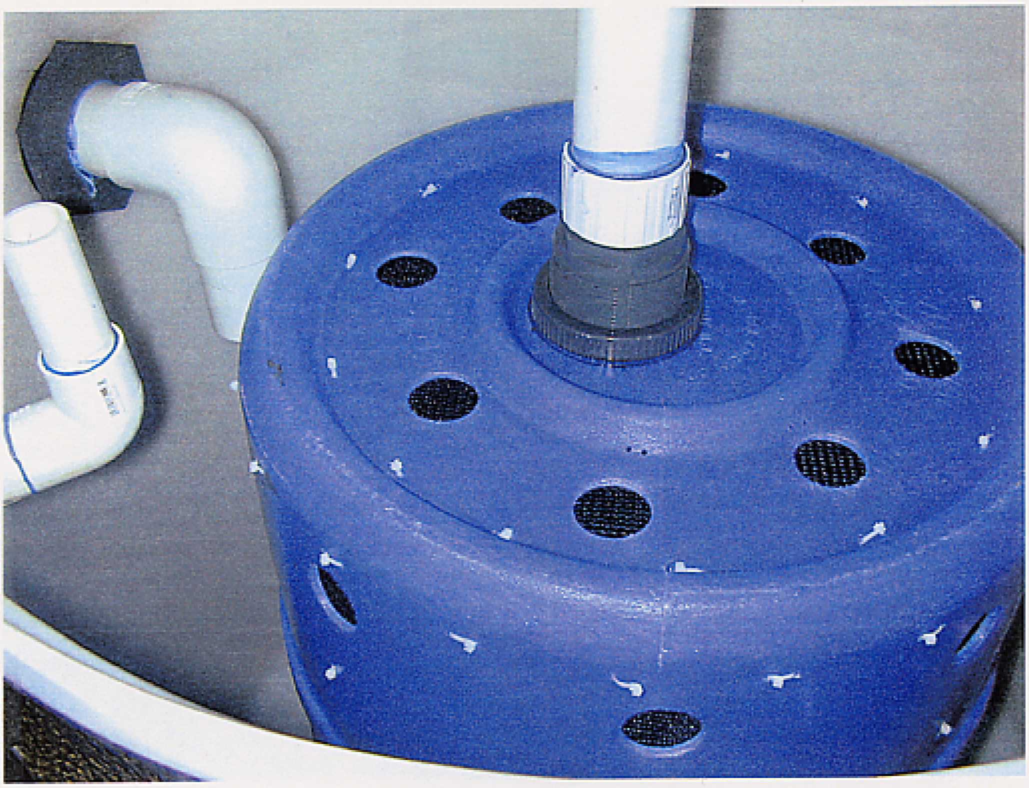
After the test, the correct O-ring was installed in the pump, and the system was modified to add a pressure gauge downstream of the pump so that pump performance could be more easily monitored. The decanter inlet was modified to add a coaxial stilling baffle/filter made from a 35-gallon polyethylene drum and polypropylene screen cloth. The baffle/filter, shown in Figure 5-4, was intended to prevent floating crystals from exiting the decanter through the drain line near the top of the decanter. In addition, a downward facing elbow was placed in the drain fitting, and pressure gauges were installed at the outlet of the large plate frame heat exchanger and at the inlet to the crystallizer.

The intent of the initial testing with tap water was to shake down the system while leaving it clear of seawater. Although the subsequent tests were to use filtered surface seawater there was some concern that between tests with seawater there might be some biofouling. Starting with tap water and moving to seawater testing would not require cleaning the system. It turned out that biofouling was not a problem during later seawater tests. The installation of the wrong O-ring in the R141b pump, however, put a residue of some compound used in making Buna rubber into the R141b storage drum. There was no practical way to remove this material and it appeared in virtually all of the tests that followed, producing a red/brown foam that colored the clathrate slurry.

5.3 First Seawater Experiment. The system was drained and the R141b that had been injected was recovered. Then on January 13, 2000 the test rig was refilled with seawater and the first experiment with seawater was started. Multiple runs were made under varying conditions but without accomplishing equilibrium operation.

Initially R141b was injected at all three injection points. About eight minutes after R141b flow was initiated, the flow was shut off because unreacted R141b was collecting at the inlet to the positive displacement pump at the bottom of the decanter. Very few clathrate crystals were observed. During this period the R141b pressure was low and it was thought that the nozzles were not working properly.

Figure 5-4: Decanter Inlet Stilling Baffle/Filter



The highest of the three R141b injection nozzles was shut off for a second test run. During this test run the R141b pressure was substantially higher, but the results were quite similar to the first test run. Liquid R141b was observed and little crystal formation.

The stilling baffle/filter was then removed and replaced with a clear section of PVC pipe, temporarily attached to the decanter inlet with duct tape. Only the lowest spray nozzle was active during this test run. The seawater flow rate was increased to about 16 gpm, about double the amount needed to absorb the heat of fusion. The visibility into the decanter was better but only for a brief period. Large amounts of floating foam began to collect on the surface of the seawater decanter, and that obscured the view into the decanter. It was thought that air was leaking in through the duct tape, so the test was again shut down so that a pipe coupling could be installed.

The pipe coupling was installed and a 3" tee was attached at the bottom of the clear PVC to reduce the velocity of the stream entering the decanter. The system was restarted and shortly afterward (3 to 5 minutes) the flow into the direct contact crystallizer began to decrease until zero flow was indicated. The pressure gauges indicated that the blockage had occurred upstream of the direct contact crystallizer. Unreacted R141b was again observed in the clear section of PVC upstream of the positive displacement pump

Several additional attempts to start the system were made, and each time the flow blockage developed shortly after R141b injection was initiated. The results of these attempts were assessed and it appeared that one cause of the difficulties might be that the injector head protruded too far into the pipe and that the R141b was impinging on the wall of the pipe, promoting local crystal formation and blockages. A decision was made at this time to replace the lowest injector with a different design made of clear PVC, shown previously in Figure 5-3, so that the injection process could be observed directly. In addition, it was decided to install a clear PVC tee as an R141b trap/drain in the event R141b was coalescing on the pipe inner wall and draining back down the direct contact crystallizer. Finally, the decision was made to increase the setpoint pressure on the R141b pump to increase the nozzle pressure.

5.4 Second Seawater Experiment. After the modifications described above were completed, another set of test runs was attempted on January 20, 2000. The seawater flow rate was set at 16 gpm, primarily to minimize the tendency to plug the system. R141b was injected through the modified injector with the intent to accept a lower production rate of crystals if necessary to operate the test rig in equilibrium.

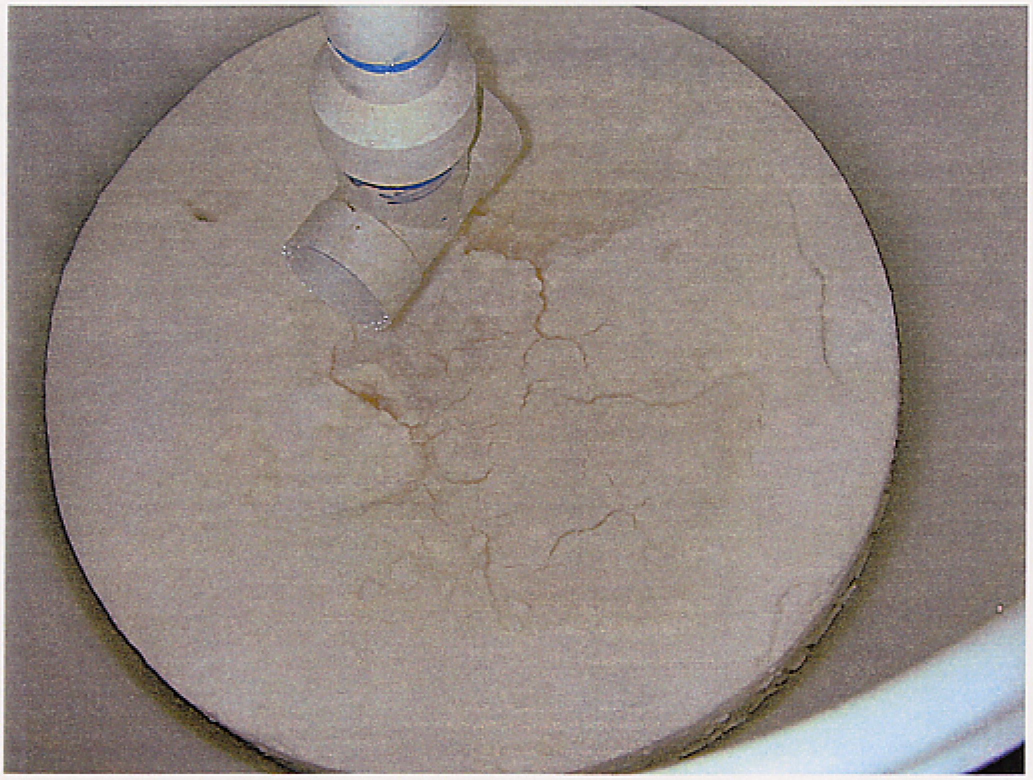
About five minutes after R141b injection was started, small crystals began appearing in the drain of the seawater decanter. In addition, foam with crystals was observed floating on the surface of the decanter. Within the next minute or two, the system again plugged and the primary flow ceased. The small metal screen filters upstream and downstream of the plate frame filter were removed and were found to be plugged. Flow was restored and the system was permitted to warm up for several hours, in part to permit recovery of unreacted R141b.

The wash column did not fill and small crystals were noted in the liquid emerging from the drain holes. It appeared that some of the holes were bridged by crystals, but many were not and continued to flow freely, and the brine carried substantial amounts of crystals from the wash column back through the drains to the seawater storage tanks. Inspection later showed that a gallon or more of R141b had accumulated in the system seawater tanks.

The system was again cooled down and R141b injection again initiated. Crystals appeared promptly but distributed around the system. The primary rotometer indicated the presence of crystals by immediately showing a large increase in flow rate, and then moving to the high flow limit. This was caused by the greater density and effective viscosity of the slurry moving through the rotometer. Eventually it was found that the plate frame heat exchanger had become plugged with ice crystals, and the test was terminated at that point.

The seawater decanter was found (Figure 5-5) to have accumulated a large quantity of clathrate crystals. The cone angle at the bottom was evidently too large (the sides were not steep enough) and the crystals did not slide down and out of the decanter. It is clear that the decanter must have a smaller included-angle if one is used in the final design.

Figure 5-5: Clathrate Accumulation in Decanter



5.5 Third Seawater Experiment. The third seawater experiment was done on January 25, 2000 with Harry Remmers of the Bureau of Reclamation present to observe. The test rig operated for a fairly long period and the wash column did fill and operate for a brief period. Although the wash spray was operated, no samples were taken so the quality of product water was not determined.

The test process was slightly modified by manually stirring the decanter to prevent a buildup of clathrate crystals in the bottom. This was deemed acceptable because the straight rod used for stirring the decanter imparted essentially no vertical velocity to the crystals but did prevent them from collecting in the bottom of the decanter.

Initially, the primary seawater flow was set at approximately 8.5 gpm, in an attempt to get a slurry concentration on the order of 4 - 7% by weight. The seawater temperature ranged between 36.3° and 39.7°F. The test rig was operated for only a few minutes with the top and lower injectors open. Crystals were observed within a minute of the start of R141b injection. Shortly thereafter there was an indication that the system was again freezing up, so the upper injector was shut off. When the filters were checked, some crystals were found but the filters were not plugged. The chiller was turned off briefly and the system temperature increased to 40.2° – 41.6°F. The test run was continued with only the lower injector operating.

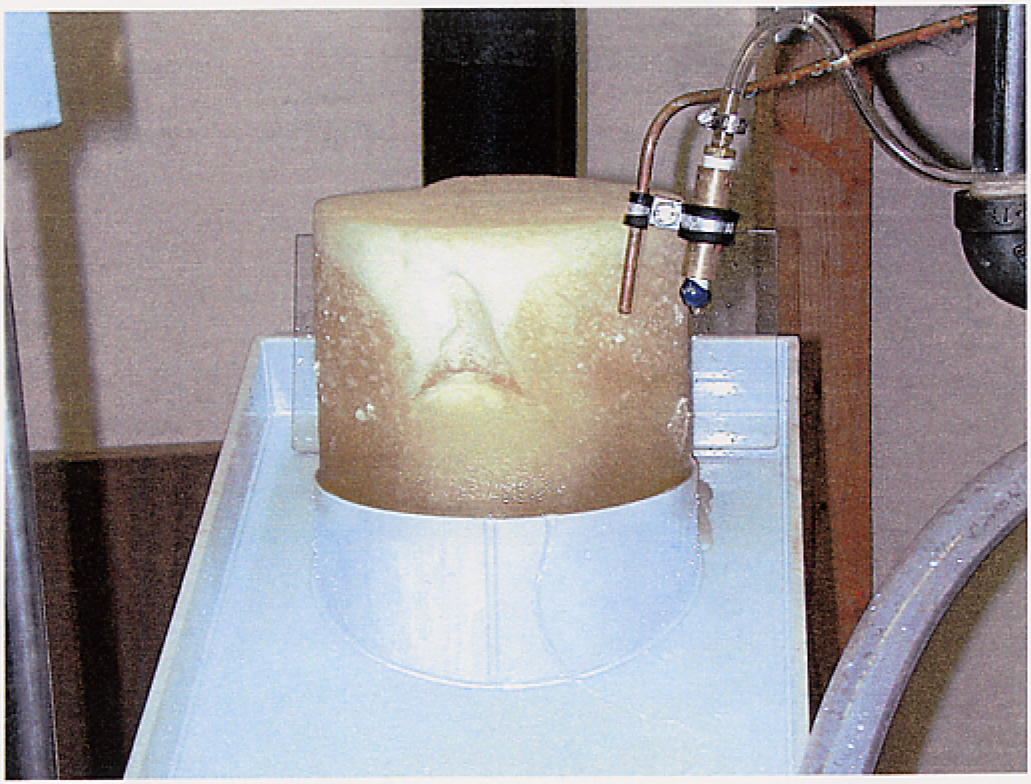
There were indications that the system was beginning to freeze, so the R141b injection was shut off and the chiller setpoint temperature was increased. The small filters were removed from the system and R141b injection was resumed. The production of clathrate crystals was significant and the crystals had the appearance of larger flakes than previously. The wash column began to fill but did not form a coherent "ice" pack. Instead, as some of the drain holes in the wash column began to bridge, an annular layer of crystals much like a filter cake began to accumulate on the inside of the column at the lower end. The crystal pack that bridged the drain holes was not a coherent structure and from time to time various drain holes would open, and a steady stream of dilute slurry would escape, preventing a continued accumulation of crystals,

In order to promote capture of crystals and bridging of the drain holes, a metal screen was wrapped on the outside of the wash column. This was effective in preventing the escape of crystals from the wash column and promoted the development of an annular filter pack of crystals that extended to the topmost row of drain holes. Subsequently, the slurry filled in the center of the column. The annular filter pack appeared to have "geared" into the drain holes with small extrusions, so as the column continued to fill with the clathrate pack extruded up through the center with occasional breakthroughs of low concentration slurry.

The slurry flow rate into the column was reduced in an attempt to match the actual drain rate of the column but at the lowest flow rates, the variable speed motor on the positive displacement pump provided very little torque and the pump occasionally stalled. To maintain operation, the pump was operated at a flow rate somewhat greater than the minimum speed but at flow rates still lower than the nominal drain rate of the wash column.

With the lower flow rate, the wash column began to fill with a high concentration slurry that developed a crystal bed with some strength and which extruded from the top of the wash column, as shown in Figure 5-6. No attempt was made to wash to crystals. The top inch or so of the clathrate column drained well as indicated by the nearly white color.

Figure 5-6: Clathrate "Ice" Pack Extruding from Wash Column



As the column filled, the seawater rotometer began to indicate very high flow rates, a symptom of the presence of clathrate crystals in the seawater circulating through the test rig. Operation of the test rig became progressively more difficult and unstable because of the formation of crystals in the piping, rotometers, and seawater storage tanks. Eventually the crystals formed plugs in the rotometers and plugged the plate frame heat exchanger, requiring a shutdown of the system.

During this experiment the permeability of samples taken from the wash column was measured with the permeability tester. The samples were taken at the top of the extruded cylinder of clathrate crystals. As a consequence, the crystals in the sample had the greatest amount of time in close contact with other crystals, estimated as about 30 minutes. The temperature at the inlet to the crystallizer during the third seawater experiment was generally in the 38 – 41°F range. The permeability results yielded crystal size estimates of approximately 130-microns, significantly larger than those obtained in the small batches made at 32 – 34°F range. The results do not permit assessing the relative importance of slurry concentration, contact time, and formation temperature but do indicate that a relatively simple experiment is possible that would permit such an assessment. Because R141b will be unavailable for future use, an experiment to determine the initiation and growth characteristics for this chemical would not have been helpful in the design of a new system. Those experiments would be helpful in characterizing a more environmentally benign replacement chemical for R141b.

5.6 Fourth Seawater Experiment.

The results of the third experiment made it clear that the drain rate from the wash column was not sufficient given the slurry concentration obtained in test rig operation. For the fourth experiment, done on February 26, 2000 the wash column was modified by tripling the number of drain holes. The external screen used in the third experiment was re-installed as a means of preventing the dilute slurry from escaping through the drain holes. In addition, two high capacity filters were installed on the inlet to the plate frame heat exchanger to prevent an accumulation of crystals from plugging the heat exchanger.

Initially the chiller was set to maintain temperatures of 41.6 – 42.4°F, but in this temperature range crystal initiation was not observed. R141b was initially injected through two injectors, but because of the lack of crystals and "marbles" of liquid R141b present it was concluded that little or no clathrate was forming. At this point the R141b flow was shut off briefly. At the same time, the chiller setpoint was reduced to give slightly lower temperatures, between 38.5 – 41.3°F.

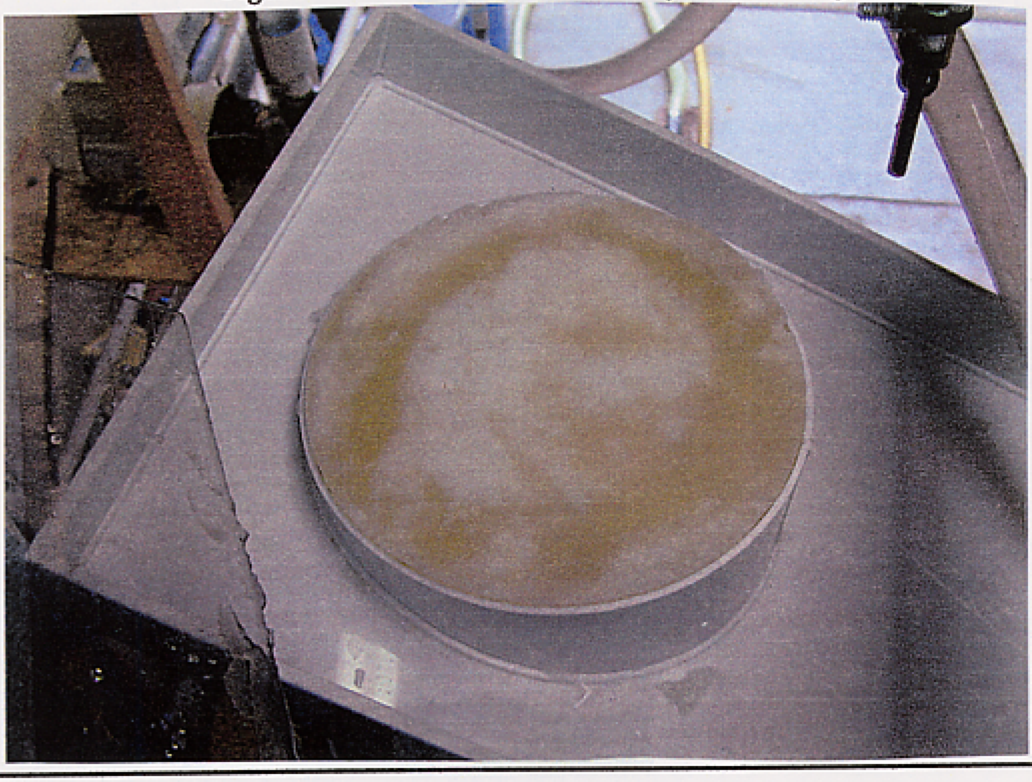
The second (mid-level) nozzle was shut off, and R141b was directed to the lower injector only and the R141b flow was re-established. Visual examination indicated a well-dispersed cloud of small particles of R141b.

Crystal initiation and growth became apparent after these changes, and the wash column began to fill with crystals. As in the third experiment, an annular filter pack began to develop, eventually reaching the top row of the drain holes. As the crystals accumulated, the central region gradually filled in and then extruded through the filter pack. The drain flow through the pack did tend to promote small radial extrusions of the crystals into the drain holes. Even though the strength of the protrusions into the drain holes is not great, the cross-section area that must be sheared once the protrusions exist is fairly large so the upward crystal flow tends toward the center. The central extrusion, as shown in Figure 5-7, indicated that the annular pack was prevented from moving upward and that the crystal pack was weakest in the center, where there had been less fluid drained away and no drain flow tending to push the crystals together which would enhance the prospects for them bonding together to form larger crystals and a coherent structure.

Figure 5-7: Crystal Annular Filter Pack and Central Extrusion

The wash column continued to fill through the central area, and as shown in Figure 5-8 there was sufficient drainage for the column to begin working. The column continued to operate and the wash spray was initiated after the column filled. The column operated nearly at equilibrium for approximately one hour and 40 minutes, and three samples of the washed crystals were taken during this period. An additional sample was taken two hours after the first sample, but by then crystals which had escaped from the wash column and the decanter had begun to plug various components and cause loss of control of the system.

Figure 5-8: Wash Column Shortly after Filling



The large filters accumulated a substantial quantity of crystals fairly quickly and created a substantial flow resistance. After the filter elements were removed, cleared, and replaced the amount of crystals captured was substantially less. It was not possible to determine whether this was because fewer small crystals were circulating in the system or because the filters were not capable of withstanding the pressure and permitted some of the crystals to escape and continue circulating.

There is reason to believe that crystals continued to circulate and that seems more likely from subsequent events, but no permanent damage to the filter elements was discernable. Eventually the crystals accumulated in the rotometers (both the primary and the decanter drain) and plugged both rotometers. Other flow restrictions were indicated by pressure readings so an attempt was made to thaw out the test rig and to continue the experiment. That attempt was unsuccessful and the test was terminated.

During the relatively stable operating period during which samples of the washed clathrate crystals were taken, the characteristics of the crystal pack changed somewhat as shown by the lighter color near the top, shown in Figure 5-9. As each of

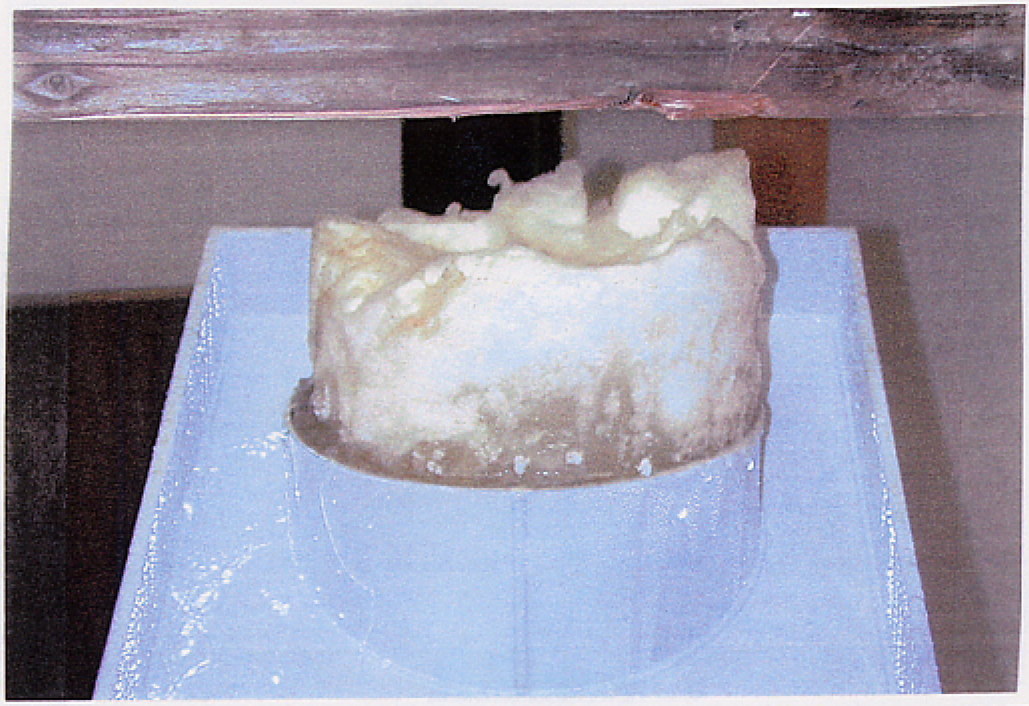
Figure 5-9: Wash Column Equilibrium Operation

the first three samples were taken; the top of the cylinder of crystals was scraped off into the fresh water decanter and was replaced by crystals moving upward in the wash column.

The last sample was taken after the symptoms of loss of control of the system were observed. As can be seen in Figure 5-10 the appearance of the region where the sample was taken had changed appreciably. During the testing it was clear that the wash column operation had been adversely affected. Other photos indicate that by the time the fourth sample was taken the wash column was no longer operating properly.

The samples of washed crystals were melted, and the R141b was driven off by heating the samples. The samples were checked with a handheld meter which gave readings of 166 to 440 ppm, and were then sent to an analytical laboratory for measurement of total dissolved solids. The results of the laboratory analysis are given in Table 5-1. The handheld meter is fairly sensitive to temperature, and in most instances the samples were still hot after the R141b had been driven off. This is thought to account for the large difference between the spot check and the laboratory results.

Figure 5-10: Wash Column Late Stage Operation



Given the conditions when the samples were taken, it is likely that long-term equilibrium operation of the system would have produced potable water with total dissolved solids around 90 ppm, similar to the levels for Samples 2 and 3.

Table 5-1: Water Sample Total Dissolved Solids

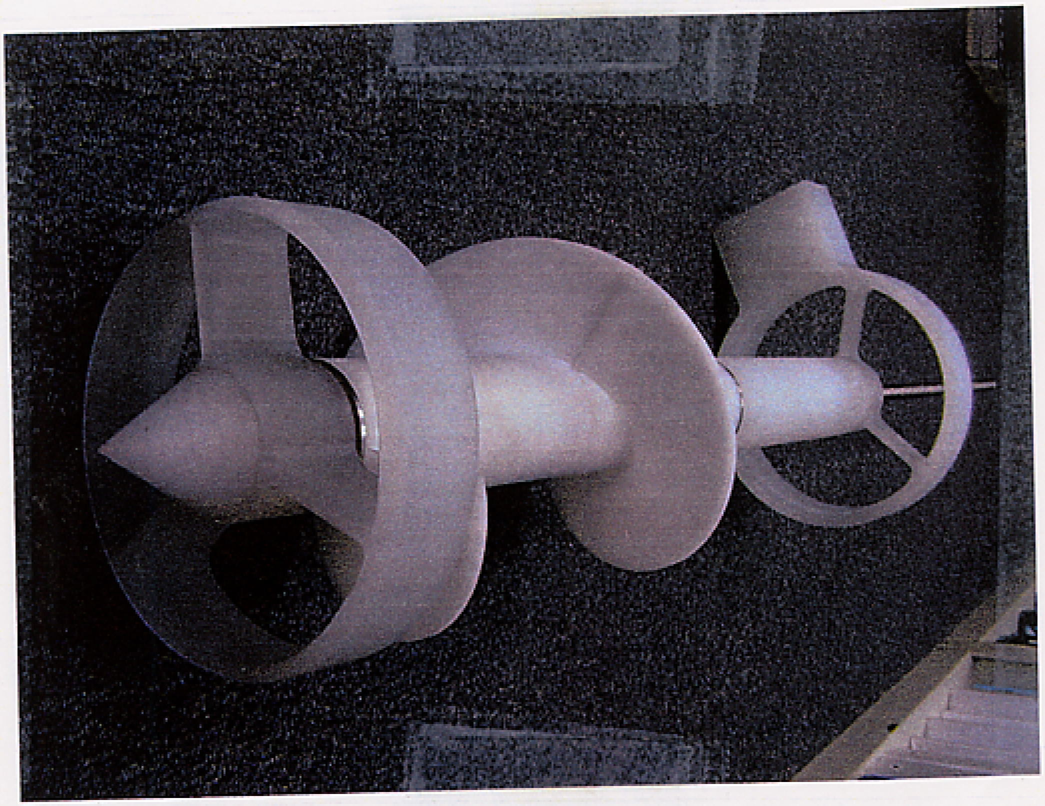
Sample	Time taken	Total Dissolved Solids
1	2/25/2000 @ 13:40	139 ppm
2	2/25/2000 @14:00	85 ppm
3	2/25/2000 @ 15:20	90 ppm
4	2/25/2000 @ 15:40	340 ppm

The initial sample was taken before the test rig reached equilibrium, and the final sample clearly was taken after an upset because of freezing in the system.

5.7 Fifth Seawater Experiment.

The encouraging results from the fourth experiment led TESI to make modifications in the small test rig that would yield longer-term operation of the test rig and wash column. The primary change included the addition of an auger (shown in Figure 5-11) inside the wash column that was intended to provide a lifting force to move the clathrate crystal pack upward through the wash column to clear the drain holes. In addition a scraper was added at the top of the wash column so that longer term operation would be possible without manual scraping. A variable speed drive was provided for the auger that permitted rotational speeds from 1 to 30 rpm. The direct contact crystallizer on the roof of the facility was eliminated, the R141b injector location was moved to just upstream of the decanter, and the decanter inlet was modified in an attempt to improve the effectiveness of the

Figure 5-11: Wash Column Auger



decanter. The decanter stilling baffle/filter was removed and replaced with a section of 2" clear PVC perforated with 1/2" holes and lined with 40 mesh stainless steel screen.

The fifth experiment was conducted on May 19, 2000, with temperatures initially controlled in the range of 39.2 – 41.1°F. Initially the auger and the scraper which was attached to the auger shaft at the top were set to rotate at 2 rpm. The flow rate into the wash column was initially set at approximately 13 gpm. Within one minute of beginning R141b injection (using a single injector) smoke-like wisps of tiny particles of unreacted R141b or very small crystals could be observed exiting from holes in the clear PVC decanter inlet.

Long before the wash column filled with crystals, water began to overflow the top of the column, indicating the inability to drain the higher flow rate, and perhaps the presence of smaller crystals than in the last experiment. The auger functioned as intended, lifting crystals to the top flight of the auger long before the column filled with crystals to that level. Despite the higher flow rate and apparent presence of smaller crystals there was a smooth startup of the wash column, without the annular plug developing.

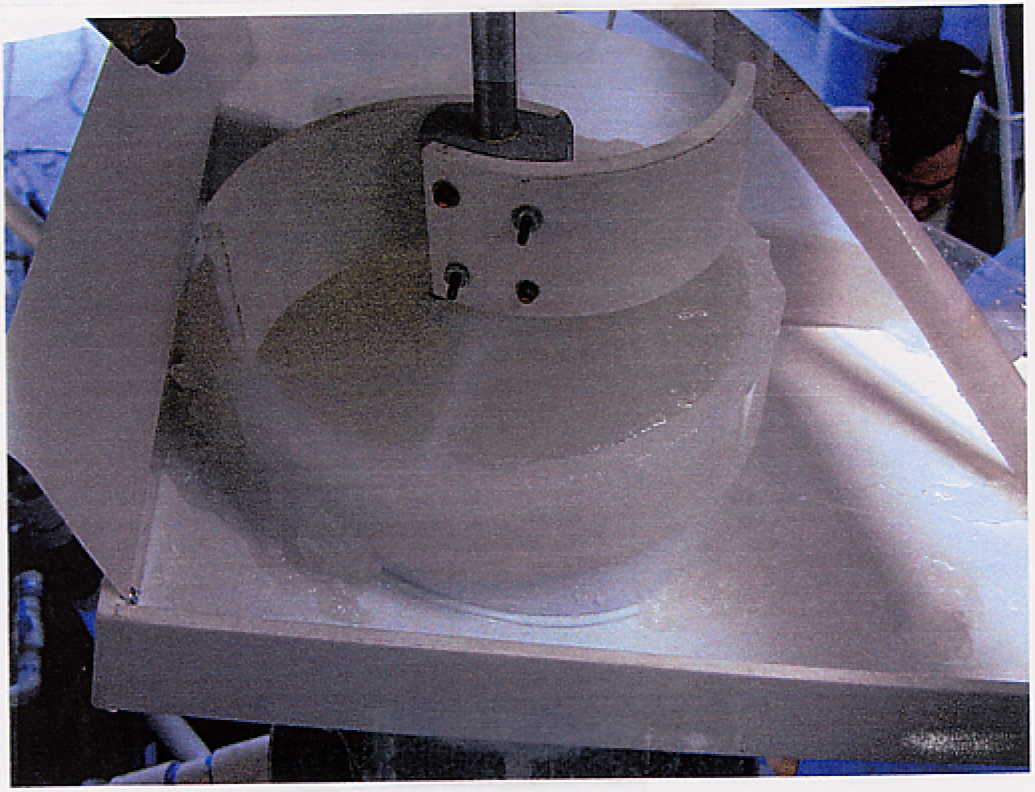
The auger speed was varied during this period and little effect was noted. The transfer flow rate from the decanter to the wash column was reduced to approximately 2.5 gpm and the wash column overflow diminished substantially, but continued at a much lower level. During the entire period, crystals were observed in the wash column and decanter drains, and approximately 30 minutes into the test run the primary rotometer indicated a substantially increased flow, a symptom of clathrate crystals in the primary seawater flow.

At this time the R141b injection was shut off and the active 50-micron filter upstream of the plate frame heat exchanger was valved off and replaced by a parallel filter. Upon examination, the filter was found to be filled with crystals. Because the flow rate had not diminished much, it seems likely that the filter was deformed by pressure and began to permit an unfiltered bypass.

The R141b injection was resumed and the wash column filled with crystals to a level above the drain holes. Then the R141b injection was stopped because of a flow imbalance on the decanter that indicated plugging. After adjusting the flow control valves R141b injection was resumed until the primary flow was reduced to a level that no longer registered on the rotometer. The modified inlet to the decanter and the R141b injection port were examined, and both were found to be filled with crystals and plugged.

At this point the test rig was shut down, and the stilling/filtration assembly (Figure 5-4) was reinstalled. In addition, a temporary decanter was installed on the wash column drain so that crystals escaping through the drain holes would be captured rather than circulating through the system. During the shutdown the system was warmed up and R141b that had accumulated at various points in the system was collected and returned to the R141b storage tank. Following that the system was cooled down again, with the setpoint on the chiller slightly higher than in the last test run, in an attempt to generate larger crystals. R141b injection was again resumed, and after some reductions in chiller setpoint temperature to get crystal formation the wash column filled with a dense slurry of clathrate crystals and seawater as shown in Figure 5-12.

Figure 5-12: Wash Column Scraper in Operation



The slurry scraped from the top of the wash column contained too much water to permit starting the wash flow. The slurry was estimated as being 60 to 90% clathrate by weight, and at this point the response would have been to reduce the flow from the decanter to the wash column. But at about this time the rotometer measuring

R141b indicated zero flow. By this time there was also evidence of crystals distributed throughout the system. The rotometers were reading off-scale high and in the past this had been an indicator of an imminent freeze-up so the test was paused to examine the R141b pump. The pump appeared to have worn excessively on the rotating gear faces, developing the internal bypass that prevented the pump from developing significant pressure. Given that R141b could no longer be injected, the test was terminated.

5.8 Lessons Learned. The fifth and last experiment provided the following valuable information even though equilibrium operation of system was not established: 1) The auger was useful in providing a smooth startup of the system wash column filling with crystals without the annular plug developing. 2) There were more small crystals in evidence than during the last experiment, even though the initial chiller temperature settings had not been changed. This appears to be a startup transient that occurs because there is a statistical distribution of crystal sizes that includes very small crystals early in the operation. 3) Small crystals were evident in all parts of the system, indicating that they escaped in quantity either from the wash column or the decanter, or both. Although the wash column filled, it did not function long enough to begin separating out the very small crystals, nor did it drain adequately, and crystals were found in the drain from the decanter. 4) The small crystals caused plugging in the loop at high and low flow rates, especially at turns and sharp edges such as are present in the rotometer.

The failure to separate the small crystals was probably caused by the action of the auger that prevented the annular "filter pack" that was observed in previous tests. The lack of this filter pack permitted the small crystals to escape the wash column and continue circulating through the system. In retrospect, it is likely that the auger would have worked better if it had been somewhat shorter and allowed more column height for a crystal bed that would act as a full diameter filter pack to form.

The modification of the test loop made during the test series used a 35-gal drum to act as a decanter downstream of the wash column drain. With it in place a large quantity of crystals accumulated (10-12 gal approximately 40% by weight slurry). Clearly, many small crystals escaped through the wash column drain holes.
At the same time, the wash column did not drain quickly, indicating that the crystals in the column were generally smaller than expected. Prior runs indicated that a crystal size of about 100-microns could be expected but they were smaller. As the column filled, the crystals were accumulating between the wash column and the screen wrapped on the outside. Moving the screen released the small crystals and

promoted rapid draining of the column.

Some crystals seemed to be present everywhere shortly after the system was started. It is possible that these had been left in the secondary seawater storage tank and were siphoned into the primary tank and loop after the system was cooled to operating temperatures. These crystals promoted formation and plugging in the wrong places.

The initiation of crystallization seems to require subcooling of 5 – 6°F. After that the subcooling need not be as great for crystals to continue to form. This suggests that it may be helpful to have a small initiation stream flow that is cooled to initiate crystallization upstream of the main R141b injection point. This flow could then "seed" the formation and growth of crystals in somewhat higher temperature water.

It seems likely that the crystal "size" is a distribution of sizes having some average or other characteristic dimension that determines its properties. The subcooling for initiation may produce more of the very small crystals and result in a smaller effective crystal size, and lower permeability. If seed crystals from an initiation stream are injected into slightly warmer water along with the main R141b flow, the effective crystal size may be larger.

The results of the experiments, taken together lead to several conclusions about the process and the design of the equipment. The primary conclusion to be drawn is that the wash column will not work with large drain holes and an external small screen. In this experiment the drain holes were too large and permitted the small crystals to escape. The drain section would work better if it were constructed of a fine mesh material, perhaps in the 80 – 120-micron range. The wash column would also work better with the drain section positioned above the auger.

6. HIGHER TEMPERATURE CLATHRATE FORMERS

Prior searches for a clathrate suitable for desalination of seawater by hydrate formation led to the selection of R141b. It is an excellent candidate from an engineering perspective for the following reasons:

- it forms a crystal that separates salt from the crystal at a temperature significantly higher than the normal freezing point of water, making freeze desalination more economical than it would otherwise
- it forms crystals more readily than R11 which was used in earlier clathrate former desalination research
- it is in high-volume production as a foam blowing agent and solvent
- it forms a Structure II hydrate and in volume is relatively economical
- it is non-flammable, has low toxicity, and is generally unreactive at the temperatures involved in operations

Unfortunately, R141b contains chlorine and has an ozone depletion potential of 0.11, and for that reason the EPA has ruled that production of the chemical must cease in year 2003.

Other clathrate formers are available, including common chemicals such as methane, carbon dioxide, propane, and other hydrocarbons and halogenated hydrocarbons. Some of these chemicals could be useful in desalination and have characteristics that are in some instances beneficial.

The company engaged Dr. John Ripmeester to survey potential clathrate formers with the objective of satisfying the criteria given in Table 3-1, but with the goal of finding clathrate formers having a higher formation temperature than R141b. This would produce better economic returns in regions where cold seawater is available, and could make the process economical in regions where seawater temperatures are higher.

6.1 Candidate Clathrate Formers.

Two classes of materials that are readily available as clathrate formers are the hydrocarbons methane and isobutane and the

Table 6-1: Hydrofluorocarbon Clathrate Former Candidates

HFC	Formula	B. P (°C)	Hydrate. Structure	Ozone Depletion Potential	Global Warming Potential	Flammability	Commercial Availability.	Temp, Press (°C, atm) (decomp, in sealed tube)
23	CHF_3	-84.4	I	0.02	11,700	N	x	21.8, -
32	CH_2F_2	-51.7	I	0	650	Y	x	17.6, -
41	CH_3F	-78.5	I	0	150	Y		18.8, 32
125	CF_3CHF_2	-48.5	II	0	2800	N	x	11.8,
134	CHF_2CHF_2			0	1000	N		
134a	CF_3CH_2F	-26.1	?	0	1300	N	x	9.9, 4.1
143	CHF_2CH_2F	+5	II	0	300	Y		
143a	CH_3CF_3	-47.3	II	0	3800	Y	x	
152	CH_2FCH_2F	30.7	II	0		Y		
152a	CH_3CHF_2	-24.7	I	0	140	Y	x	14.9, 4.3
161	CH_3CH_2F	-37.1	I	0		Y		22.8, 8

Table 6-2: Clathrate Former Candidates

HFC	Formula	B. P (°C)	Hydate Structure	Ozone Depletion Potential	Global Warming Potential	Flammability	Commercial Availability	Temp, Press (°C, atm) (decomp, in sealed tube)
	CO_2		I	0	1	N	x	9.9, 44.4
	propane		II	0		Y	x	5.7, 5.45
	cyclopropane		I	0		Y	x	17.0, 5.9
	CF_4		I	0	6500	N		
	C_2F_6		II	0	9200	N		
	NF_3		I	0	8000	N		
	SF_6		II	0	23900	N	x	14, 19.9

refrigerants based on fluorinated hydrocarbons (HFCs). In addition, gases such as CO_2 and SF_6 are potentially useful. Several of the HFCs form clathrate at considerably lower pressure and higher temperatures than the hydrocarbons.

Tables 6-1 and 6-2 list several chemicals that are known, or likely form, clathrates at relatively high temperatures, along with proper data on the material where it is available. Promising candidates include HFCs 125, 134a, and 143a. Although the clathrate-forming properties of these HFCs are not known completely, knowledge of the properties of the other HFCs suggest that each of these should form a Structure II hydrate of good stability. These three materials are constituents of blends used in new refrigerants that are produced in commercial quantities.

The table lists the hydrate former, the structure it is known to form, the boiling point, the ODP and GWP (if known), flammability, commercial availability, and the hydrate decomposition temperature and pressure (if known).

6.2 Clathrate Former Blends. In addition to the pure materials listed in Table 6-1, a number of refrigerant blends are now commercially available as replacements for refrigerants with significant ODPs. Although some of the components of these blends are flammable, the blends themselves are not. Unfortunately, no information on hydrate formation with blends was found. Nevertheless, some blends may be able to form reasonably stable clathrates. Some possibilities are Refrigerants 410A, 410B and 407C. Based on comparison with other clathrate formers these chemicals could produce Structure II clathrates. Consequently, these chemicals are also candidates for further evaluation.

7. IMPLICATIONS FOR PLANT DESIGN AND COMMERCIAL VIABILITY

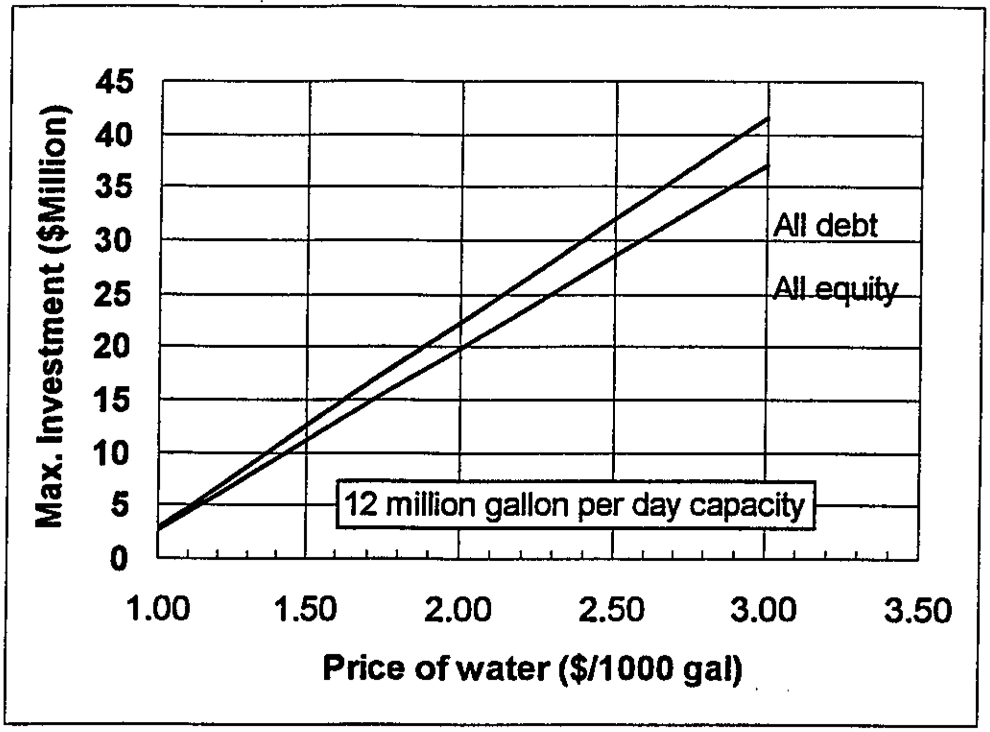
The results of the analysis and testing provide a stronger information base and greater confidence that a pilot-scale development testing will permit the design of a commercial sized system. The scope of this effort did not include an assessment in any detail of the effect of what was learned on a commercial-scale plant. Some implications are apparent, however, from the results of this program.

The control of crystals formed in the process will require filters. Conceptually the filters could be the primary means of capturing and concentrating the crystals before they are delivered to a wash column. Alternatively, they could be a supplement to a decanter and these are questions that could be resolved in a pilot-scale test. The design of filters is an art that is well-established so that should not be a difficult engineering effort. Filters are relatively expensive by contrast with decanters, so they may have a significant effect on the plant capital cost.

The higher-temperature clathrate formers will require a plant designed for closed operation at a pressure of nominally 100 psig. This will also increase the capital cost somewhat but probably not greatly because most piping, valves, instrumentation and such is easily capable of this relatively low pressure. Because the higher formation temperature permits more heat to be absorbed by the cooling water, there is an offsetting capital economy. In that significantly less water must be pumped the plant components would be smaller, and the energy expended in pumping cooling water would be lower (less water pumped and pressure energy partially recovered). In the pilot plant at NELHA, the original design anticipated a 3.5°F temperature rise but with one of the new clathrate formers with the lowest formation temperature (50.5°F in seawater) the temperature rise would be approximately 8°F. This would reduce the cooling flow by some 56%.

On balance the cost results given in Reference 1 remain useful as an indicator of the total cost of fresh water produced by a clathrate desalination plant. Working from those earlier estimates, the capital cost that could be incurred while producing water at various prices was estimated for a plant having a capacity of 12 million gallons per day, and that is shown in Figure 7-1. A competitive range of prices indicates that the process will support a significant capital cost, and that the process is viable in the desalination equipment market.

Figure 7-1: Maximum Capital Investment



8. REFERENCES

1. Thermal Energy Storage, Inc., "Build and Operate a Clathrate Desalination Pilot Plant," Final Technical Report, Bureau of Reclamation Assistance Agreement No. 1425-5-FC-81-20690, May 1998.

2. Thermal Energy Storage, Inc., "Clathrate Desalination Plant Preliminary Research Study," Bureau of Reclamation Contract 1425-3-CR-81-19520, Water Treatment Technology Program Report No. 5, June 1995

APPENDIX

Appendix A:	**Heat Load Test** **Fresh Water Test** **First Sea Water Test** **Second Sea Water Test** **Third Sea Water Test** **Fourth Sea Water Test** **Fifth Sea Water Test (Auger)**

APPENDIX

Appendix A: Date Record

HEAT LOAD TEST

TIME	FLOW RATE GPM	T1 (Deg F) DCC In	T2 (Deg F) DCC Out	T3 (Deg F) Hx In	T4 (Deg F) Hx Out	T5 (Deg F) Ambient	Barrel Temp (Deg F)	Comments
9:31am	13.75	38.19	38.77	42.63	39.3	61.7	45.2	Had been stable, just cycled, chiller @30F
9:35am	13.75	41.26	40.79	44.51	40.48	61.94	46.9	Chiller cycled once in 5 min
9:50am	13.75	41.09	41.07	46.7	41.15	63.62	49	Chiller not cycling
9:57am	13.75	41.33	11.8	47.53	41.89	63.65	50.3	Chiller not cycling
10:04am	13.75	42.42	42.44	48.2	42.5	64.93	51	Chiller not cycling
10:16am	13.5	43.27	43.26	47.07	43.31	64.72	52.3	Chiller not cycling
10:22am	13.6	43.72	43.72	49.54	43.76	64.2	52.4	Chiller not cycling
10:30am	13.6	44.14	44.15	50	44.18	66.2	52.7	Chiller not cycling
10:36am	13.6	44.47	44.48	50.34	44.51	66.3	53	Chiller not cycling
10:44am								Heater Off
10:53am	13.75	40.14	40.75	44.48	39.8	66.89	46	
11:03am	13.75	35.92	36.51	39.78	35.71	66.95	41.8	
11:10am			32.37					Close flow through R141b Hx
11:17am	13.6			33.23	31.33	67.61	35.6	
11:19am		33.15						Reset chiller to 30F - Time heater on
11:45am	13.8	37.75	37.7	43.04	37.91		46	Missed T5 reading
12:00pm	13.75	40.53	40.5	46.03	40.6	65.5	49.3	Moved T5 warm air from sea water pump changing
12:40pm	13.75	44.12	44.13	49.94	44.16	65.03	52.5	Chiller not cycling
12:50pm	13.75	33.94	39.52	43.2	38.6	64.76	45.2	Chiller not cycling
12:54pm	13.75	36.86	37.44	40.94	36.6	64.7	43.4	Heater cycles on, chiller not cycling
1:00pm	13.75	37.04	36.93	42.07	37.15	64.49	45.1	Heater still on, chiller not cycling
1:05pm	13.75	38.02	37.92	43.18	38.11	64.02	46.3	Heater still on, chiller not cycling
1:10pm	13.75	39.02	38.94	44.32	39.1	63.93	47.4	Heater still on, chiller not cycling
1:15pm	13.75	39.77	39.68	45.16	39.84	63.93	48.2	Heater still on, chiller not cycling
1:20pm	13.75	40.47	40.4	45.95	40.54	63.34	49.1	Heater still on, chiller not cycling
1:25pm	13.75	41.15	41.09	46.7	41.2	64.45	49.8	Heater still on, chiller not cycling
1:30pm	13.75	41.81	41.75	47.41	41.85	63.97	50.7	Heater still on, chiller not cycling
1:35pm	13.75	42.35	42.32	48.03	42.39	64.19	51.2	Heater still on, chiller not cycling
1:40pm	13.75	42.78	42.75	48.54	42.83	63.95	51.3	Heater still on, chiller not cycling
1:45pm	13.75	43.24	43.21	49.04	43.28	64.24	52	Heater still on, chiller not cycling
1:50pm	13.75	43.66	43.65	49.51	43.7	64.34	52.5	Heater still on, chiller not cycling
1:55pm	13.75	44.02	44.02	49.91	44.05	64.21	52.9	Heater still on, chiller not cycling
2:00pm	13.6	43.25	43.82	48.11	42.89	64.09	50	Heater off, chiller not cycling
2:05pm	13.75	40.35	40.97	44.86	40.03	64.21	47.5	Heater off, chiller not cycling
2:11pm	13.75	37.42	41.58	41.58	37.15	64.17	44.1	Heater off, chiller not cycling
2:13pm								Heater cycled on between
2:15pm	13.75	36.6	36.54	41.56	36.7	64.27	44.9	

FRESH WATER TEST

Time	Flow Rate Supply (GPM)	T1 (Deg F) DCC In	T2 (Deg F) DCC Out	T3 (DegF) Hx In	T4 (Deg F) Hx Out	T5 (Deg F) Ambient	Barrel Temp (Deg F)	Flow Rate Rtn (GPM)	Sea Water Decanter Flow Rate (hz)	R141b Flow Rate (%)	Comments
13:45	9.1	35.3	35.61	35.68	33	64.89	60.2	7	4%	30%	Initial Reading
13:50	9.1	33.85	36.01	35.64	32.26	64.76	60.5	7	4.4	30%	Chiller Off
13:56										15%	Adjust R141b flow rate down
14:00	9.1	32.35	35.31	35							Chiller On
15:40											Reset chiller temp to 25F
15:47											
15:50	9.1	36.05	36.99	42.44	35.73	63.64	61.6	7	4.4	15%	Start R141b flow
16:03	9	33.6	32.5	37.9	35.9	63.1	61.7	6	4.4	15%	
16:07										30%	Increase R141b flow
											System creates ice
											Ball, unable to
											Fwr R141b or
											Sea Water (fresh water)
											1/10/2000
											2 1/2 Pts of R141b found
											"free" in system

FIRST SEA WATER TEST

Time	Flow Rate Supply (GPM)	Lg Pl Fr Hx Outlet Press (psig)	Inlet Press DCC (psig)	DCC in T1 (Deg F)	DCC Out T2 (Deg F)	Hx In T3 (Deg F)	Hx Out T4 (Deg F)	Ambient T5 (Deg F)	Barrel Temp (Deg F)	Sea Water Decanter Overflow Rate (hz)	Wash Col Supply Flow Rate (hz)	R141b Flow Rate(%)	R141b Flow Meter Inlet Press (psig)	Comments
10:32	16.25	12	0	34.36	35.55	37.73	34.62	62.14	45.4	14.5	3.9	0	0	Set chiller at 29F
												10%	10psi	R141b on @ 10:35 @ 10%all three
10:36	16.25			36.55	35.55	37.34	36.99	62.37	45.5	14.5	3.9	10%	10psi	valves open (crystals observed at
10:40														10:36)
10:48		12	0	35.7	34.8	36.06	35.9	63				10%	30psi	
10:50														Remove SW basket
11:33	16.5	12	0	33.57	34.95	35.34	32.95	65.38	46.3	14.25	3.9			
11:35														Start injection of R141b
11:36	16.5	12	0	33.45	34.86	35.1	32.84	65.53	46.3	14.5	3.9	10%	45	Single Injection
11:40	16.5	12	0	35.16	34.83	34.97	34.27	65.56	46.2	14.5	3.9	10%	45	Lots of Liq with crystals
11:42														Stop injection of R141b
12:00														Install clear line with union
12:44	16.5	12	0	34.3	33.5	34.3	34.66	68.05	47.2	14.5	3.7			
13:00	16.5	12	0	32.99	32.4	34.21	33.64	67.96	47.7	14.5	3.9			Install 3" Tee on 2" clar puc
13:01														Start R141b injection
13:05	16.5	12	0	34.28	33.72	34.2	34.54	68.14	47.8	14.5	3.9	10%	30	Single injector only
13:06														See crystal R141b
13:10	5	18	0	31.9	34.8	34.8	29.87	68.2		0				Frozen shut
														System plugged , think it is in 1" line
														before Dcc
														Close bottom injector open
13:30														middle injector
13:37	16	12	0	36.04	36.16	37.52	36.66	69.25	46.3	14	3.9			
13:46	16	12	0	33.6	34.1	36.58	34.71	69.53	45.9		3.9			R141b on @13:46 - injector plugged
														about 13:47
13:54	16	12	0	33.06	33.84	35.76	33.72	69.48		14	3.9	14%	45	Close Inj #2, Open Inj #3
13:57	15													
13:58	14													

SECOND SEA WATER TEST

Time	Flow Rate Supply (GPM)	Lg Pl Fr Hx Outlet Press (psig)	Inlet Press DCC (psig)	DCC In T1 (Deg F)	DCC Out T2 (Deg F)	Hx In T3 (Deg F)	Hx Out T4 (Deg F)	Ambient Thermometer (Deg F)	Barrel Temp (Deg F)	Sea Water Decanter Overflow Rate (GPM)	Wash Col Supply FlowRate((hz)	R141b Flow Rate(%)	R141B Flow Meter Inlet Press(psig)	Comments
11:22	16	12	2	38.29	38.47	42.08	38.19	66	54.2	13	3.9			LWR sprayer only!
11:26														Start flow lower only
11:27	16	12	2	36.96	37.4	40.42	36.79	66	52.9	13	3.9	19%	85	No crystals!
11:31														Starting to see very small
11:32	16	12	2	36.22	36.56	39.6	36.07	66	52	13	3.9	19%	85	crystals Floating foam
														(crystals on top)System
														plugged off within next few
														minutes.Filters found
														plugged
--	--	--	--	--	--	--	--	--	--	--	--	--	--	
14:30	17.4	12	2	37.62	38.05	17	37.41	65	53.7	15	3.9			
14:35	17	12	2	36.38	36.79	17	36.21	65	53.8	15	3.9	19%	85	Lower injector only
14:37														Small sand noted at base
14:39	17	12	2	35.44	35.95	18	35.31	65	53.9	15	3.9	18%	80	of S.D. Lots of crystals
14:41	17	12	2	35.24	35.89	18	35.02	65	53.9	18	3.9	17%	80	Good flow of crystals
14:45	21	13		35.54	37.55	20	35.02	65	53.9	23	3.9	18%	80	Crystals in S. D. out flow
14:48														Crystals in supply F. M.
14:50	22	13	2	35.22	37.07	20	34.69	65	54	24	3.9	17%	85	Crystals all around loop
14:56	24	13	2	35.2	34.96	20	36.3	65	54.1	22	3.9	18%	80	
15:01	24	13	2	36.73	35.76	20	36.58	65	54	22	3.9	17%	80	
15:09	24	13	2	36.61	35.56	20	37.03	65	54.1	20	3.9	17%	85	
15:28	24	13	2	35.33	36.42	20	36.11	65	54.6	20	3.9	17%	80	Chiller off

THIRD SEA WATER TEST

Time	Flow Rate Supply (GPM)	Lg Pl Fr Hx Outlet Press (psig)	Inlet Press DCC (psig)	DCC In T1 (Deg F)	DCC Out T2 (Deg F)	Hx In T3 (Deg F)	Hx Out T4 (Deg F)	Ambient Temp T5 (Deg F)	Barrell Temp (Deg F)	Sea Water Decanter Overflow Rate (hz)	Wash Col Supply FlowRate (hz)	R141b FlowRate (%)	R141b Flow Meter Inlet Press (psig)	Comments
11:47	8.5	17	5	38.2	39.06	39.69	36	64.77	62.5	6.25	3.9			
11:49	8.5	17	5	38.82	36.3	39.53	39.56	64.93	62.6	6.25	3.9	28	48	Top & lower injectors open
11:51														1st tiny crystal seen in
									62.6					clear line below S.D.
11:53	8.5	17	5	36.65	38.34	39.4	38.09	64.93		6.5	3.9	29	52	Shut upper injector @ 11:55
														System started to freeze up.
														Shut down & check filters.
														Some crystals found on filters,
														RMB pump flow rate stopped.
														No explanation
														LWR sprayer only test
12:23	13.75	14	5	41.43	41.62	40.68	41.49	64.19	65.1	13	3.9	20	85	Lwr Sprayer only on
														Lots of crystal below S. D.
														Rtn flow meter still looks clean
12:27	Crystals below sea water decanter look like large wet snow forces													
	Sea Water decanter flow meter still clear													
12:29				41.92	42.08	41.3	42.17	64.73						Turn chiller back on
12:30	System starting to plug, turn R141b off, turn chiller off, remove filters @ 12:34													
	Set chiller slightly warmer													
12:40	15	13	5	39.22	41.04	42.54	39.3	64.64	65.7	16	3.9	19	85	Restart flow of R141b
12:42	Lots of large snow flakes being created below sea water decanter.													
12:43	16	12	3	42.36	41.81	42.8	42.8	64.63	65.8	17	3.9	20	85	Lots of large clumpy crystals
12:51	18	12	3	40.23	42.71	42.35	39.37	64.36	65.7	20	3.9	18	85	Tiny crystals in SWD FM
13:00	20	13	3	39.4	41.06	42.34	40.6	64.66	65.9	20	3.9	19	85	
13:04	Screw installed on wash column. Wash column flow = 20 hz													
13:06	20	13	2	39.8	42.7	42.5	38.73	64.81	65.9	20	2	17	85	Lots of Large crystals
13:11	Stop R141b supply													
14:27	Place 60 x 40 cres screen on wash column and restart chiller.													
14:39	16	16	6	40.7	40.6	43.66	42.15	65.28	66.1	17.5	2	20	85	Start flow of R141b lwr only
14:41	Still see only unreacted R141b (saw this before I started to inject)													
14:45	Crystals seen at pump below sea water decanter													Only traces of unreacted R141b
14:46	16	16	8	38.85	41.72	43.07	40.47	65.32	66.3	17	2	19	85	
14:51	Maybe some very small crystals coming through, mostly unreacted R141b													
14:54	Flow through sea water decanter flow meter looks flax colored													
14:59	Mostly unreacted R141b													
15:00	Stop flow or R141b													
15:10	Found ice cake at base of wash column													
15:26	Wash column ice rising													

FOURTH SEA WATER TEST

Time	Flow Rate Supply (GPM)	Lg Pl Fr Hx Outlet Press (psig)	Inlet Press DCC(psig)	DCC In T1 (Deg F)	DCC Out T2 (Deg F)	Hx In T3 (Deg F)	Hx Out T4 (Deg F)	Ambient Temp T5 (GPM)	Barrell Temp (Deg F)	Sea Water Decanter Overflow Rate (GPM)	Wash Col Supply FlowRate (nz)	R141b FlowRate (%)	R141b Flow Meter Inlet Press(psig)	Comments
11:01				39								20%		R141b opn
11:03												28%		Middle on
11:04														Crystals with some small globs
11:08	16.5	11		42.37	42.08	42.05	41.6	61.07		156PM	3.9	20%		Turn second sprayer off
														Turn chiller down to 34F
	Seeing lots of R141b marbles, no accumulation of clathrate in wash column but some in pipe form decanter. Will remove cover or lower holes and use screen. Gap in lower cover may be letting crystals through. Chiller now cycles off at T=38.5 & 04 at T1=41.3. Restart flow of R141b in lower only.													
11:41	106PM	12	40.53	39.29	43.29	41.99	41.99	61.26		7	3.9	20%	85	
11:41	106PM	12	8	40.53	39.29	43.29								
11:51	Notice crystals getting thi		8				41.47	61.49		7	3.9	20%	85	
11:52	126PM	11	8	40.47	40.04	42.26	39.89	61.65		7	3.9	18%	85	
11:57	12.56PM	12		41.81	40.5	42.06								
12:00	Note ice crystal ball (donut in decanter) up welling seen in center at 5 rows down from top of hole													
	pattern. Huge snow flakes						38.86	61.7		8.5	3.9	24%	85	
12:03	12.5	12	8	37.52	42.04	41.97								
12:06	Partially dry ice pack 3 rows down from top, sea water still bores a small hole through pack.													
12:07	Pack solid at 3 holes down from top									8.5	3.9	23%	85	
12:09	136PM	11	8	38.45	41.56	41.98	39.82	61.8						
12:16	It appears as if the last draining holes are now about 4 rows down													
12:30	Top row of holes on W.C. are weeping, packed 1/2" from top, appears to be dry for 2-3"													
12:37	16	9	2	41.84	41.72	42.49	41.7	62.28						
12:39	Began scraping clathrate off W. C.									11	3.9	85	209%	
13:01	14	10	5	41.84	43.2	44.32	42.39	62.13		5.5	3.9	0.85	18%	
	Thaw system out													
14:47	10	12	0	41.28	41.85	45.33	41	63.47		16	3.9	28	85	
15:12	17.5	11	0	41.4	40.6	43.77	41.95	63.14		9.5	3.9	22	85	

FIFTH SEA WATER TEST (AUGER)

Time	Flow Rate Supply (GPM)	Lg Pl Fr Hx Outlet Press(psig)	Sea Water Decanter Inlet (psig)	Sea Water Decanter Inlet-T1 (Deg F)	Post R141b T2 (Deg F)	Hx In T3 (Deg F)	Hx Out T4 (Deg F)	Ambient Temp - T5 (Deg F) (T/C)	Barrel Temp (Deg F)	Sea Water Decanter Overflow Rate (GPM)	Wash Col Supply FlowRate (hz)	R141b FlowRate (%)	R141b Flow Meter Inlet Press (psig)	Comments
8:13	9	16	0	39.22	39.45	41.06	39.99	65.7		0	21hz	0	0	Pretest
														8:18 - R141b injection started
8:19												20%	85	Start R141b
8:21	Note: Crystal coming through 40 mesh screen in sea water decanter.													
8:25														
8:26				38.96	39.73	39.65	36.27	66.2		0	19	20	85	
8:29	Wash column overflowing with water. Note: Crystal starting to 15hz.													
8:33	10hz sea water still overflowing wash column.													
8:35														
	Large quantity of crystals being p8ulled through wash column and into sea water decanter.													
8:38	Speed of auger is having little or no effect.													
8:40	18	18	0	43	42.88	48.72	41.62	65.7		0	10	18	85	Lots of crystals everywhere.
	With 50 micron filter.													
8:42	Discontine R141b injection													
	50 micron filter found full of crystals, screen slid up on column and it quit overflow, liquid level 7 rows from top holes.													
10:05	6	17	0	38.71	38.97	49.55	38.41	70.6		4.5	4	0	0	Pretest
10:08	6	18	0	38.47	38.69	49.14	38.21	70		4.5	4	20	85	Start flow; note fog below sea D
10:16	6	18	0	37.47	37.63	47.66	37.08	70.2		4.5	4	20	83	All holes covered in W. C.
10:21	4.5	18	0	34.77	35.23	45.85	45.7	70.6		4.5	4	20	83	
10:24	6													Open flow on supply to maintain 6
10:26	Stop R141b flow rate because sea water decanter getting to cold.													
10:32	Restart injuecting R141b Sct supply valve. Back 4 - 6 6Pm mark													
10:33	10	20	0	36.58	37.42	46.32	31.4	69.9		0	4	20	83	
10:41	20	17	0	37.04	38.76	43.5	36.48/	70.4		4.5	4	20	85	
10:43	20	18	0	39.14	39.42	43.29	39.01	71.2		4.5	5	20	85	Increase flow rate to WC because it is freezing.
	System froze up - have to thaw out.													
	System thawed out, line from wash coluymn cut and put into tank.													Start R141b flow
13:32	16	16	0	41.4	42.66	48.7	41.15	74.7		6.5	4	20	85	Very fine crystals below decanter
14:44														R141b on
	System plugged with crystals, expecially right at injector.													
	Put filter basket into system (blue drum)													
16:01	12	12	0	37.96	38.91	42.1	37.64	75.4		14	4	20	85	Start new test
16:30	Slight flow through top of WC flow meter plugged, reset SW decanter pump to 2 hz- got wet clathrate out of wash column, system froze up.													
	Thaw system out; set chiller to cycle at warmer temps													
21:25	10	10	0	39.61	40.37	42.95	40.92	68.9		18	2	20	78	Start flow
21:30	10	10	0	41.35	41.7	42.63	40.43	68.6		18	2	19	72	
21:35	10	10		41.11	41.62	44.7	40.95	68.6		17	2	18	70	
21:40				40.91	41.43	44.3	40.66	69.2		17	2	18	70	marbles & some sand
21:42	10	10	0	41.02	41.47	42.93	40.27	67.7			4	18	70	Set higher flow rate
													72	
21:50	Set chiller slightly colder due to few crystals.													
22:00		10	0	39.45	40.05	42.79	39.15	67.8		17	4	17		not much for crystals
22:03	Set chiller slightly colder was 39.2 - 41.5 of cycling													37.88 - 41.08
22:07	See Sloppy flakes starting to come down.													
22:11	10	10	0	39.25	43	41.81	38.04	68.9		18	4	15	70	
	R141b pump quits; watery crystals rising near top of wash column; 50 micron filter. Have a lot of crystals in them; crystals are all over the system.													