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UNITED STATES
DEPARTMENT OF THE INTERIOR

THE KOPPERS HYDRATE PROCESS
FOR SALINE WATER CONVERSION
EXPERIMENTAL AND ENGINEERING STUDIES



OFFICE OF SALINE WATER

RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 90

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RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 90

THE KOPPERS HYDRATE PROCESS FOR SALINE WATER CONVERSION
EXPERIMENTAL AND ENGINEERING STUDIES

BY

KOPPERS COMPANY, INC.

FOR

OFFICE OF SALINE WATER

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MARCH 1964

FOREWORD

This is another of a series of reports designed to present accounts of progress on saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea or other saline waters.

Except for minor editing, the data herein are as contained in a final report submitted by the Koppers Company, Inc., Pittsburgh, Pennsylvania, under Contract No. 14-01-001-204, covering project activities from June 1960 to June 1963. The data and conclusions given in this report are essentially those of the Contractor and are not necessarily endorsed by the Department of the Interior.

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SUMMARY AND CONCLUSIONS

This report covers the research and development work on the Koppers Hydrate Process which is based upon U. S. Patent 2,904,511 (1959) assigned to Koppers Company, Inc. This investigation, partially supported by the Office of Saline Water under Contract No. 14-01-001-204, was carried out from June 1960 to June 1963 by personnel of the Research Department of Koppers Company to establish the technical and economic feasibility of the Koppers Hydrate Process as a means of desalting sea water. Most of the work was carried out in bench-scale equipment including a 10-gallon reactor-crystallizer with a capacity equivalent to 150 gallons of potable water per 24 hours. In addition, some laboratory research was done on the hydrate forming reaction and calculations were made to evaluate the processing steps and to determine the order-of-magnitude of the production costs.

The Koppers Hydrate Process is a chemical process in which a hydrating agent, such as propane or dichlorodifluoromethane, and water combine to form insoluble crystals. The crystals are separated from the mother liquor by filtration, washed free of mother liquor and decomposed into two immiscible liquids: Liquid hydrating agent which is recycled and salt-free water.

Technical Feasibility

The major portion of this report describes the work that was done in laboratory and bench-scale equipment. This work proves the technical feasibility of the process using synthetic "sea water" and various hydrating agents, especially propane, to produce hydrate crystals. Filtration studies show it is feasible to wash the crystals sufficiently free of brine so that, upon decomposition by contact with relatively hot vapors of the agent, potable water can be produced.

A great many experiments were made on this general process outline so that the important process variables were investigated on batch and continuous hydrate formation, batch washing and batch decomposition.

Batchwise filtration and washing experiments were made using various hydrate crystals as well as sand so that filtering and washing equipment could be evaluated in comparison with work reported in the literature. Consistent results were obtained with the sand and various hydrate crystals through a 12" square filter using various bed depths. Large-scale filtration and washing experiments were conducted using sand in a 5.5 ft. diameter compartment of special design with beds 24 inches deep. Performance of the equipment agreed with that expected from the literature. The work with sand was not repeated on a large scale using hydrate because the contract did not provide for hydrate formation on this scale of operation. However, the 5.5 ft. diameter compartments are the size recommended for a 10,000 gallon per day pilot plant as well as commercial plants up to approximately 250,000 gallons per day. Beyond this capacity the diameter would be increased.

Economic Feasibility

The Koppers Hydrate Process has an inherent flexibility related to the physical properties of a wide range of hydrating agents and dependent upon the temperature and pressure chosen for use with any particular agent. This flexibility offers possibilities for cost reductions.

As an example, if the incoming sea water is available at a temperature lower than the hydrate reactor temperature (i.e., sea water at 60°F or lower, using ethyl fluoride as agent in a reactor at 65°F) the energy consumption for refrigeration would be small compared to that used in the above estimate. The decomposition would be conducted at a low temperature using a waste heat source (100°F or higher).

The demonstration of the flexibility and the solution of most of the problems connected with filtration and washing of hydrate, as accomplished under this contract by the Koppers Research Department, justify the expectation that the Koppers Hydrate Process will develop into a saline water conversion system which will be economically attractive for many years.

Recommendations for Further Work

Based on the work in this report, it is recommended that the U. S. Government erect a 10,000 gallon per day pilot plant at Wrightsville Beach to demonstrate, on a larger scale and on a completely integrated basis, the hydrate process for potable water production with special attention given to the following:

- a) In the bench scale work, the crystal filtration and washing steps were conducted batchwise because of the limited rate of crystal production. A mathematical model and computer program were developed to relate the batch data to a projected multi-stage, counter-current procedure which would greatly reduce the wash water usage. The pilot plant is designed to test the latter procedure.
- b) Decomposition studies should be made with the present system (condensation of gaseous hydrating agents in the washing compartments) as well as with alternate procedures.
- c) Studies of hydrate formation will be performed in a vertical cylindrical reactor with a turbine agitator and in another type of crystallizer-reactor which will be chosen later.
- d) Evaluation of pilot plant data will result in production cost predictions for larger scale operation under standard conditions as well as for conditions especially favorable for the Koppers Hydrate Process.

1. INTRODUCTION

In 1959 Koppers Company was assigned U. S. Patent 2,904,511, by W. Donath, which discloses the use of gas hydrates for the desalination of aqueous saline solutions. The method described in this patent consists of combining a hydrating agent and an aqueous solution to form an insoluble hydrate. The hydrate crystals are separated from the mother liquor and are washed free of salts. The resulting pure hydrate is decomposed into hydrating agent and pure water.

A preliminary experimental and engineering investigation was carried out by Koppers to explore this process in greater detail. This investigation showed that propane could be used as the hydrating agent and that propane-hydrate crystals could be washed free of dissolved salts.

Based upon the results of this initial study, the Office of Saline Water, U. S. Department of Interior, contracted with Koppers Company to perform experimental and engineering studies for the purpose of establishing the technical and economic feasibility of the Koppers Hydrate Process as a means of desalting sea water.

This report summarizes the research and development work carried out by the Research Department of Koppers Company during the period June 1960 to June 1963 under Contract No. 14-01-001-204.

2. THE NATURE OF GAS HYDRATES

Berthollet found in 1785 that chlorine gas produces a crystalline yellow precipitate with ice cold water. Davy identified this product in 1810 as chlorine hydrate. Subsequently Villard and de Forcrand^{1/} showed that many gases and volatile liquids are capable of forming similar hydrates. Even though a considerable amount of research on hydrates had been done in the last part of the 19th century, the chemical structure of gas hydrates has only recently been elucidated through X-ray diffraction work by von Stackelberg and his school.^{2/} Claussen^{3/} also played an important part in clarifying the structure of gas hydrates. Gas hydrates belong to a type of compound known as clathrates. The word clathrate, coined by Powell^{4/}, applies to those compounds "in which two or more components are associated without ordinary chemical union, but through complete enclosure of one set of molecules in a suitable structure formed by another."

2.1 Structures of Gas Hydrates

Simple hydrates crystallize in either of two cubic lattice structures.* There is a structure, designated by von Stackelberg as Structure I, which has a unit cell consisting of 46 water molecules enclosing two nearly spherical cavities which have a free diameter of about 5.2 Å and six larger and slightly oblate cavities having a free diameter of approximately 5.9 Å. Small hydrating molecules (such as Ar, Kr, H₂S, CO₂, CH₄, etc.) are capable of occupying all 8 cavities, and the formula of the hydrate when all cavities are occupied is 8M·46H₂O, i.e. M·5.75H₂O. Slightly larger molecules, such as CH₃Cl, CH₂FCl, CH₃Br, etc., fit only into the larger cavities, and the resulting hydrate has a theoretical formula of 6M·46H₂O, i.e. M·7.67H₂O.

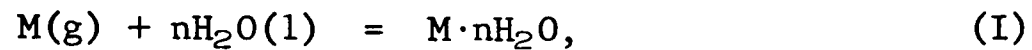
Another structure (Structure II) arises with hydrating agents whose molecules are too large to fit into the voids of the Type I lattice (e.g. C₃H₈, CF₂Cl₂, CFC₂Cl). The unit cell of Structure II comprises 136 water molecules enclosing 8 cavities with a free diameter of about 6.9 Å and 16 small cavities with a free diameter of about 4.8 Å. Type II hydrates have the formula 8M·136 H₂O or M·17H₂O when all large cavities are occupied. Excellent and more detailed discussions of the structure of gas hydrates have been presented by von Stackelberg and Müller^{2/}, van der Waals and Platteeuw^{6/}, and Barduhn^{7/}. van der Waals points out that "a common feature of all clathrates is a host lattice, by itself thermodynamically unstable, which is stabilized by the inclusion of the second component." He regards a clathrate compound as "a solid solution of the second (guest) component in the (metastable) host lattice."

- - - - -

* Allen and Jeffrey recently reported^{5/} that bromine hydrate is an exception and crystallizes in a tetragonal structure with a unit cell composed of 172 water molecules and containing 20 polyhedral cavities large enough to accommodate Br₂-molecules.

2.2 Composition of Gas Hydrates

If clathrates are considered as solutions, it is meaningful to speak of their composition only when the temperature and pressure at which they have been formed are defined. The variation in the composition of gas hydrates can be quite appreciable. Barduhn^{7/} has proved that the Clapeyron equation applies to the hydrate-gas-water equilibrium of simple hydrates even though this equilibrium involves more than one component. This equilibrium corresponds to the equation:



in which M symbolizes the hydrating agent. In the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad (II)$$

as applied to hydrates, dP/dT is the slope of the hydrate equilibrium line at conditions (P, T), ΔH is the change in enthalpy and ΔV is the change in volume involved in reaction (I). The term ΔV for reaction (I) is, at low pressure, approximately equal to the volume of one mole of gaseous M at (P, T), since the difference in volume between n moles of liquid water and one "mole" of hydrate is small by comparison with the volume of the gas:

$$\Delta V \cong V \quad \text{and} \quad V = \frac{zRT}{P} \quad (III)$$

where z, the compressibility factor of the gas measures the deviation from the perfect gas law.

The term ΔH can be replaced by $n \times \Delta h$, where Δh is the change in enthalpy for reaction (I) per mole of water and n is the number of moles of water reacting to form one "mole" of hydrate. Substituting in the Clapeyron equation:

$$\frac{dP}{dT} = \frac{n \Delta h}{zRT^2/P} \quad (IV)$$

which integrates to:

$$\ln P = - \frac{n \Delta h}{zRT} + C, \quad (V)$$

in which C is the integration constant. Hence on a log P vs. $1/T$ plot, the hydrate equilibrium line is straight only when $n \Delta h/zR$ is constant, i.e. when $n \Delta h/z$ is constant. Since for many hydrating agents, z varies considerably along the hydrate equilibrium line, there is no theoretical reason to expect that the hydrate equilibrium line would be straight on a log P vs. $1/T$ plot. The value of n is also not a constant. Near the critical hydrate point, the hydrate lattice is nearly completely filled, but as one moves to lower pressures, an increasing fraction of the cavities becomes vacant, i.e. n increases. This is expected from theoretical considerations^{6/} and it has

recently been confirmed by A. van Cleef^{11/} who found for the composition of nitrogen hydrate at 9°C: $n = 5.7$ moles of H_2O and at 0°C: $n = 6.0$ moles of H_2O .

2.3 Prediction of Critical Properties of Hydrates

Stackelberg^{2/} derived an approximate equation to calculate the equilibrium pressure of hydrates as a function of temperature. Barduhn^{7/} extended this work by deriving an expression for the critical hydrate temperature. This is the highest temperature within the pressure range under consideration at which the hydrate is thermodynamically stable. Barduhn points out that several assumptions had to be made in the derivation and application of this equation and concludes that it is of qualitative rather than quantitative usefulness.

We have found that an approximately linear correlation exists (Figure 1) between the logarithm of the critical hydrate pressure (P_c) (this is the decomposition pressure of the hydrate at the critical temperature when liquid and gaseous agent are present) and the normal boiling point of the hydrating agent (T_b). Within the limits of accuracy of this correlation, it applies to hydrates of both structures. Knowing the critical hydrate pressure, the corresponding critical hydrate temperature can, of course, be readily estimated from vapor-pressure data of the hydrating agent.

The central line of Figure 1 permits an approximate prediction of the critical pressure of any hydrate. Somewhat better estimates are possible by noting certain trends on Figure 1. Straight-chain hydrocarbon molecules (ethane, propylene, propane) tend to fall near the lower limit of the band, i.e., they have relatively low critical hydrate pressures. Ethylene is not shown on this figure. The work of van Cleef and Diepen^{12/} indicates that ethylene does not exhibit a critical hydrate point, since, at the critical pressure of ethylene, the hydrate equilibrium temperature is higher than the critical temperature of the gas. Spherical or nearly spherical molecules with no permanent dipole (chlorine, bromine, cyclopropane, etc.) tend to cluster around the central line. Polar molecules such as H_2S , H_2Se and C_2H_5F lie near the upper limit, i.e., have higher critical hydrate pressures. The presence of a double or triple bond in a molecule also makes hydrate formation more difficult, thus the critical pressure of acetylene is near the central line whereas that of ethane is near the lower limit. Isobutane does form a hydrate, but isobutene does not.

Trends within homologous series of compounds can also be detected on Figure 1. Thus the critical pressure of refrigerant-11 (CCl_3F) is above the central line and that of refrigerant-12 (CCl_2F_2) is below the central line. If we draw a line through the refrigerant-11 and refrigerant-12 points and extend it to the boiling point of refrigerant-13 ($CClF_3$), we predict that its critical pressure should be considerably lower than that predicted by the central line, and indeed, preliminary laboratory experiments performed at the Koppers Research Laboratories with refrigerant-13 have confirmed this. Similarly, the points corresponding to $CHCl_3$, CH_2Cl_2 and CH_3Cl lie on a straight

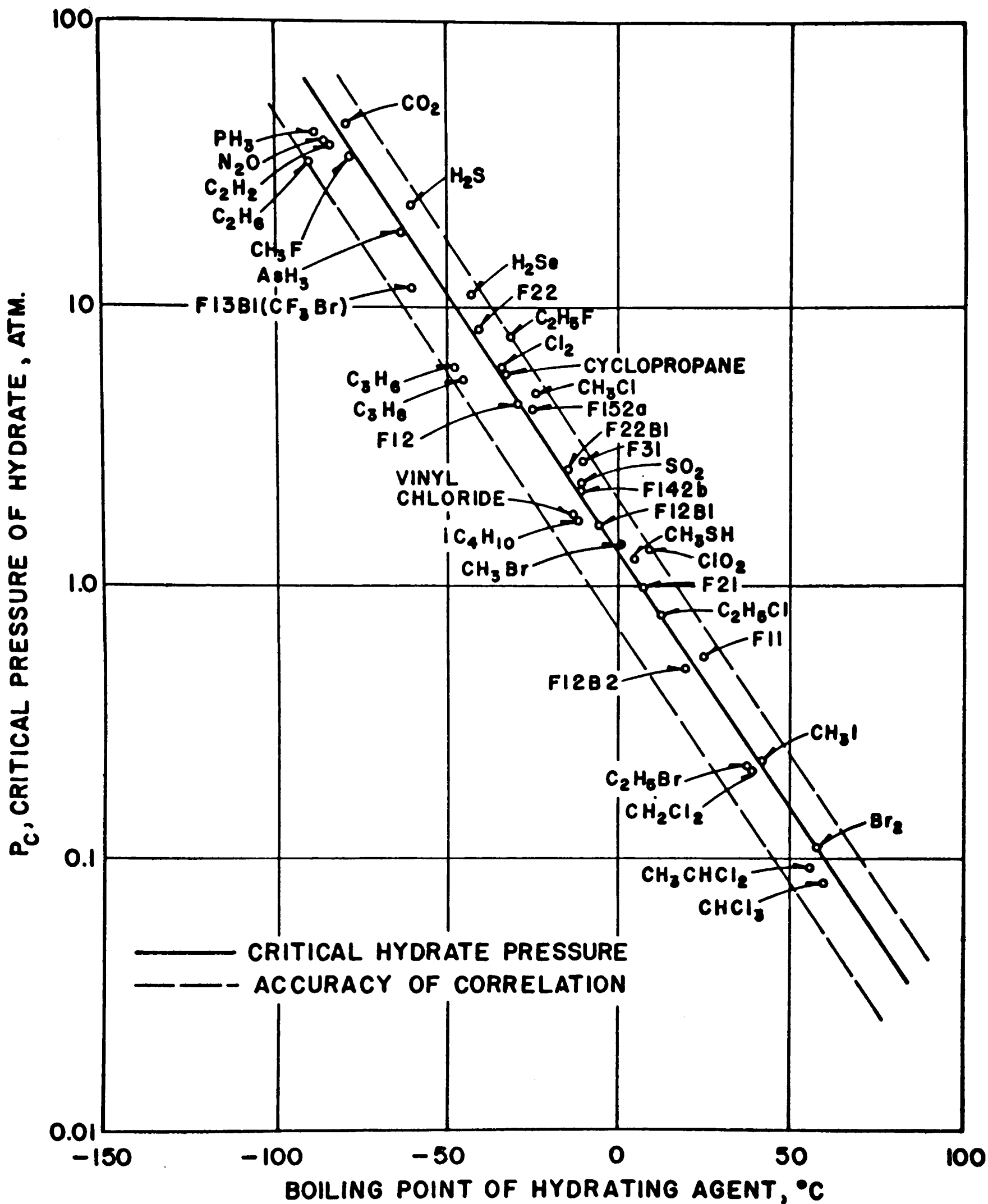


FIGURE 1
CRITICAL PRESSURE OF GAS HYDRATES

line, as do those of C_2H_5Br , C_2H_5Cl and C_2H_5F , and those of CH_3F , CH_3Br and CH_3I ; but the point for CH_3Cl lies considerably above the line joining the other mono-halogenated methanes.

No hydrates are known for substances with boiling points higher than approximately $60^\circ C$. This phenomenon has not yet been explained. There are many other compounds having molecules of the appropriate size and boiling point which do not form hydrates (e.g. NH_3). Although this has not yet been clarified, it seems that compounds which are strongly hydrated in solution cannot form gas hydrates. Ionized compounds can only be incorporated in hydrate structures in exceptional cases.^{9/}

2.4 Other Properties of Hydrates

Barduhn^{8/} presents equations to calculate the densities of gas hydrates having a full lattice. Most gas hydrates are heavier than water, but a few (e.g. propane hydrate) are lighter.

Gas hydrates are generally precipitated from an aqueous phase when water is contacted with the hydrating gas at a temperature lower than the critical formation temperature (between 0° and approximately $30^\circ C$, depending on the hydrating agent) and at a pressure higher than the equilibrium pressure. This equilibrium pressure decreases with temperature and depends on the hydrating agent. If a hydrate decomposes (this can take place at a temperature higher than the critical temperature or at a pressure that is too low for equilibrium), the heat effect per unit weight of water is of the same order of magnitude as that for the melting of ice.

If one tries to form hydrate using pure water and a gaseous hydrating agent under conditions at which the hydrate is thermodynamically stable, the formation is frequently strongly retarded. The formation is however catalyzed by small amounts of ice or hydrate. It appears that in a clean system it is almost impossible to form hydrate from gaseous propane and water without using a nucleating agent such as ice or hydrate^{10/}. Small amounts of hydrate "condition" the system so that hydrate formation and spontaneous nucleation will take place everywhere in the solution. It is remarkable that this "conditioned" state of the aqueous phase is preserved for many hours after a propane hydrate slurry has been decomposed completely by decreasing the pressure. Heating the clear aqueous phase above the critical decomposition temperature destroys this conditioned state. Bubbling nitrogen under low pressure through the cold solution has the same effect. However, gaseous propane hardly influences the system under similar circumstances.

The effects described are pronounced only when the solubility of the hydrating agent in water is low. A hydrating agent such as refrigerant-21 (CH_2Cl_2) is so soluble that the retardation of nucleation cannot be demonstrated.

Dr. C. M. Adams found^{10/} that the decomposition of propane hydrate is very slow when the hydrate is in contact with liquid water only and not

with the gas phase. He submerged propane hydrate in water of +2°C and heated the hydrate slowly to about 9°C (almost 4° over the critical formation temperature) at a pressure much lower than the critical decomposition pressure. Under these conditions, he did not obtain any gas bubbles, but observed after a certain time that the cold water suddenly gelatinized (with the exception of the top one-inch layer which was in contact with the gas phase, and which remained liquid). These experiments suggest that propane hydrate might dissolve into a partially dissociated state and form a metastable solution.

Gases such as methane, ethane and ethylene which do not exhibit critical hydrate points, because the critical temperatures of the gases are too low, have remarkably stable hydrates at high pressures. Recent high pressure research at Rice University^{13/} indicates that methane hydrate is stable at a temperature of 50°C when the pressure is several thousand atmospheres and it is possible that higher pressures will stabilize this hydrate at temperatures over 50°C. This could suggest that locations might exist on this earth with temperature and pressure conditions under which natural occurring gases could form hydrates.

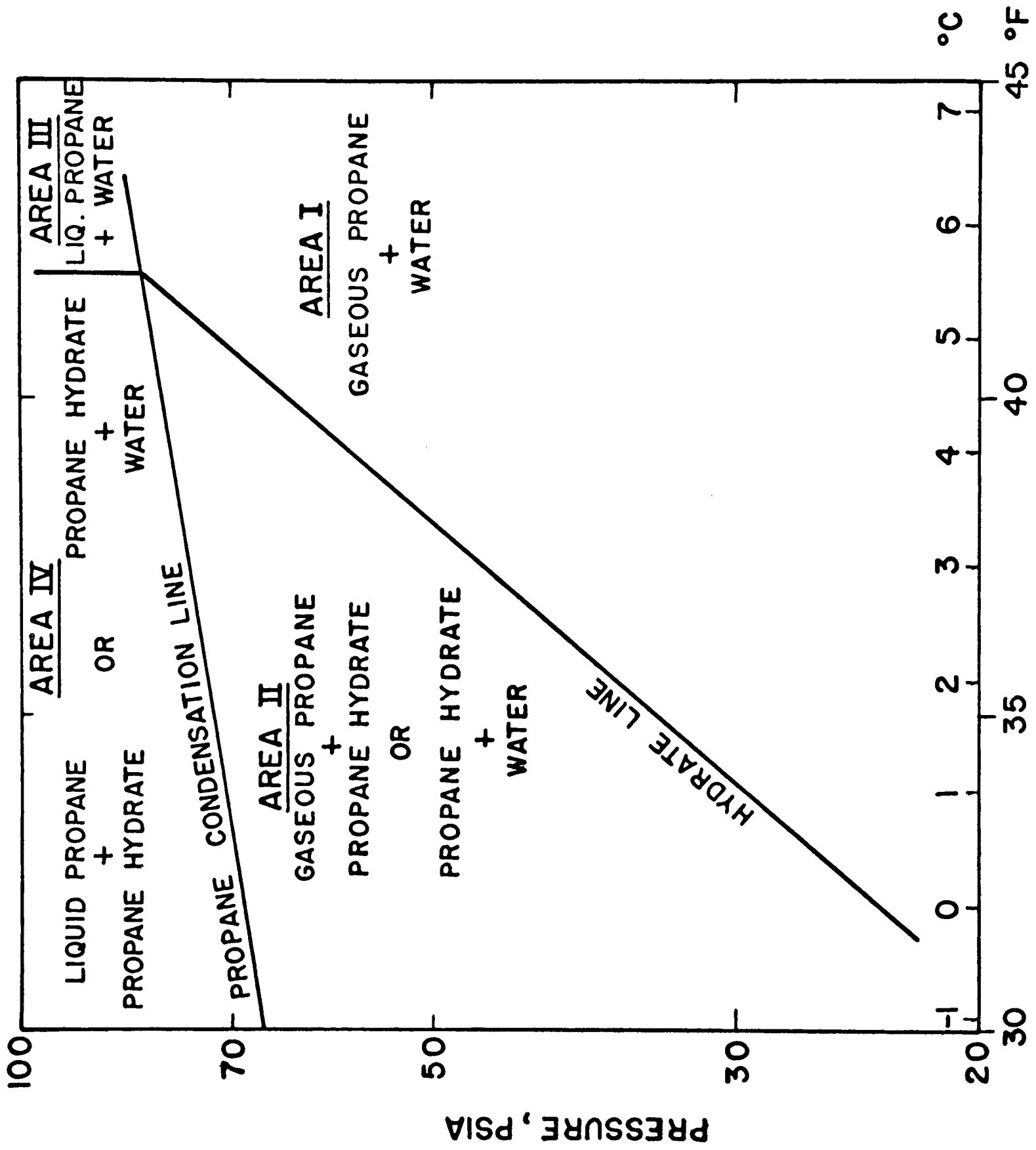
2.5 Selection of Hydrating Agent

Initially propane was selected as the hydrating agent for the experimental work because it possesses a number of desirable features: it is readily available, inexpensive, and non-toxic; its solubility in water is low, so that it can be readily recovered; it can be used as a direct heat transfer medium, thereby eliminating the use of heat exchangers to remove the heat of hydrate formation; and preliminary experiments indicated that propane hydrate forms at a useful rate.

Later in the program, other hydrating agents, such as dichlorodifluoromethane (refrigerant-12), were studied in detail, mainly to gain a better understanding of the factors governing the rate of formation and the characteristics of hydrate crystals. Some of these compounds are capable of forming hydrates at higher temperatures and lower pressures than propane and do not form explosive mixtures with air. The possibility of using different hydrating agents under different circumstances is an important advantage of the Koppers Hydrate Process. Several of the hydrating agents, which have been investigated, are satisfactory for saline water conversion. At this time, it is not possible to state that any one of these agents is clearly superior. It is likely that local conditions, such as sea water temperature, cost and availability of a particular hydrating agent, etc., will be important for the selection of the hydrating agent for each particular commercial installation. It is also quite possible that further research will uncover hydrating agents that are superior to any hydrating agent known today.

2.6 The Phase Diagram of Propane Hydrate

The phase diagram^{14/ 15/} which has been verified in this laboratory, is illustrated in Figure 2. The slightly inclined line, labeled as the propane



TEMPERATURE
 °C °F
 FIGURE 2
 DIAGRAM FOR PROPANE HYDRATE

condensation line, is the vapor pressure curve for propane. The steeply inclined and the vertical lines are known as the hydrate lines. To the right of these lines in Areas I and III, hydrate does not occur and only liquid water exists in the presence of either gaseous or liquid propane. To the left of the hydrate line, in Areas II and IV, all water is converted into hydrate if an excess of propane is present, or all propane is converted into hydrate if an excess of water exists.

When propane is introduced at constant pressure into a propane-water system in Area I, and heat is removed from the system, the temperature will fall until the system reaches the hydrate line. If more heat is removed the temperature will stay constant while propane hydrate is being formed. Upon complete conversion of either component, the temperature will continue to fall.

The quadruple point where the hydrate lines cross the propane condensation line gives the conditions under which liquid propane, gaseous propane, liquid water, and propane hydrate can co-exist. The corresponding temperature and pressure are commonly designated as the "critical decomposition temperature" and "critical decomposition pressure."

The effect of salt on the phase diagram as determined at the Koppers laboratories is shown in Figure 3. The addition of salt to the system has the effect of shifting the quadruple point along the condensation line with a resultant parallel shift of the hydrate lines.

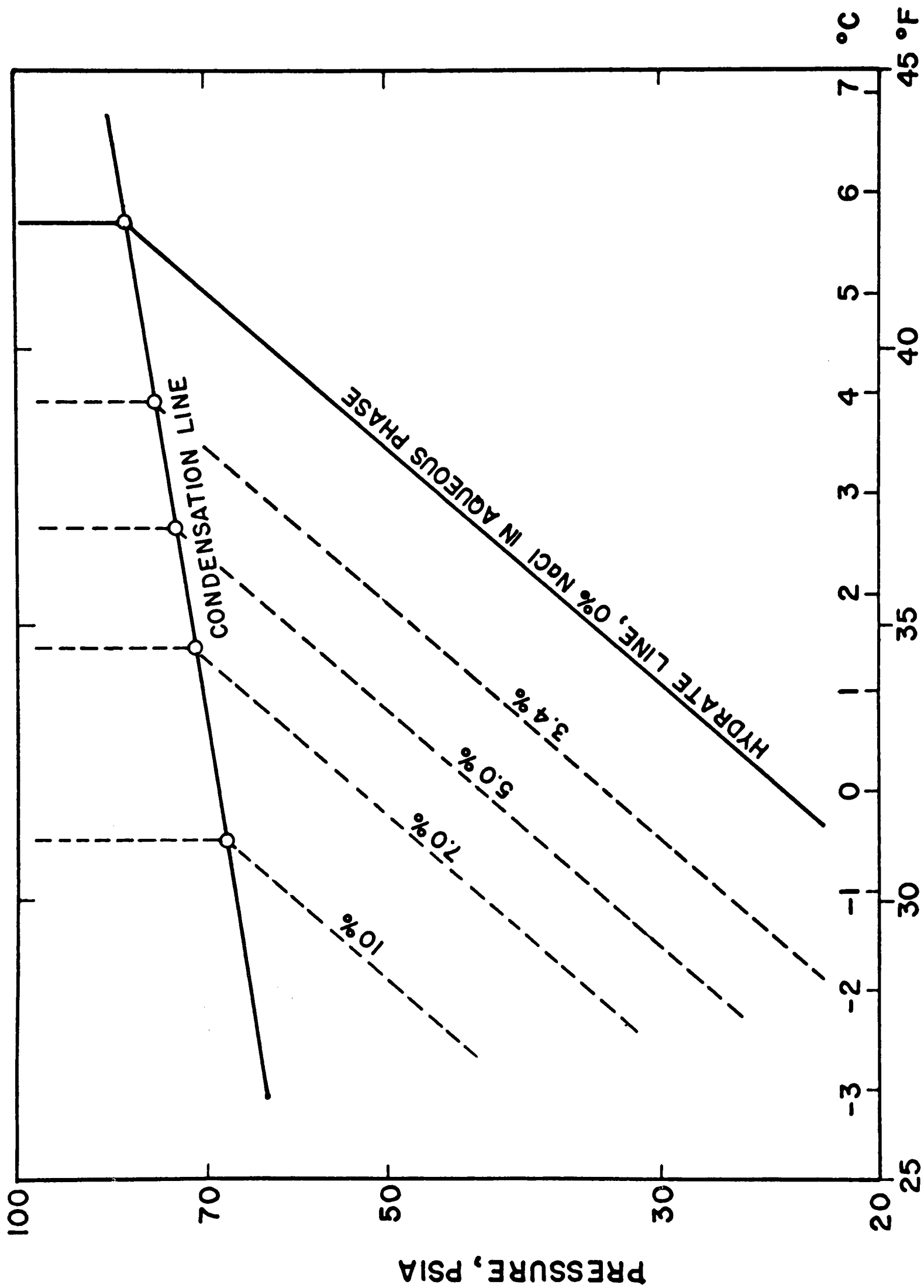
2.7 Process Description

In the Koppers Hydrate Process, a hydrating agent and water combine to form an insoluble hydrate. The resulting hydrate crystals are separated from the mother liquor by filtration, washed and decomposed to form salt-free water as well as liquid hydrating agent, which is recycled to the reactor.

Figure 4 presents a simplified material balance for a commercial plant using propane as the agent and producing 10 million gallons of potable water per day using a continuous process. The reactor or hydrate formation vessel operates at about 35°F and 57 psig and the decomposition vessel operates at about 45°F and 70 psig. The temperature range in the washer of 35°F to 45°F eliminates the possibility of freezing the wash water and of plugging the washer. Figure 4 is based on 40 per cent of the sea water feed being converted into potable water.

The flow streams for this process are shown in Figure 5.

Sea water is pumped into the process and is cooled by heat exchange with the product water and the effluent brine. It is then fed into the hydrate reactor where it comes in contact with the hydrating agent and is partially converted into solid gas hydrate. The heat of reaction is removed by the evaporation of an equivalent amount of liquid hydrating agent. A pressure control in the gas outlet line keeps the reaction temperature at



TEMPERATURE
 FIGURE 3
 PHASE DIAGRAM FOR PROPANE HYDRATE

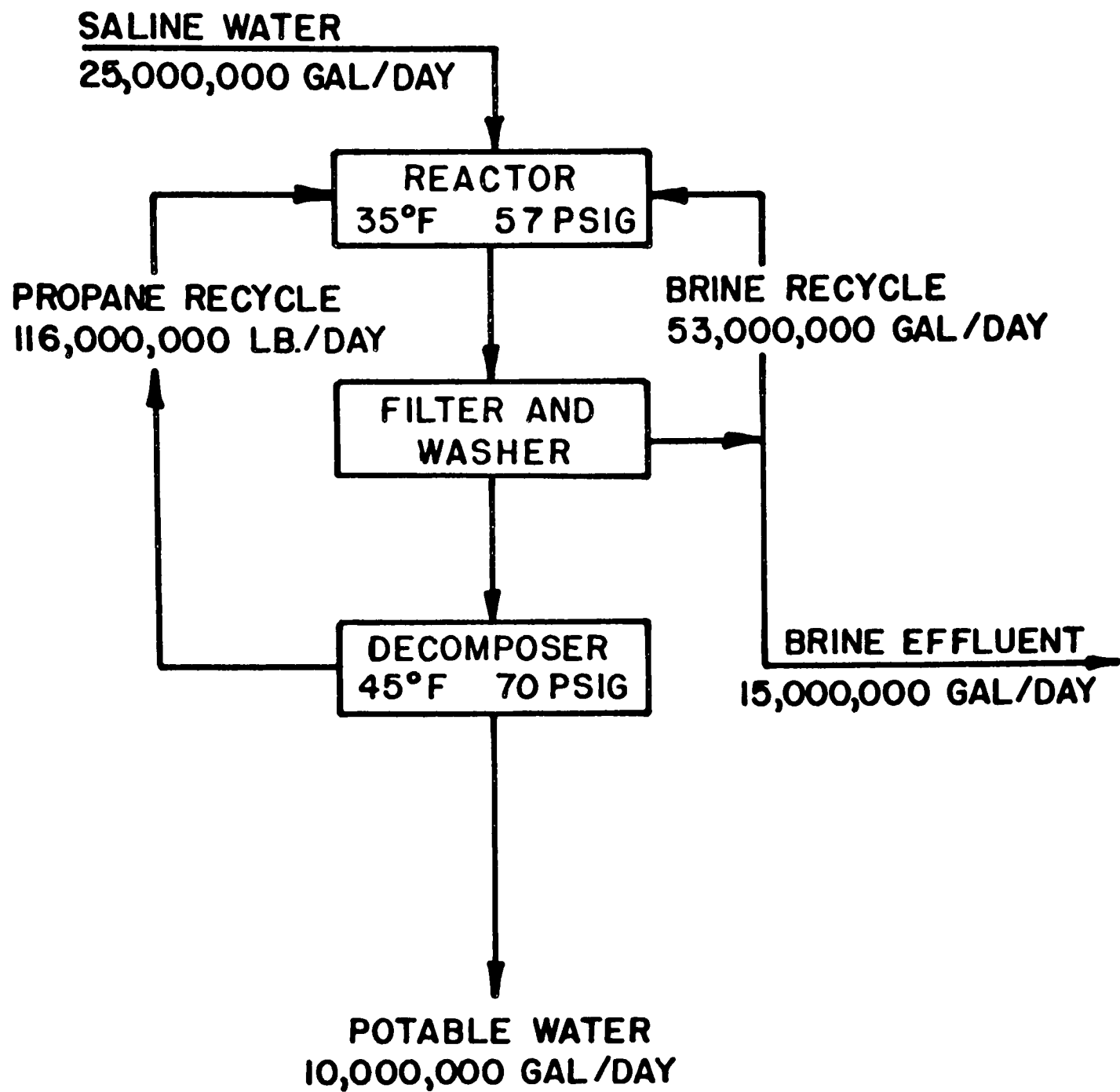


FIGURE 4
SIMPLIFIED FLOW DIAGRAM
COMMERCIAL PROPANE HYDRATE PROCESS
FOR POTABLE WATER

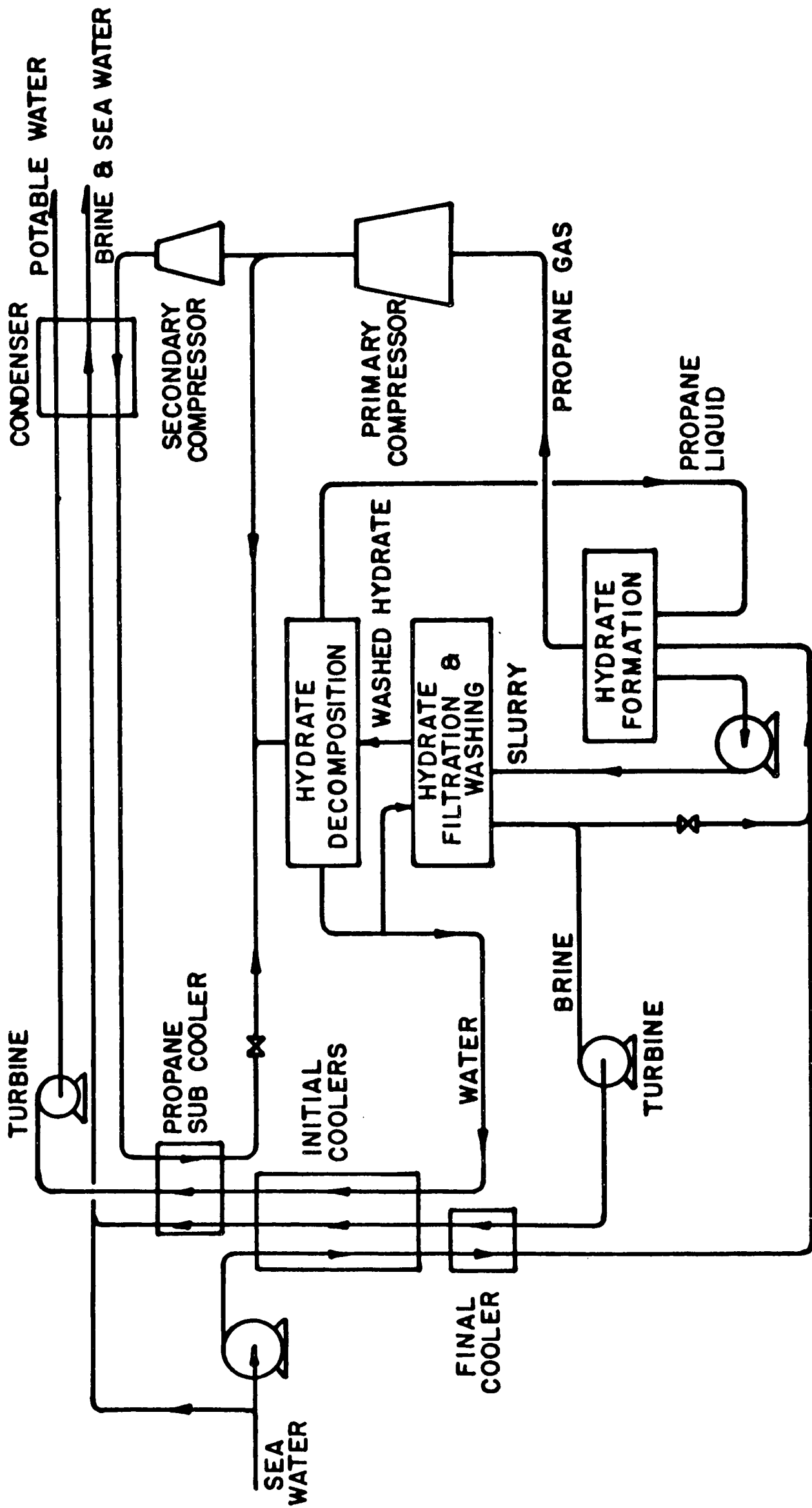


FIGURE 5
PROPANE HYDRATE POTABLE WATER PROCESS

the required level. A slurry containing hydrate crystals is transported to the filter-washer where washed hydrate crystals and brine are produced. Part of the brine is recycled to the reactor and the remainder is discharged as an effluent after heat exchange with both the inlet sea water and the propane recycle system. The recycled brine is required to maintain the slurry concentration at a level low enough to permit the slurry to be readily transported and at the same time allow an overall conversion which could be as high as 40 per cent of the incoming sea water. The washed hydrate crystals are moved to the decomposer where product water and liquid agent are produced. The product water is discharged after heat exchange with both the inlet sea water and the propane recycle system. Liquid agent is recycled to the reactor.

The refrigeration system consists of two stages--a low-temperature primary system and a high-temperature secondary system. Heat liberated in the reactor by the formation of hydrate vaporizes the agent. The vapor, plus additional vapor generated by heat leaks into the system, is compressed in the primary compressor. Most of the vapor leaving this compressor flows to the hydrate decomposition equipment where it condenses, providing the heat of decomposition of the hydrate.

Excess vapor discharged by the primary compressor is further compressed in the secondary compressor. The compressed vapor is condensed and cooled by heat exchange with the potable water product, the brine effluent, and additional sea water. Heat removed by the additional sea water represents the energy used by the compressors, heat leaks into the system, and temperature differences between feed and products.

There are many problems associated with the transport of large volumes of water, the recovery of heat, the compression and recycle of hydrating agent, the clean-up and preparation of the inlet sea water, the degasification of the potable water, etc. Most of these problems can be handled by established engineering techniques. The problems associated with the formation, washing and decomposition of the hydrate crystals have been the major subject of the experimental efforts. The rate of hydrate formation, the rate of crystal growth, washing characteristics of hydrate beds, and the condensation rate of propane vapor on hydrate crystals, are examples of the variables which have been studied on bench scale.

3. BENCH SCALE EQUIPMENT

A majority of the experiments in the bench unit were carried out using propane as the hydrating agent; the following description of the equipment and its operation is based on the use of propane. With minor modifications, the system was also used to investigate other hydrating agents. These latter studies are discussed in Section 8, "Hydrating Agents Other Than Propane."

A 10-gallon Pfaudler kettle equipped with a variable speed, three-bladed, retreating blade agitator was used for the hydrate reactor. Auxiliary equipment included: a product heater and rotameter, a feed tank, a feed pump and rotameter, a feed cooler, liquid propane supply tanks, a liquid propane rotameter, and a back-pressure control valve. Figure 6 is a simplified flow diagram of the bench-scale apparatus and Figure 7 is a photograph of the equipment.

Salt water was pumped from the feed tank through the cooler where its temperature was reduced to about 0.1°C above the reaction temperature. Liquid propane joined the salt water feed stream after the cooler and the mixed stream entered the reactor. Hydrate slurry which was formed continuously was removed from the bottom port of the reactor and flowed through the product heater to the feed tank. A fixed charge of salt water was maintained in the reactor and the reaction time was controlled by adjusting the salt water feed rate. The hydrate in the slurry was decomposed in the heater. Salt water was recycled to eliminate the preparation and storage of large quantities of salt water. Gaseous propane, flashing from the brine, was vented to atmosphere from the feed tank. Propane, which was vaporized in the reactor, vented through the back-pressure control valve. The hydrate formation temperature was controlled by adjusting the pressure in the reactor. The temperature of the slurry could be held to $\pm 0.1^{\circ}\text{C}$. A coolant held within 0.1°C of the reaction temperature was pumped through the reactor jacket to simplify the temperature control.

Brine samples were withdrawn from the reactor through a small tube containing a filter. The amount of hydrate in the slurry was calculated from a material balance based on the salt content of the brine. Salt analyses were determined with a conductivity bridge (Model RC-16B of Industrial Instruments, Inc.). Two conductivity cells used with the bridge made it possible to measure salt contents in the range of 10 to 100,000 ppm.

Artificial sea water or artificial sea water brine was used in all of the experimental work carried out in the bench unit. The composition of the artificial sea water was based on the analysis of "normal" sea water, a standard solution distributed to oceanographic institutes by the Hydrographic Laboratories of Copenhagen, Denmark.^{16/} The following table shows the analysis of normal sea water and the composition of the artificial sea water used. The normal water contains an additional 43 ppm of trace elements such as strontium, fluorine, iodine and silicon which are not shown. The salts listed in the right hand column give the same ion concentrations as shown in the other column except that Cl^- is 63 ppm higher.

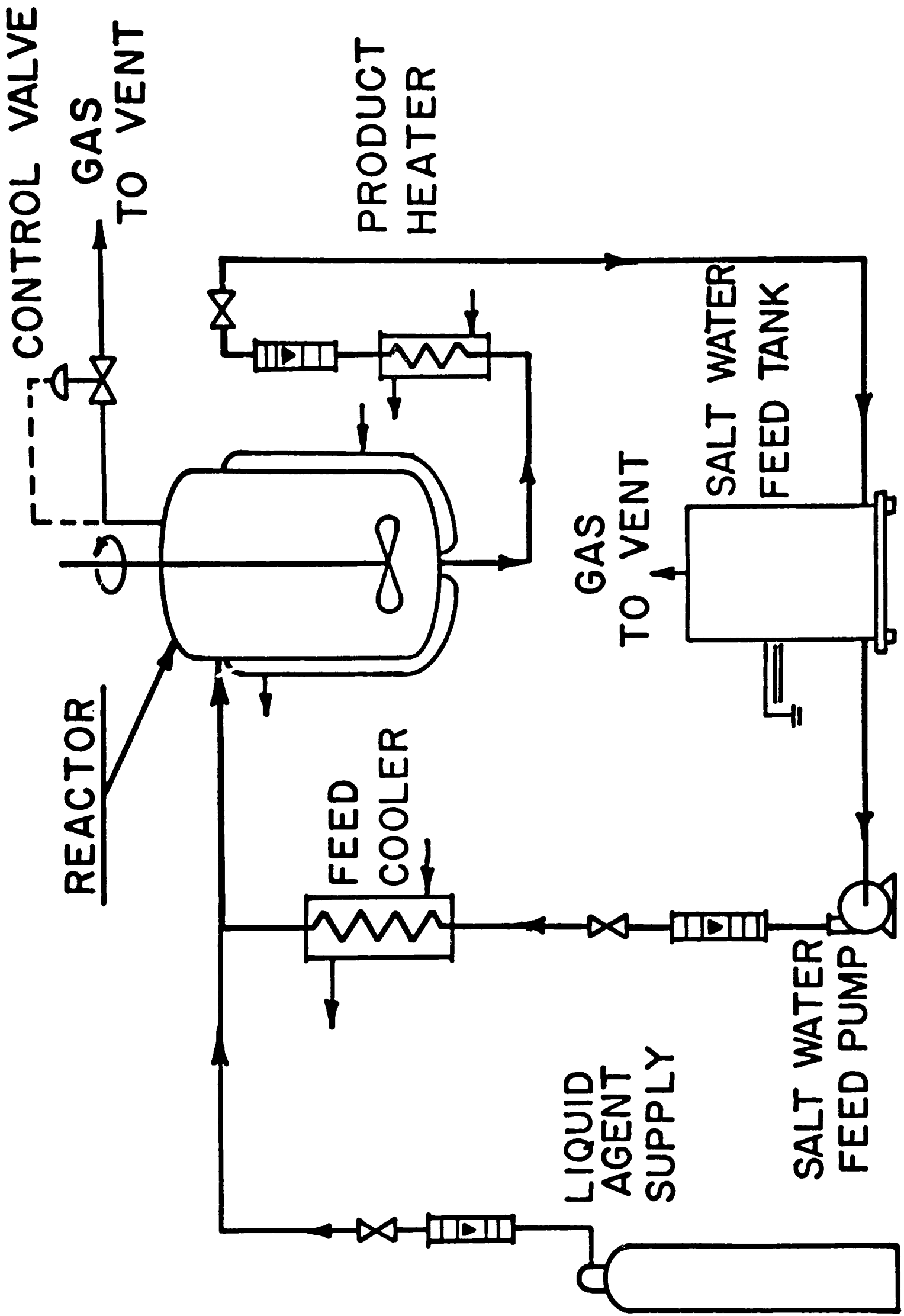


FIGURE 6

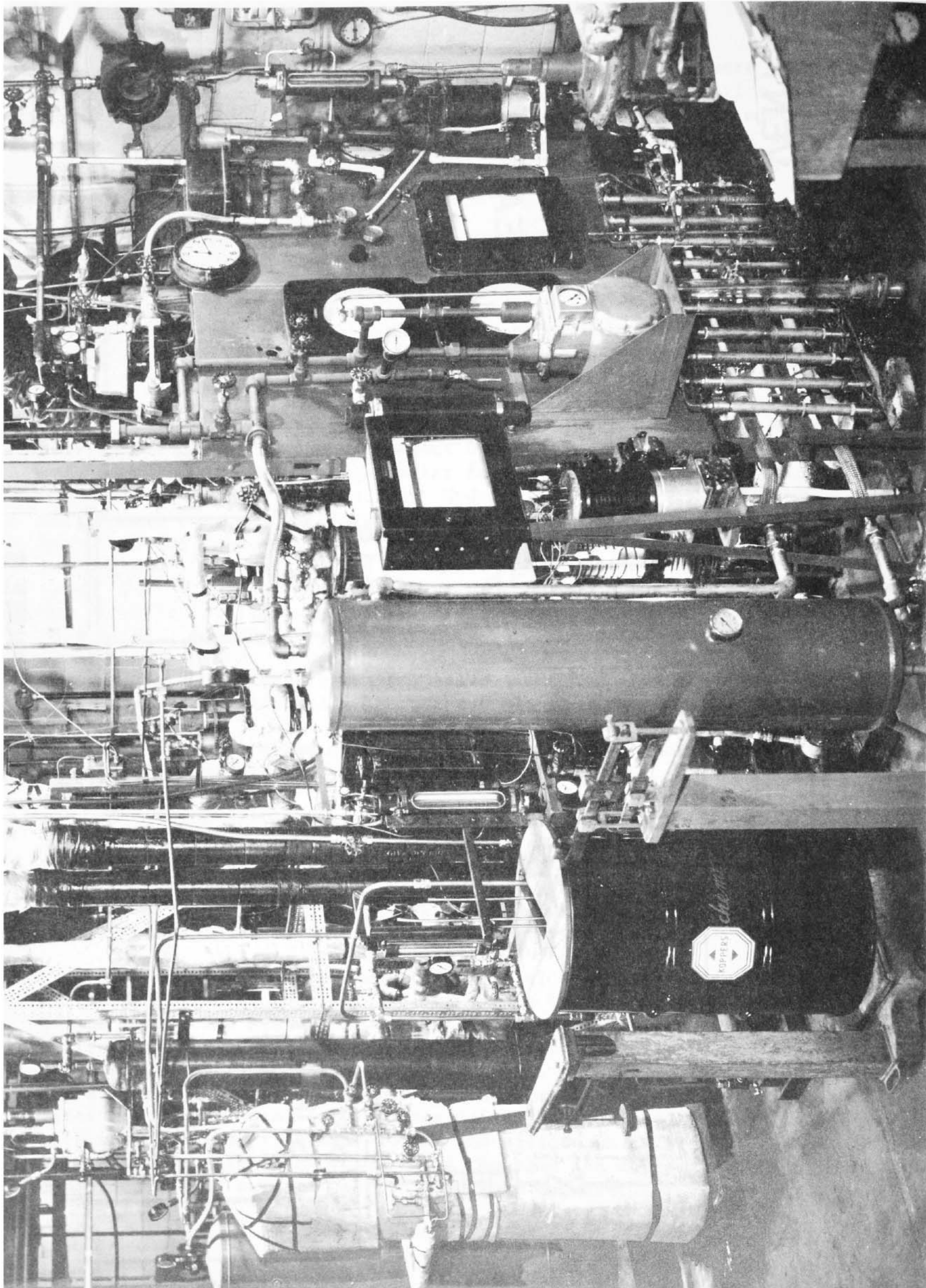


FIGURE 7 - PHOTOGRAPH OF BENCH-SCALE APPARATUS

Composition of Artificial Sea Water

<u>"Normal" Sea Water</u>		<u>Artificial Sea Water</u>	
<u>Ion</u>	<u>PPM</u>	<u>Salt</u>	<u>PPM</u>
Sodium	10,768	Sodium Chloride	27,251
Chloride	19,361	Magnesium Chloride	2,895
Sulfate	2,702	Calcium Chloride	1,133
Magnesium	1,298	Magnesium Sulfate	2,781
Calcium	408	Potassium Sulfate	865
Potassium	388	Sodium Bicarbonate	196
Bromide	<u>66</u>	Magnesium Bromide	<u>76</u>
Total	35,134	Total	35,197

4. HYDRATE FORMATION STUDIES

4.1 Effect of Salt Concentration

During the early part of the investigation, the effect of the salt concentration in the brine on the formation rate of propane hydrate was examined. Feed stocks containing 3.6%, 4.8% and 6.0% salt were used. At equivalent formation conditions, no change was detected in the rate at which the hydrate formed and in the characteristics of the hydrate crystals. It was decided to use artificial sea water containing 4.8% salt for most of the bench-unit experiments.

4.2 Effect of Average Residence Time and Thermal Driving Force

The thermal driving force is the difference between the actual reaction temperature and the equilibrium temperature of the hydrate-salt-water system at the operating pressure. The critical decomposition temperature for the actual salt concentration in the reactor has been used instead of equilibrium temperature. For example: assume the brine in the reactor contained 5.4% salt and the reaction temperature was 1°C. Since the critical decomposition temperature of propane hydrate in brine containing 5.4% salt is 3°C, the thermal driving force would be 2°C. The average residence time is defined as the quotient of the weight of the aqueous slurry in the reactor and the weight of aqueous feed per unit time.

The rate of propane hydrate formation in a steady state system is affected by the thermal driving force and by the residence time. Figure 8 presents results of hydrate formation experiments. The production rate of the hydrate reactor working under steady conditions with a thermal driving force of 1°C, depends on the residence time of the reacting salt water. The highest reaction rate is obtained with a feed rate equivalent to an average residence time of 15 minutes. Smaller feed rates result in a hydrate slurry with more suspended hydrate, which slows the reaction down. If the thermal driving force is 2 or 3°C the same effect also occurs at shorter residence times.

An average residence time of 23 minutes and a driving force of 1°C resulted in a slurry of 18% hydrate by weight. Similarly with 2°C, 22% was obtained. If, in a similar experiment, all streams leaving and entering the reactor were stopped and the existing slurry was isolated in the reactor, the hydrate concentration in the slurry increased from 18% to 35% within one hour. This test showed that slurries containing a relatively high concentration of hydrate could be formed if desired. Useful reactor operation was generally obtained with slurries containing 8-10% hydrate.

4.3 Crystal Characteristics

The effect of the formation conditions on the effective particle size of the hydrate crystals was investigated by conducting tests on beds containing propane hydrate produced at different reactor conditions. The test

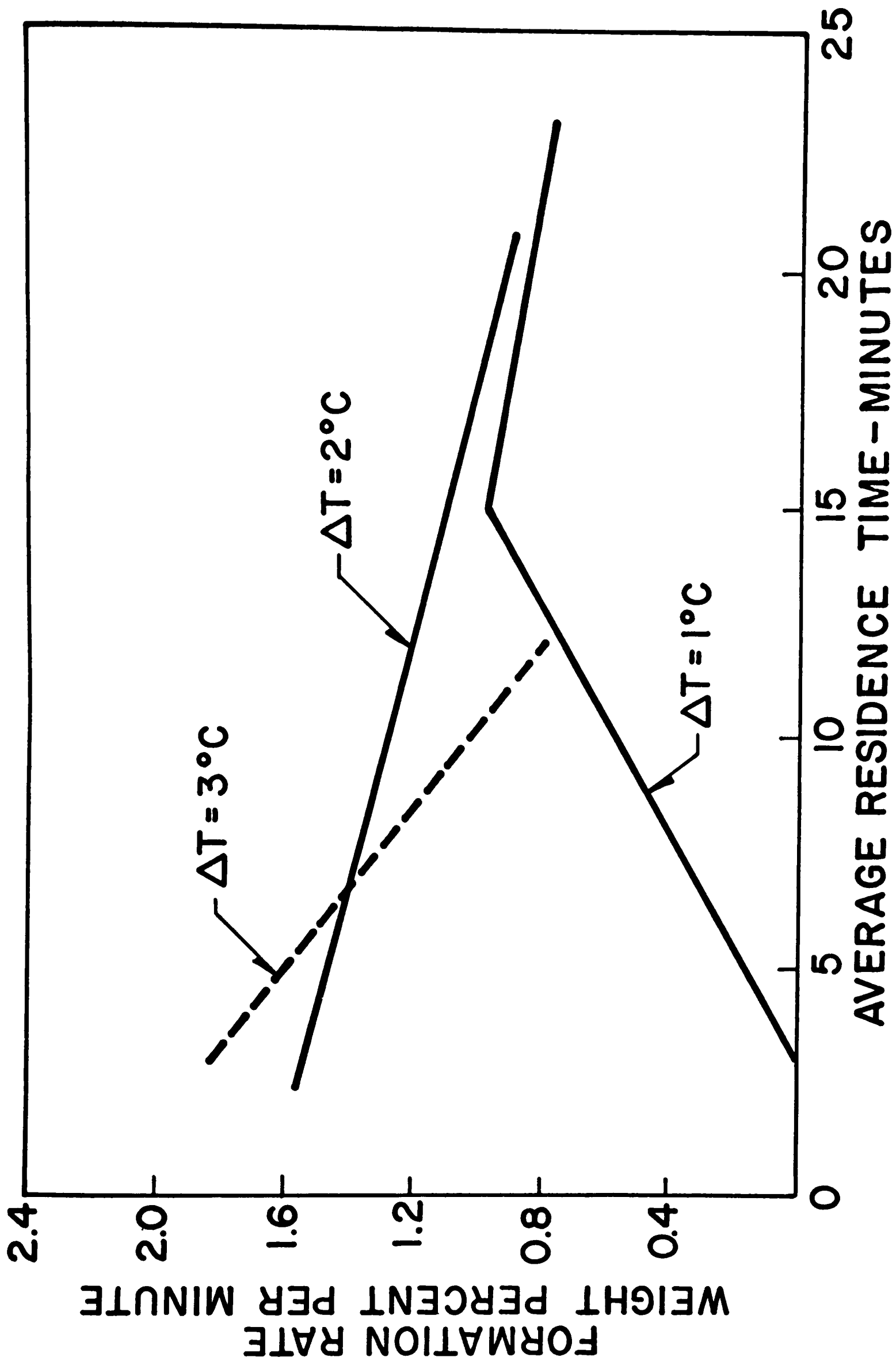


FIGURE 8
 RATE OF PROPANE HYDRATE FORMATION
 IN STIRRED TANK REACTOR

method involved the measurement of the flow rate of water through the hydrate bed at various pressure drops across the bed. The hydrate bed was formed in a 2-inch glass column which was jacketed for the flow of a coolant.

The average effective particle size of the hydrate crystals was calculated with the Carman-Kozeny equation:^{17/}

$$D_p = \frac{5.6 \mu L U (1-E)^2}{\phi^2 E^3} \quad (I)$$

where D_p = average particle diameter, ft.

μ = viscosity, lb. mass/ft.-sec.

L = depth of bed, ft.

U = superficial velocity, ft./sec.

ϕ = particle shape factor (unity for spheres),
dimensionless

E = fractional free volume in bed, dimensionless.

The equation gives particle sizes in feet. For reasons of convenience they are given below in microns.

This equation is not considered to be rigorous for particles smaller than 100 microns, but it does permit a comparison of such particles. With the assumption that the hydrate particles were uniform in size and were spherical in shape, the calculated particle diameter varied from about 3 microns to 30 microns depending upon the driving force during the formation of the crystals. Propane hydrate, formed at a drive of 2.5° to 3.5°C, had an average particle diameter of 3 to 7 microns, whereas that formed at lower thermal driving forces produced crystals which had an average particle diameter of 25 to 30 microns. No appreciable differences were detected in the characteristics of propane hydrate formed at thermal driving forces less than 2°C.

4.4 Rates of Nucleation and Growth

The interpretation of the results obtained in the bench unit could be improved if it were possible to calculate separately the rates of nucleation and growth of hydrate crystals. The rigorous calculation of such rates would be complex, but with certain assumptions, simplified equations can be derived that are useful to establish trends.

An average linear growth rate, G, can be calculated if it is assumed: (a) that the reactor is perfectly mixed, so that a theoretical distribution of residence times is obtained; and, (b) that the nuclei, generated at a uniform rate, grow in accordance with the " ΔL -law" of crystallization. This law^{18/} states that the increase in a linear dimension of any crystal in a given time interval is independent of the size of the crystal:

$$D_t = G t \quad (I)$$

where D_t is the diameter of a crystal leaving the reactor after having remained

in the reactor for a time t , G is the linear growth rate and t is the elapsed time between nucleation of that particular crystal and the time when it leaves the reactor. The distribution of residence times of the crystals in the reactor is:

$$f(t)dt = \frac{dN_t}{N} = \frac{1}{\theta} e^{-t/\theta} dt \quad (II)$$

where N_t is the number of crystals that remain in the reactor for time t , N is the total number of crystals in the reactor and θ is the average residence time (equal to weight of the reaction mixture in the reactor divided by the feed rate).

The average particle diameter D_p measured by the Carman-Kozeny method is defined by the equation:

$$D_p^2 = \frac{\int_{t=0}^{t=\infty} D_t^2 dN_t}{\int_{t=0}^{t=\infty} dN_t} \quad (III)$$

In equation (III), dN_t can be substituted by the equivalent expression derived from equation (II)

$$dN_t = \frac{N}{\theta} e^{-t/\theta} dt \quad (IV)$$

and D_t is defined by equation (I). Hence:

$$D_p^2 = \frac{\int_0^{\infty} \frac{G^2 t^2 N}{\theta} e^{-t/\theta} dt}{\int_0^{\infty} \frac{N}{\theta} e^{-t/\theta} dt} \quad (V)$$

Upon integration:

$$D_p^2 = G^2 \frac{2\theta^3}{\theta} = 2G^2\theta^2 \quad (VI)$$

$$G = \frac{\sqrt{2} D_p}{2\theta} \quad (VII)$$

The rate of nucleation can be derived by equating the total weight of crystals obtained per unit time per unit reactor volume to the sum of the weights of the individual crystals.

The mass of one crystal which remains in the reactor for time t is:

$$m = \frac{\pi\rho}{6} G^3 t^3 \quad (\text{VIII})$$

and the total mass of crystals is:

$$M = \int_{t=0}^{t=\infty} m \, dN = \frac{\pi\rho G^3}{6} \int_{t=0}^{t=\infty} t^3 \, dN_t \quad (\text{IX})$$

$$M = \frac{\pi\rho G^3 N}{6\theta} \int_0^{\infty} t^3 e^{-t/\theta} \, dt \quad (\text{X})$$

Upon integration

$$r_n \text{ (rate of nucleation)} = \frac{N}{\theta} = \frac{X}{\pi\rho G^3 \theta^4} \quad (\text{XI})$$

For propane hydrate, $\rho = 0.88 \text{ g/cm}^3$

$$r_n = 1.21 \times 10^{15} \frac{X}{G^3 \theta^4} \quad (\text{XII})$$

where r_n is the rate of nucleation expressed as nuclei formed per minute per gallon of reactor volume, G is the growth rate in microns per minute and θ is the average residence time and X is the hydrate yield expressed as the weight of hydrate per unit weight of slurry.

Rates of growth and nucleation were calculated from experimental data on propane hydrate using equations (VII) and (XII). These calculations indicated that, in general, there was little variation in growth rate with driving force and/or reaction time. The average growth rate was calculated to be 1.23 microns per minute. The rate of nucleation increased rapidly when the driving force reached about 3°C . The nucleation rate was highest at very low residence times combined with large driving forces.

4.5 Particle Size Distribution from Various Types of Reactors

Another problem which needed to be understood prior to the design of a pilot plant was that of particle size distribution from various types of reactors. The following particle size distributions applicable to crystallization processes had been derived for continuous flow stirred tank reactors (CFSTR) and tubular reactors. The equations given by McMullin and Weber^{19/} were used in arriving at the equations below:

<u>Type of Reactor</u>	<u>Frequency Distribution, (t)</u>
Single CFSTR	$e^{-t/\theta}$
Two-Stage CFSTR	$e^{-t/\theta} \left(1 + \frac{t}{\theta}\right)$
Three-Stage CFSTR	$e^{-t/\theta} \left[1 + \frac{t}{\theta} + \frac{1}{2!} \times \left(\frac{t}{\theta}\right)^2\right]$
n Stage CFSTR	$e^{-t/\theta} \left[1 + \frac{t}{\theta} + \frac{1}{2!} \times \left(\frac{t}{\theta}\right)^2 + \frac{1}{3!} \times \left(\frac{t}{\theta}\right)^3 + \dots + \frac{1}{(n-1)!} \times \left(\frac{t}{\theta}\right)^{n-1}\right]$
Tubular Reactor	Constant

(t is the residence time for a given crystal in the reactor, θ is the average residence time.) The above equations assume an equal θ in each stage.

At a given total residence time θ_t ($\theta_t = n\theta$), the following average particle diameters result, assuming the ΔL -law to be valid:

<u>Number of Stages, n</u>	<u>Relative Particle Diameter, Dp</u>
1	1.414
2	1.000
3	0.860
4	0.790
5	0.758
10	0.663
20	0.620
Tubular ($n = \infty$)	0.577

These figures indicate that a single continuous flow stirred tank reactor results in the largest average particle diameter.

4.6 Mass Transfer Studies

4.6.1 Agitation Tests

In order to determine the effect of agitation on the yield of propane hydrate, runs were made at different agitator speeds. These runs were made using 4.8% salt water at a 15-minute residence time and 1.95°C. The table which follows presents the data from these tests.

Effect of Agitation on Propane Hydrate Production
(Bench-Scale Reactor)

<u>Agitator Speed (RPM)</u>	<u>Calculated Power Input-H.P./gal.</u>	<u>Per Cent Hydrate in Slurry</u>	<u>Formation Rate Wt. Per Cent Per minute</u>
150	0.0051	6.1	0.406
200	0.0117	9.1	0.606
250	0.0230	11.9	0.766
300	0.0408	14.6	0.973
355	0.0673	14.8	0.986

The data obtained at the various agitator speeds indicate that the rate of hydrate formation varies as the 0.4 to 0.5 power of the agitator power input. This is the same exponent as the dependence on power of the specific surface of two immiscible liquids according to Calderbank^{20/} and to Vermeulen.^{21/} Above the agitator speed normally used in the bench-scale reactor (300 RPM), the yield hardly increased.

4.6.2 Effect of Liquid Propane Feed Rate

An experiment was made to demonstrate the need for an excess of liquid propane in the reactor. The bench-unit reactor was operated in the usual manner but the amount of liquid propane fed to the reactor was varied throughout the test. Each of the propane feed rates was held constant for a period of three hours. The agitator speed was held at 300 RPM during the whole run. The following table shows the rate of hydrate formation at the various levels of liquid propane feed.

Effect of Propane Feed Rate on the Rate of
Hydrate Formation
(15 min. residence time; $\Delta T = 1.2^{\circ}C$)

<u>Propane Feed Rate - Pounds Propane Per Pound of Salt Water Fed</u>	<u>Rate of Hydrate Formation - Per Cent per Minute</u>
0.22	0.45
0.27	0.61
0.35	0.65
0.43	0.70
0.54	0.71

The data indicate that the liquid propane feed rate to the reactor affects the yield of hydrate up to a feed rate of about 0.4 lb. propane per

lb. of salt water feed. Tests were made to determine the amount of free liquid propane in suspension in the slurry at steady state. Two different propane feed rates were used, 0.32 and 0.43 lb. per lb. of feed. The volume per cent of free liquid propane in the slurry was found to be 8.4% and 15.7%, respectively.

4.6.3 Observations on the Behavior of Liquid Propane Droplets

In order to make qualitative observations on the behavior of liquid propane droplets and propane gas bubbles in a flowing (or static) stream of brine in the absence as well as in the presence of hydrate particles, a vertical glass-jacketed 2-inch diameter pipe nine feet high was erected at the bench-unit site. The following observations were made:

1. Liquid propane droplets less than about 3 mm in diameter do not have a great tendency to coalesce in 4.8% artificial sea water in the absence of hydrate particles.
2. There is very little, if any, relative motion between propane droplets less than 3 mm in diameter and the slurry when the hydrate concentration in the slurry is above about 5%.
3. No coalescence of liquid propane droplets was observed when hydrate was present in the amount of about 5% or more.

4.7 Loop Reactor

The retreating blade impeller used in the 10-gallon Pfaudler reactor served two purposes: to form small droplets of liquid agent by a shearing action on the large liquid agent globules and to impart a pumping action which turned the slurry over many times a minute. It was impossible to distinguish between the amount of power being added to the slurry for each of these functions. In order to determine the amount of shearing horsepower necessary to maintain certain levels of hydrate production, another style of hydrate reactor was used with the final aim of developing an improved reactor design which would require less agitator power for the same production level. In this design, circulation of the slurry was brought about through the use of a positive displacement pump and the power required to create liquid-liquid interface was added to the slurry through the use of a 6-bladed flat-blade turbine impeller. The power added by the impeller was varied by changing its speed. Impeller speeds up to 1300 RPM were used. The loop reactor was only used with propane as the hydrating agent.

4.7.1 General Description

A sketch of the loop reactor is shown in Figure 9. The reactor was made up of four main parts connected together in the form of a vertical loop about 10 feet tall by 3 feet wide: (1) a Moyno Pump for internal circulation of the slurry; (2) a contacting chamber containing an agitator impeller; (3) a 10-foot length of 3-inch glass pipe which formed the reaction tube; and (4) a separating chamber where propane gas was separated from the slurry.

4.7.2 Method of Operation

The loop reactor was inserted in the bench-scale system and used the same auxiliary equipment. In general, the loop reactor was operated in the same manner as was the 10-gallon kettle reactor. Figure 9 shows the various streams flowing to and from the unit and the location of the control thermocouples. The temperature of the slurry at the top of the 3-inch column was used to calculate the thermal driving force.

4.7.3 Agitator Power Input

Three different agitator impellers were used in this series of tests: a 2-inch and a 3-inch 6-bladed, flat-blade turbine and a 2-inch propeller. Through the use of these impellers and by varying the speed of rotation of the impellers, the power added to the fluid in the loop reactor was varied through the range of from 0.009 to 0.12 horsepower.

Additional power was added to the contents of the loop by the circulation pump. It varied from 0.006 to 0.114 horsepower for circulation rates of 57 and 150 pounds per minute, respectively. The total horsepower per gallon of water and hydrate which was added to the system amounted to 0.004-0.05 HP.

It was difficult to obtain reproducible results. Averages over many experiments gave the following results:

Formation Rates in the Loop Reactor

<u>Power Input HP/Gallon</u>	<u>Thermal Driving Force</u>	<u>Average Residence Time</u>	<u>Formation Rate Weight % per Minute</u>
0.004	2.0	16.7	0.25
0.020	1.5	26.0	0.25
0.025	2.0	14.0	0.3
0.050	1.55	16.7	0.7

Formation rates of 1% or larger could only be obtained with a driving force of at least 3°C.

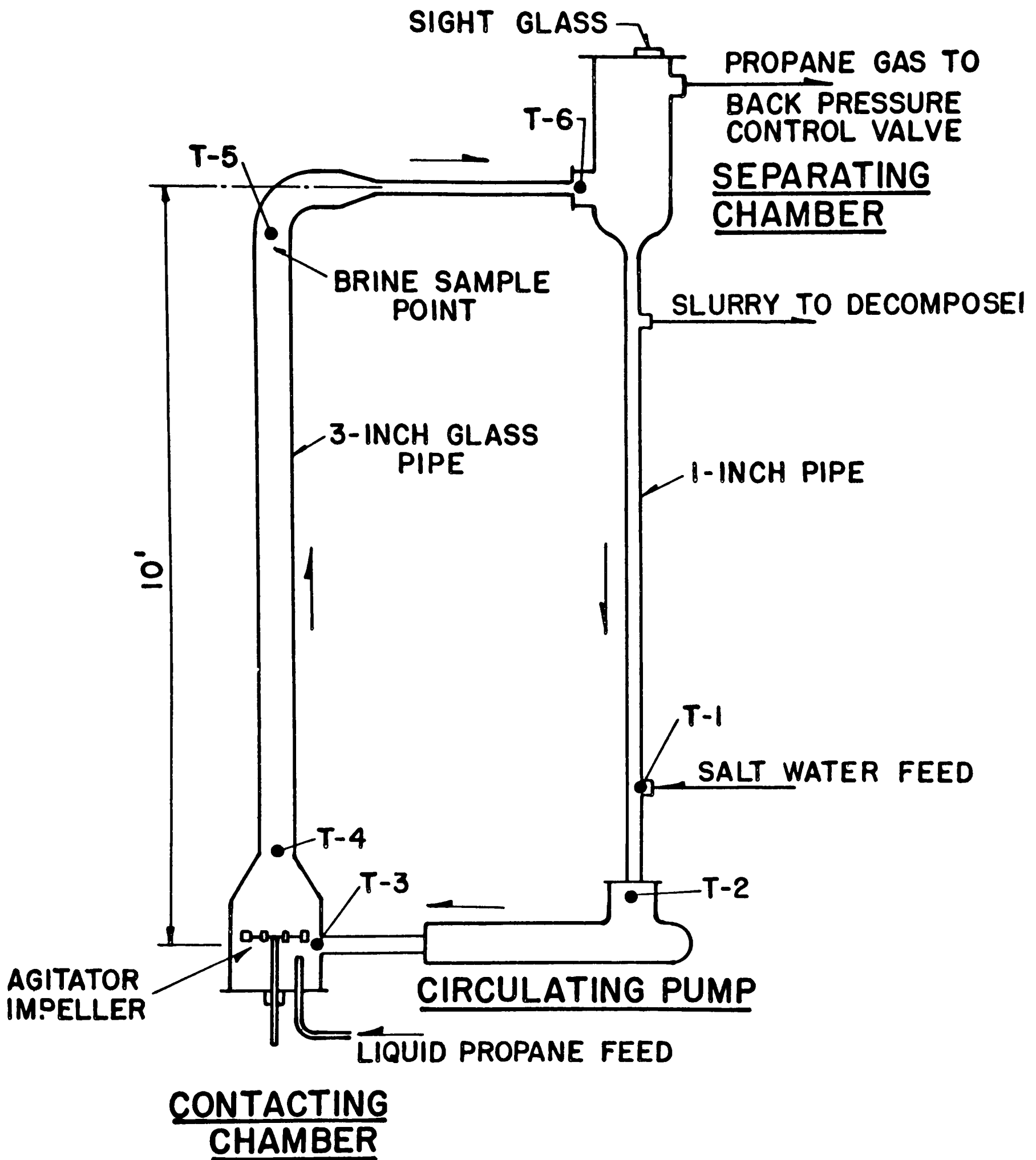


FIGURE 9
DIAGRAMATIC SKETCH OF
PROPANE HYDRATE LOOP REACTOR

The volume of the loop reactor was modified by changing all the piping to one-inch lines, and later, by changing to two-inch lines. The hydrate formation rates were again somewhat lower than those obtained in the 10-gallon reactor at similar power input levels.

It was concluded that it was not advantageous to study this loop reactor in more detail and that a commercial or pilot plant reactor design could better be based on the results obtained in the 10-gallon kettle.

4.8 Mass and Heat Transfer Calculations on Hydrate Formation

Calculations were made to find out which resistance controlled the growth of hydrate crystals assuming that no kinetic resistance was involved.

The rate of diffusion at steady state is given by Fick's first law as:

$$-a D \frac{dc}{dx} = Q \quad (I)$$

where a = specific area through which diffusion takes place, cm^2/cm^3

Q = rate of diffusion, $\text{g}/\text{cm}^3 \text{ sec.}$

c = concentration, g/cm^3

x = distance in direction of diffusion

D = diffusion coefficient, $\text{cm}^2/\text{sec.}$

This equation was solved for dc/dx for the diffusion of propane to the hydrate crystal and the diffusion of salt away from the hydrate crystal. The diffusion coefficient of propane in water was estimated using the method of Wilke and Chang^{22/} and the diffusion coefficient of salt in water was taken from Reid and Sherwood.^{23/} The area of hydrate crystals was estimated by the Carman-Kozeny equation with a shape factor of 1.0.

The analogous heat transfer equation is Fourier's Law:

$$Q = -a k \frac{dT}{dx} \quad (II)$$

where Q = heat flow rate

k = thermal conductivity

T = temperature

a = specific area

x = distance in direction of heat flow.

This equation was solved for the conduction of heat from the crystal.

Assuming a linear concentration gradient and the whole driving force available for mass transfer to be concentrated across a diffusion layer, the thickness of the layer which would just permit the observed rate of flow is calculated for a typical run made in the slurry reactor at 1.95°C and with a

reaction time of 15 minutes. The film thicknesses calculated were 180 microns for the diffusion of propane to the crystals, 392,000 microns for the conduction of heat from the crystals, and 32,000 microns for the diffusion of salt from the crystals. The values used in these calculations are listed in the Appendix (page 111).

An estimate of the droplet size and specific area for propane was made based on data of Calderbank^{20/} and Vermeulen^{21/} for the dispersion of liquid droplets at the power level used in the experiment (0.04 HP/gallon). This calculation gave a droplet diameter of 200 microns and a diffusion layer thickness of 14 microns. The corresponding heat conduction layer was 31,200 microns. This is an entirely credible value for the thickness of the propane diffusion layer and indicates that diffusion from the propane droplet may well be the rate controlling step in the growth of hydrate crystals. It certainly is the most serious resistance to heat and mass transfer of the ones considered.

Support for the concept that diffusion from the propane droplet may be the rate controlling step comes from a number of different observations:

1. The rate of hydrate production varies as the 1.2 power of the stirrer speed. This is the dependence on stirrer speed which would be predicted using the statistical theory of turbulence, and which has been observed experimentally by Calderbank and Vermeulen.
2. Calderbank and Vermeulen also have shown that the surface area of two immiscible liquids suspended in a stirred tank increases about as the square root of the dispersed phase concentration. It was found that rate of propane hydrate production was approximately proportional to the square root of the concentration of suspended propane.
3. The rate of propane hydrate production appears to vary approximately as the propane concentration driving force.
4. The "microscale of turbulence," defined as $\eta = \frac{\nu^{0.75}}{\epsilon^{0.25}}$, has been considered^{24/} to be descriptive for the smallest eddies in an agitated reactor. In the formula, ν is the kinematic viscosity, ϵ is the energy input per unit mass. At a power level of 0.04 HP/gallon, η is 28 microns. This is the same order-of-magnitude as the thickness calculated for the diffusion layer.

Based on experimental data and the above observations, it was decided to use power input per unit reactor volume as the criterion for scale-up of the hydrate reactor.

5. WASHING STUDIES

The hydrate reactor produces a slurry with approximately 5-20% hydrate by weight. In order to make potable water, this slurry must be filtered and the resulting filter-cake must be washed and subsequently decomposed. Countercurrent washing is considered to be necessary to keep the wash water consumption low. A method has been developed to perform the filtration, washing and decomposition in filter compartments, somewhat similar in design to the frames of a filter press.

The countercurrent washing is performed in the following way:

A compartment is filled with solids by filtration and compacted up to a predetermined pressure drop. This most recently filled compartment is connected as the last member of a train of such compartments being washed and it is washed with water already used in the rest of the train. Salt free compartments are cut off the line in front where fresh wash water is added and newly filled ones are put in line behind. Then the cut-off gas is added and condensed on the bed of washed crystals producing potable water and liquid agent. Figure 10 shows this scheme diagrammatically. In the top horizontal row, compartment 1 is being filled with hydrate crystals by filtration. Compartments 2, 3 and 4 are in the washing part of the cycle with compartment 4 receiving the fresh wash water. Compartment 5, containing the washed hydrate, is in the decomposition stage of the cycle. When this part of the cycle is completed, three compartments change position in the train with respect to their function. The new arrangement is shown by the next row in the sketch. 1 is in the washing stage and 4, containing hydrate free of salt, is in the decomposition stage of the cycle. The contents of compartments 2 and 3 are still being washed. Five is being charged with hydrate crystals. The following rows show the functions of the five compartments throughout subsequent stages in the cycle.

5.1 Washing of Solids - Theoretical and Design Considerations

In the ideal washing situation, the brine in the bed is displaced by wash water in plug flow. When all of the brine is displaced, the salt concentration of the liquid leaving the bed suddenly drops from the original concentration of the brine down to the salt concentration of the wash water. This ideal situation does not occur. Figure 11 shows a typical plot of the salt concentration of the effluent versus the cumulative volume of the effluent in terms of displacement from a batch wash test. At first the salt concentration in the effluent is the same as the salt concentration of the brine. When the brine in the bed has been displaced once with fresh water, the average salt concentration in the effluent is approximately half the original value. After 2-3 displacements have passed through the bed, the salt concentration decreases much less rapidly than before. Essentially all the washing by simple displacement has taken place. From this point on the salt which was trapped in "pockets" within the bed is removed by a slower process which is a combination of displacement and molecular diffusion.

The washing tests carried out during the development of the hydrate process have been run batchwise using pure water. The commercial washing

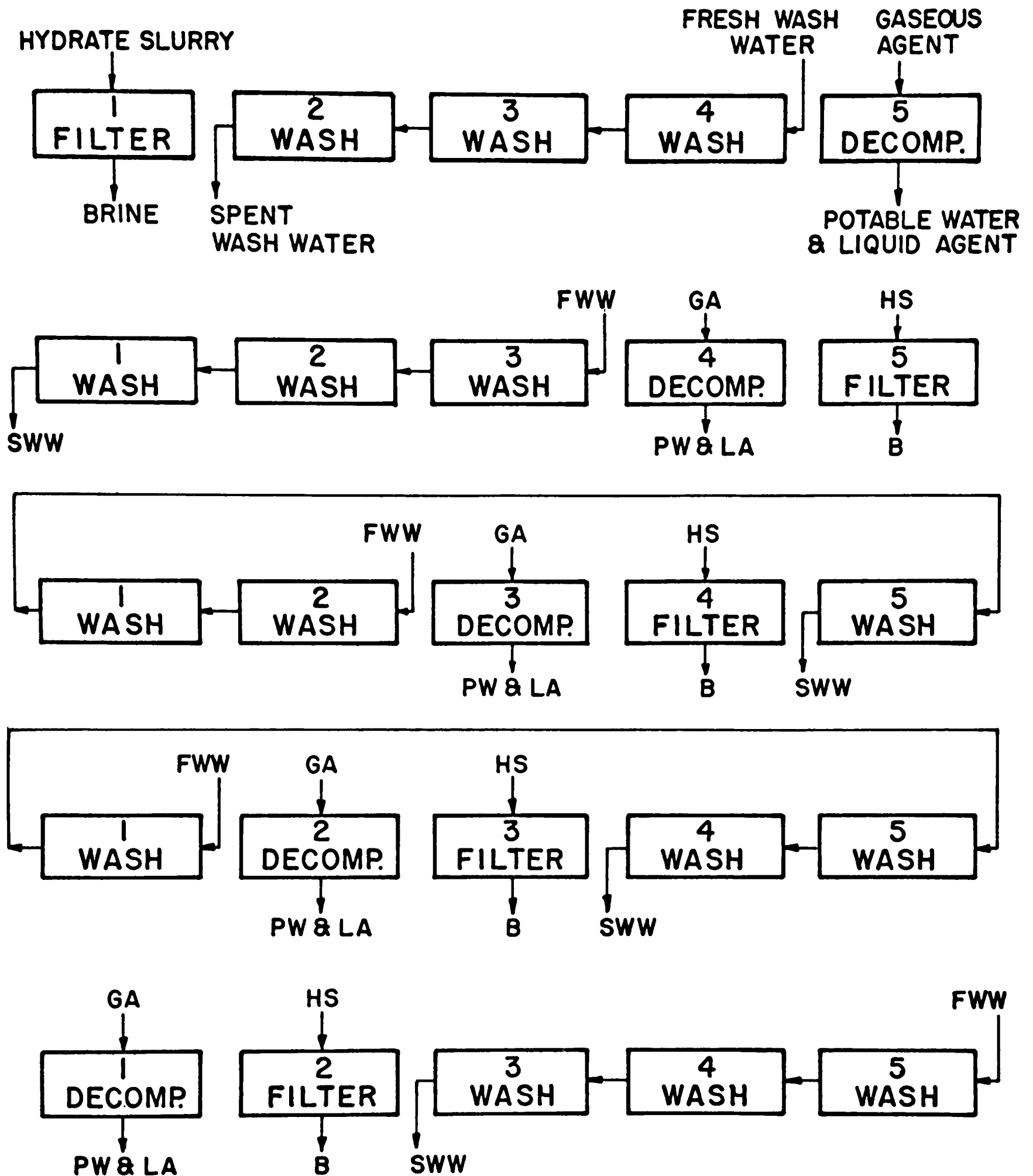


FIGURE 10
PRINCIPLE OF OPERATION OF A
FILTER-WASHER-DECOMPOSER WITH FIVE COMPARTMENTS

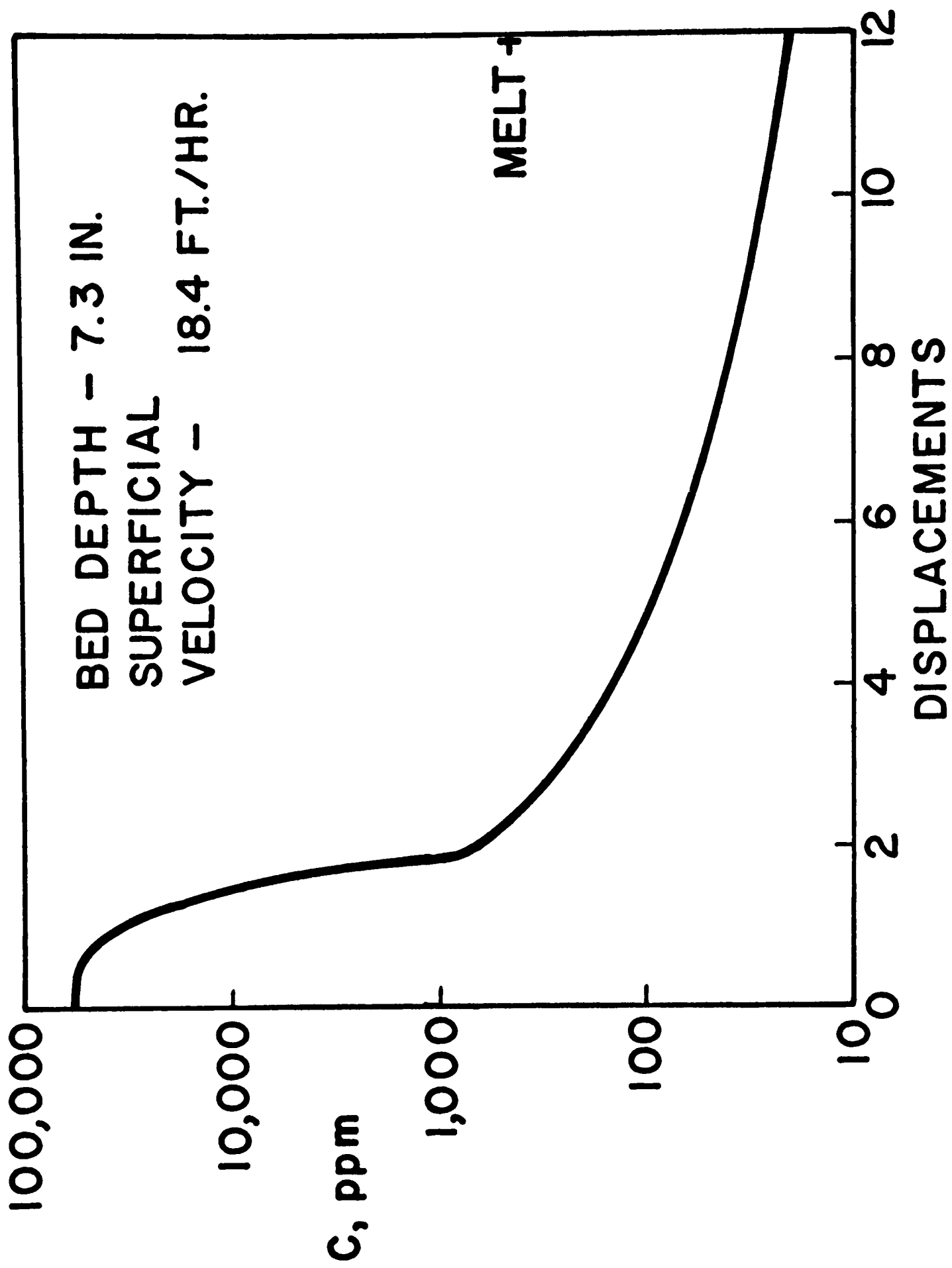


FIGURE II
 WASH CURVE

process should be a countercurrent scheme. With such a scheme, it would be possible to keep wash water consumption to a minimum. For that reason, it is important to have a method of estimating the total length of beds which have to be washed in series for a given wash water consumption.

The displacement of one fluid by another miscible fluid in a packed bed has been studied from a number of different points of view. Beran^{25/} used a statistical approach and by using the central limit theorem was able to show that for beds longer than a few particle diameters the diffusion equation (see following) could be expected to hold. Kramers and Alberda attacked the problem by considering a packed bed analogous to a series of perfectly mixed vessels. Cairns^{26/27/} and also Rifai^{28/} applied a statistical method. In all cases, except for very short beds, results were obtained which are equivalent to the diffusion analysis described below which was first presented by Danckwerts^{29/}. He used diffusion equations to describe the mixing which occurs at the boundary between two miscible fluids, one of which is displacing the other. This approach has been selected for the analysis of the washing data, and has been extended for the development of design methods for a continuous countercurrent washer and also for a staged countercurrent washer.

The mixing occurring at the boundary between two miscible fluids when the plane of reference is considered to move at the velocity of the fluids may be described by an equation analogous to Fick's first law for molecular diffusion:

$$q_A = -E \frac{dc}{dy} \quad (I)$$

where q_A = rate of diffusion across a boundary
 E = dispersion coefficient
 c = salt concentration
 y = distance across the boundary layer in a coordinate system moving at the fluid velocity.

Another relationship is derived from (I) by differentiation with respect to time and the use of a material balance:

$$\frac{\partial c}{\partial t} = E \frac{\partial^2 c}{\partial y^2} \quad (II)$$

where t = time.

Using a fixed coordinate system equation (II) can be transformed to:

$$\frac{\partial c}{\partial t} = E \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (III)$$

where x = distance in a fixed coordinate system
 v = interstitial fluid velocity.

Danckwerts^{29/} has presented the following approximate solution for the diffusion equation for the case in which a fixed bed containing brine is washed with pure water.

$$C = \frac{C_0}{2} \left(1 - \operatorname{erf} \left(\frac{N-1}{2\sqrt{\frac{E_i N}{LV_i}}} \right) \right) \quad (\text{IV})$$

$$\text{or } C = \frac{C_0}{2} \left(1 - \operatorname{erf} \left(\frac{N-1}{2\sqrt{\frac{E_s N}{LU}}} \right) \right) \quad (\text{V})$$

where C = salt concentration in effluent (in % by weight)

C_0 = salt concentration in brine

N = number of displacements of void volume of bed

V_i = interstitial velocity of wash water through the bed

U = superficial velocity (in cm/sec.)

E_i = dispersion coefficient based on V_i (in $\text{cm}^2/\text{sec.}$)

E_s = dispersion coefficient basis on V_s

erf = error function.

If ϵ is the void fraction of the bed, $U = \epsilon x V_i$, E_s is defined as $E_s = \epsilon x E_i$.

The dispersion coefficient, E_s , can be calculated using two points taken from the washing curve. The ones chosen were the value at $N = 1$ where $C/C_0 = 0.5$ and the value of N where $C/C_0 = 0.01$. Substituting in (V):

$$\operatorname{erf} \left(\frac{N \cdot 0.01 - 1}{2\sqrt{\frac{E_s N \cdot 0.01}{LU}}} \right) = 1 - \frac{2C}{C_0} = 0.98 \quad (\text{VI})$$

The value of the argument of the error function of 0.98 can be found from tables of functions, Jahnke and Emde.^{30/} Then:

$$\frac{N \cdot 0.01 - 1}{2\sqrt{\frac{E_s N \cdot 0.01}{LU}}} = 1.645 \quad (\text{VII})$$

or:

$$E_s = \left(\frac{N \cdot 0.01 - 1}{3.29} \right)^2 \frac{LU}{N \cdot 0.01} \quad (\text{VIII})$$

and:

$$N_{.01} = \frac{V_{.01}}{V_{.5}} \quad (\text{IX})$$

where: $V_{.01}$ and $V_{.5}$ are volumes of effluent where C/C_0 have the values of 0.01 and 0.5 respectively.

A simplified basis for design which neglects the effect of pockets of brine in the bed can be applied to the continuous countercurrent washer. This basis is obtained by a steady state integration of equation (I):

$$q_A - c(w-v) = -E \frac{dc}{dx} \quad (\text{X})$$

where q_A = diffusion flow/unit area free space
 w = interstitial velocity of wash water
 v = interstitial velocity of brine moving with crystals
 E = dispersion coefficient (= E_s)
 c = salt concentration
 c_1 = concentration at dilute end of washer
 c_2 = concentration at concentrated end of washer
 x = length
 L = total bed length.

This can be integrated for two cases:

- A. When $w-v = 0$. In this case, there is no fluid velocity with respect to the vessel wall, but there is a velocity with respect to the particles in the bed (w).

$$L = -E \frac{(c_2 - c_1)}{q_A} \quad (\text{XI})$$

- B. For the practical case, where there is a positive net consumption of wash water, $w-v \neq 0$ and we have:

$$L = \frac{E}{w-v} \ln \frac{c_2(w-v) - q_A}{c_1(w-v) - q_A} \quad (\text{XII})$$

Equation XII gives useful information about washing. It shows that the length of the washer required is directly proportional to the dispersion coefficient and inversely proportional to $w-v$, the net wash water velocity. Thus it is important that the dispersion coefficient be low. Increasing the net wash water ratio reduces the length of the washer required, but it increases the cost of washing. The quantity $w-v$ can also be increased by increasing the wash water velocity. However, since the dispersion coefficient is approximately proportional to the wash water velocity, no decrease in

washer length can be obtained using this approach. The fraction of solids in the bed has a strong influence on the quantity w-v for a given net wash, and on the length of washer required. Increasing solids content also has an effect on the washer area required.

For a staged washer, the solution is more complicated since the flow of trapped brine from pockets must be taken into account. The washer is no longer at steady state so that $\frac{\partial c}{\partial t} \neq 0$. The basic differential equation is developed from (III):

$$\begin{array}{ccc} \text{Diffusion Flow} & & \text{Pocket Flow} \\ \frac{\partial c}{\partial t} = E \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - F c \text{ pocket} & & \end{array} \quad \text{(XIII)}$$

In which:

$$F = \frac{V_0}{T} e^{-\frac{t}{T}} \quad \text{(XIV)}$$

where V_0 = original volume of pockets
 T = time constant of pockets
 c pocket = concentration of original brine.

V_0 and T are empirical constants describing the rate of drainage from the pockets. Computer programs for the IBM 704 were prepared and tested for two cases. One case applied to simple batch washing, as in the bench-scale washing experiment, while the other case treated the staged counter-current washer. The batch washing program was primarily used to check agreement of calculated batch washing curves with experimental data. It has also been used in checking the staged washer program.

The programs have been used in the design of a washer for the pilot plant and, to a limited extent, in the exploration of the effect of different variables on the performance of a staged washer. The controllable variables are total bed length, wash water velocity, number of stages, and the wash water consumption. In addition, there are variables dictated by the characteristics of the beds obtainable experimentally, volume percentage solids in the filter chamber, dispersion coefficient, initial pocket volume, and pocket time constant.

From the computer calculations, it was predicted that increasing the number of stages in a staged washer beyond three or four would give very little improvement in performance. For example, assuming four stages instead of two reduces the projected salt content of the melt from 490 to 350 ppm. An increase to six stages resulted in an additional predicted reduction of only 30 ppm.

Washing studies represent a major part of the experimental effort. They can be divided into four phases, each of which had a specific objective and involved a different design for the washing equipment. The initial phase of the work was directed towards the development of general concepts concerning the behavior of fixed hydrate beds during washing. This experimental work was carried out in a two-inch tube. Later a twelve-inch filter press was employed

to verify the earlier findings and also to explore filtration and washing variables in greater detail on a larger scale. The filter press was also used for the development of a wash water and gas distributor which could be used in a larger scale washer. The third step in the washing investigation involved the use of a five-inch diameter by five-foot washing column. It supplied information on the washing characteristics of deep hydrate beds. The final phase of the washing study was devoted to the development of a wash water distributor for the pilot-plant washer. It started in the five-inch column and progressed through the filter press to a "mock-up" of the pilot-plant washing chamber.

A batch technique was used in all of the washing tests. A hydrate bed was formed by filtration of a hydrate slurry. Pure water was passed through the hydrate bed and brine and spent wash water were removed through a filter medium. Samples of filtrate were analyzed for salt content. The water recovered after the washed hydrate has been decomposed was also analyzed for salt content. The experimental data from each washing test were used to calculate a dispersion coefficient. The percentage of solids in the bed, and the pressure drop through the bed during washing were also determined.

5.2 Two-Inch Column

A diagram of the test equipment which was used for propane hydrate is shown in Figure 12. It consisted of a jacketed washing column, two storage tanks, and filtrate receivers. The washing column was a 36-inch length of 2-inch glass pipe with filter screen, fabricated from 28 x 500 mesh stainless steel Dutch twill wire cloth, at the bottom. The top of the column was connected to a slurry sample line, a wash water inlet, and as a pressure equalizing line. The column was equipped with a perforated stainless steel plate 1.9 inches O.D. fastened to a rod which could be moved up or down through a pressure seal. The plate was used to retain the top of the hydrate bed during washing. The washing column was contained in a 48-inch length of 6-inch glass pipe which served as a jacket for the flow of coolant. Before entering the column, the wash water was cooled to hydrate formation temperature and flowed through a cooling coil located in the annular space between the jacket wall and the washing column. Ten receivers, each having a capacity of 150 ml, were manifolded to the bottom of the washing column. Each receiver was equipped with a quick-opening valve so pre-determined increments of filtrate could be taken without otherwise altering the flow of wash water.

A summary of data developed from washing tests of propane hydrate in the two-inch column is given in Figure 13. It was learned that beds of hydrate crystals can be washed sufficiently free of brine with pure water. Two to three displacements of the liquid surrounding the particles by pure water produced a melt containing about 500 ppm salts. This amount is sufficiently low to consider a countercurrent washing as a final solution for the brine-hydrate separation. An additional number of displacements was necessary to reduce the salt content of the melt to 100 ppm. However, if a partially washed hydrate bed is reslurried, a total of about three brine displacements was sufficient to reduce the salt content of the melt to 70 ppm. The washed beds

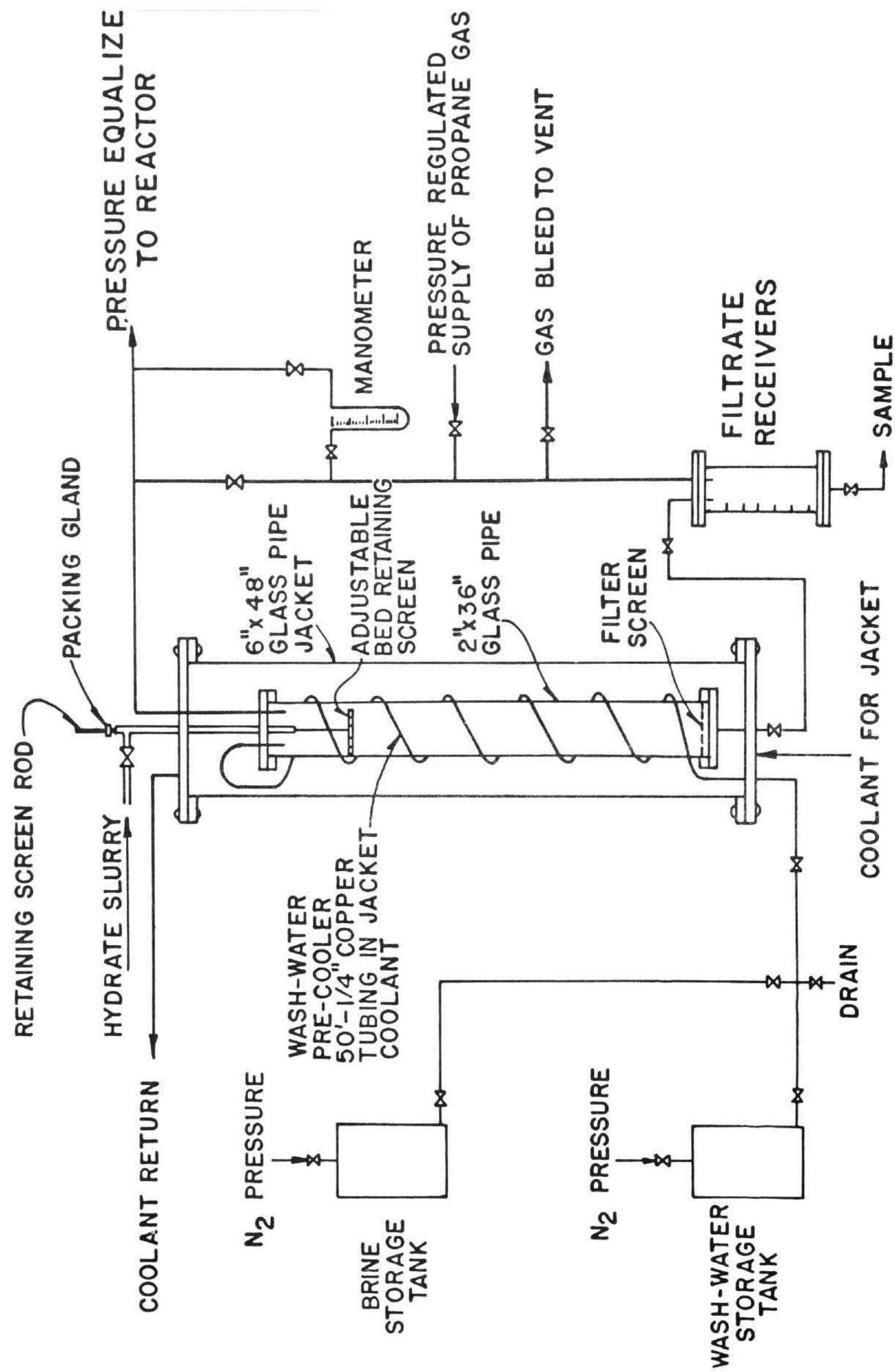


FIGURE 12
PROPANE HYDRATE WASHING APPARATUS
TWO-INCH COLUMN

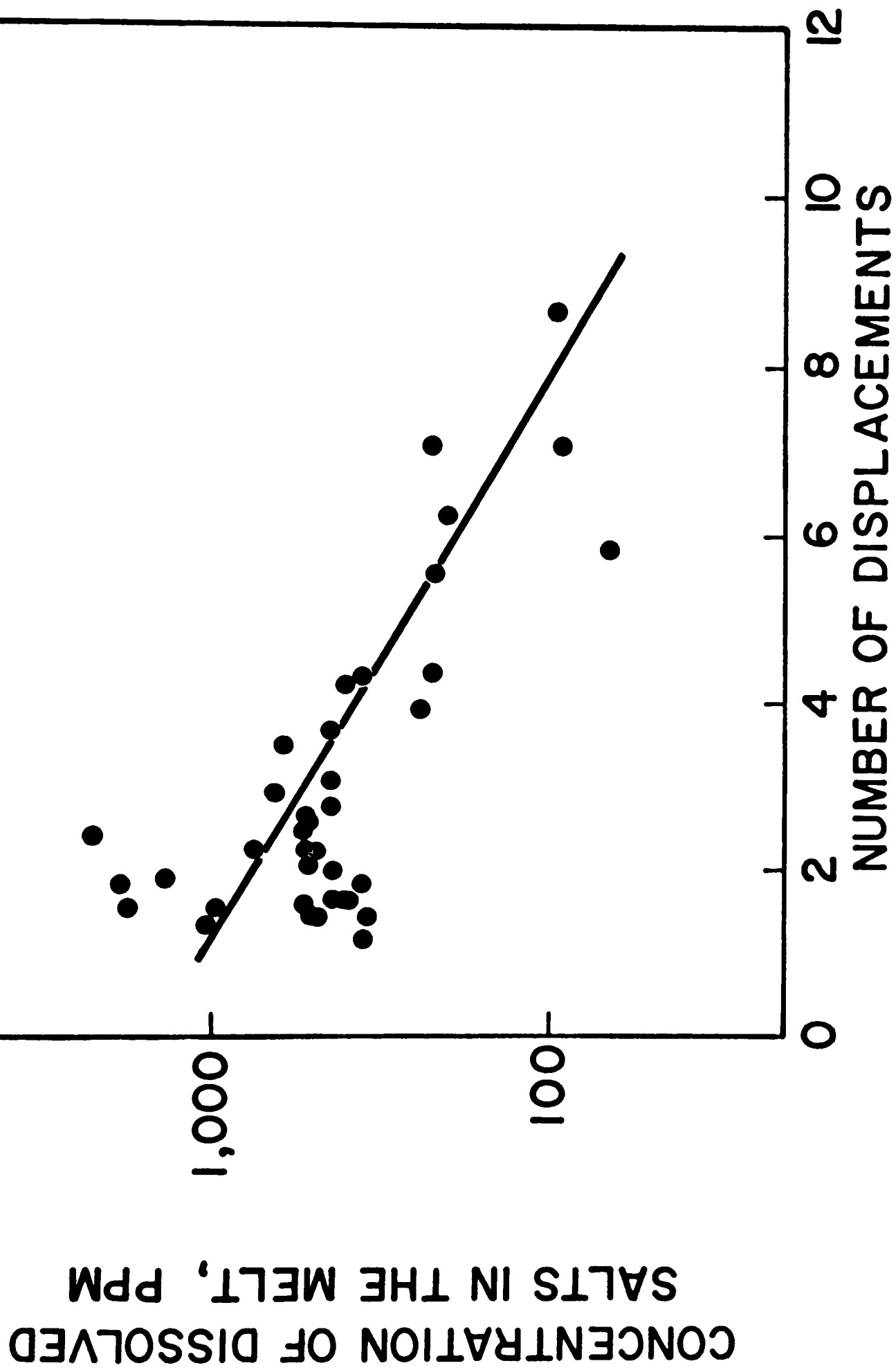


FIGURE 13
WASHING TESTS-TWO-INCH WASHING COLUMN
MELT CONCENTRATION VS DISPLACEMENTS

of hydrate formed under the latter conditions contained about 25-30 per cent solids by volume, which was not as high as obtained later. Beds drained by gravity contained less than 20% hydrate by volume.

The pressure drop through the bed varied from 2 to 18 psi per foot of bed depending upon the velocity of the wash water. Figure 14 shows the relationship between pressure drop and the superficial velocity of the wash water.

5.3 Twelve-Inch Filter Press

Although the 2-inch column produced relatively consistent data, it was considered advisable to conduct washing tests on larger hydrate beds before going to a pilot plant operation. A Shriver 12-inch plate-and-frame filter press was installed for this purpose. The frames had the inside dimensions of 11 inches square. The press was mounted in a vertical position so that the filtering surface was on a horizontal plane. Only one frame was used for filtration. The plates on top and bottom of this frame were connected to inlet and discharge lines for the wash water and filtrate. Frames immediately above and below the operating plates were connected for the flow of cooling brine so that the temperature of the operating section of the press could be controlled. A flow diagram for the filter and its supporting equipment is shown in Figure 15. Other major items of equipment were: A positive displacement pump used to transport slurry from the reactor to the filter press; a 33-gallon, stone-lined filtrate tank; a 16-gallon, carbon-steel vessel for used wash water; two 1.5-gallon tanks, fabricated from 3-inch Pyrex pipe, to receive product water and liquid agent produced during decomposition tests; a 33-gallon, stone-lined vaporizer with a steam coil, to remove liquid agent; a wash water feed system, consisting of a 55-gallon, phenolic-lined drum, an Eco gear pump and a rotameter; a gaseous hydrating agent feed system, consisting of two 100-lb. gas cylinders in warm-water baths and a rotameter to supply gaseous agent to the filter press during the decomposition step.

The hydrate slurry formed in the reactor was pumped into the filter frame. The mother liquor passing through the filter cloth was collected in the filtrate tank. The pressure drop across the bed during charging and washing was measured by a mercury manometer. Samples of filtrate were taken periodically throughout the bed formation period. The salt content of the filtrate was used to calculate the amount of hydrate in the slurry charged to the frame, and thus the amount of hydrate in the filter bed could be calculated. When the filtration pressure, which rises steadily during the filtration, reached a predetermined maximum value, the filtration was stopped.

Wash water was pumped from the wash water tank through the hydrate bed at a constant, pre-determined rate. The temperature of the wash water was about 2°C for most of the tests. Samples of wash liquor were taken during the washing period.

Experiments in the Shriver press were carried out using 3, 6 and 12-inch chambers. During the first series of tests, the flow of the wash

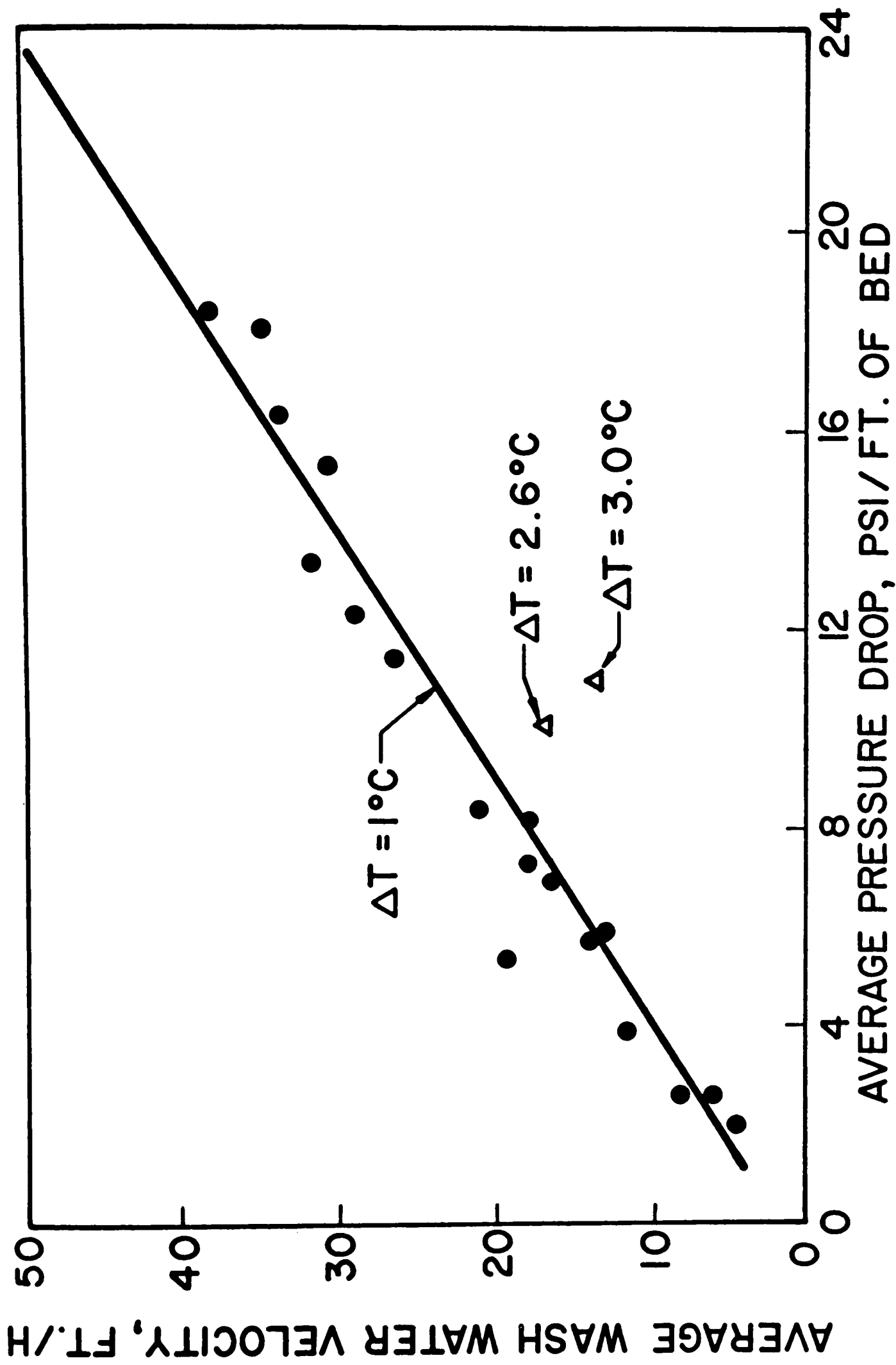


FIGURE 14
PRESSURE DROP VS WASH WATER VELOCITY
TWO-INCH WASHING COLUMN

water was from the top of the bed to the bottom. In the tests on the 3-inch bed, a 14.7 oz. nylon duck cloth (28 x 49 spun yarn) served as the wash water distributor and as the filter medium. The filtrate was removed through the bottom plate. The tests on the deeper beds were run in the same manner except a polypropylene filter cloth* was used in place of the nylon duck because of its lower pressure drop.

With a few exceptions, the salt concentration in the melts from these tests fell in the range of from 100 to 220 ppm dissolved solids. The dispersion coefficients developed from the data obtained from the tests on the 3-inch beds were in close agreement with the coefficients developed in the 2-inch glass column. The dispersion coefficients developed from the tests on the deeper beds were somewhat higher and seemed to increase as the height of the bed was increased.

Figure 16 shows the salt content of the effluent wash liquor as a function of the cumulative wash liquor collected throughout several of the tests on the 3-inch beds. The agreement of data from duplicate tests in the 3-inch bed was remarkably good, particularly within those made at the higher wash water velocity. This good duplication was not obtained in the tests on the deeper beds. The non-uniformity of the bed, which causes local by-passing and which is apparently not reproducible, is more important with deeper beds.

In order to reduce initial cost and maintenance of the filter-washer-decomposer in the pilot or commercial potable water plant, it was considered desirable to try perforated metal sheets as the filter medium rather than a fiber or metal cloth. Various combinations of perforated metal were used in the Shriver filter press to determine if a hydrate bed could be formed and washed on this type of filter medium. The distribution of wash water and gaseous agent produced by these plates was also of interest.

The first system investigated involved the use of perforated metal plates containing 0.06-inch diameter holes on 0.13-inch centers. The perforated metal was placed at the bottom and top of the 12-inch frame. It was found that a special technique had to be used to form a filter cake on this perforated plate. The slurry was charged to the filter frame and the removal of filtrate from the chamber was delayed until about 3/4 of the chamber had been filled with slurry. Then the filtrate was allowed to flow from the bottom of the frame through the perforated plate. About 10% of the hydrate charged to the frame was still lost through the plate during the early moments of filtrate removal, but a hydrate cake was always formed.

The washing of these beds was poor and the results were erratic. Melts containing as high as 1% salt were produced. It appeared that poor distribution of wash water was responsible for the inefficient washing.

* Shriver No. 334A Polypropylene; 55 monofilament in warp and 35 multifilament in filling per inch; gauge: 0.020 inch.

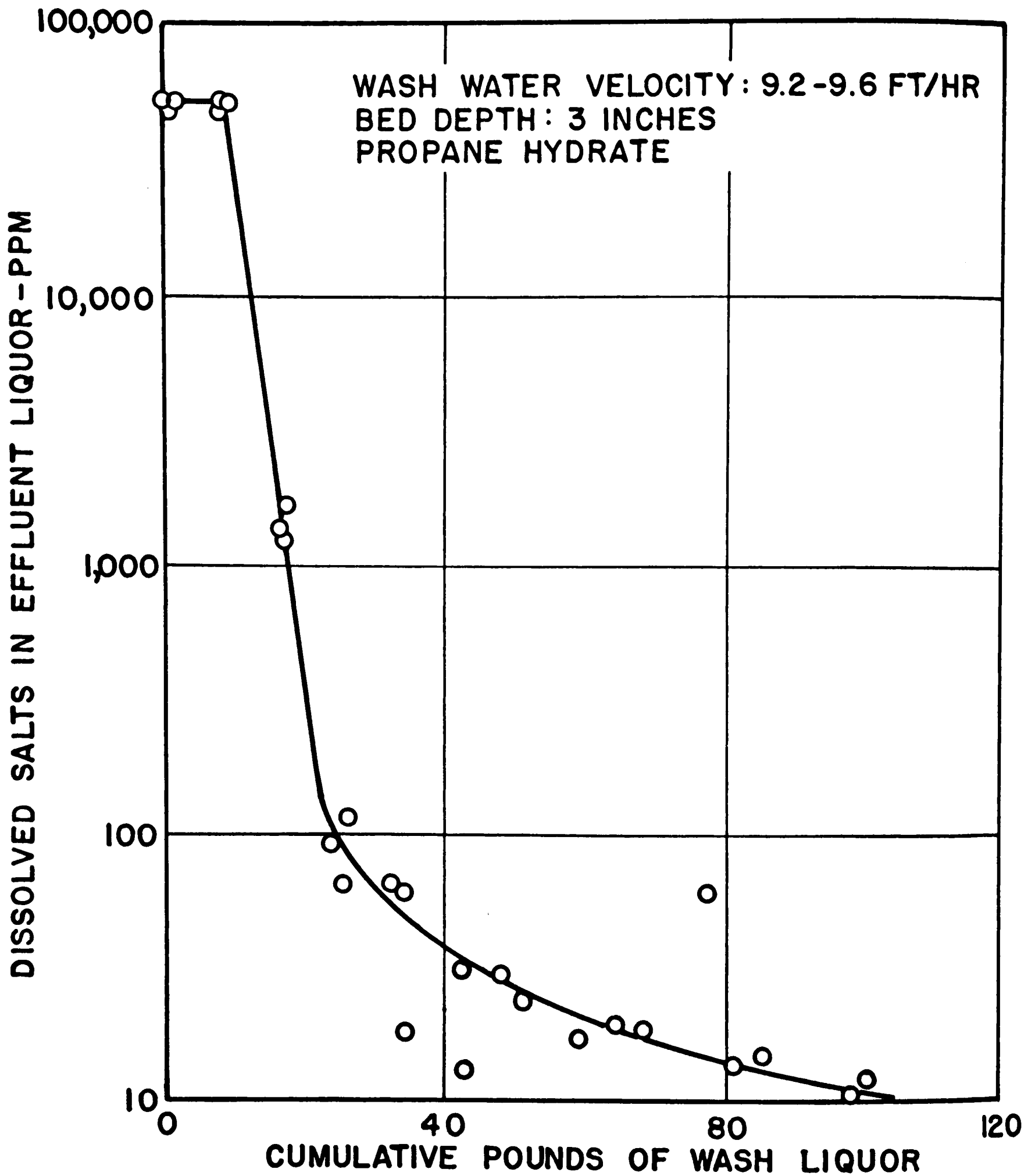


FIGURE 16
 WASHING TESTS IN TWELVE INCH FILTER PRESS
 SALT CONTENT OF WASH LIQUOR

After this, a filter medium at the bottom of the frame was fabricated from two plates containing 0.06-inch holes on 0.13-inch centers. The two plates were placed one on top of the other with a 0.01-inch spacer between them. The holes in the two plates were offset at maximum misalignment. This arrangement is quite similar in principle to a metallic filter and distributing medium called "Neva-Clog"* which also uses an offset, double layer of light gauge perforated metal sheets.

In order to improve the distribution of wash water across the top of the bed, a plate containing forty-nine 0.06-inch holes per square foot was placed in the top plate of the press.

The offset arrangement of the perforated plates acted as a much better filter medium than did one plate alone. It was not necessary to concentrate the slurry in the frame by delaying the removal of filtrate as was done in the first series of tests. The filter beds for these tests were formed by direct filtration of the slurry as it entered the press. Melts containing from 100-200 ppm of salt were obtained, with dispersion coefficients of approximately $0.150 \text{ cm}^2/\text{sec.}$, using six displacements and $U = 18 \text{ ft./hr.}$ These experiments demonstrated that a hydrate bed can be formed and washed on a filter medium such as a perforated metal plate.

A simplified design of a filter compartment could be obtained if the same distributor could be used for both wash water and propane gas for decomposition. Since it was demonstrated that the highest decomposition rates are obtained when the flow of propane is from the bottom of the bed to the top, the distributor plate for both the wash water and the propane must be located at the bottom of the bed and the wash water must also flow up through the bed. (See Section 6., Decomposition Tests.)

Washing tests were made to explore the practicability of: (a) using the same distributor plate for both wash water and propane gas; (b) washing by flowing the water from the bottom of the bed to the top; (c) charging the hydrate slurry at the bottom of the bed and removing the filtrate through a filter medium located at the top of the bed. The distributor plate contained forty-nine 0.06-inch holes/sq.ft. A perforated metal plate containing 0.018-inch by 0.5-inch slots on one-eighth-inch end centers (9% open area) served as the filter medium at the top of the bed.

This arrangement gave melts similar to those obtained in former experiments: approximately 125 ppm, with 6 displacements and $U = 10 \text{ ft./hr.}$; 200 ppm with $U = 30 \text{ ft./hr.}$ More significant were the differences in the dispersion coefficients. If the washing velocity is higher than the filtration velocity, the bed contracts during the washing. The void space immediately behind the perforated plate makes the distribution of the incoming wash water more even and the dispersion coefficient drops from $0.500 \text{ cm}^2/\text{sec.}$ (filtration velocity = $U = 30 \text{ ft./hr.}$) to $0.380 \text{ cm}^2/\text{sec.}$ (filtration velocity = 5 ft./hr. ;

* Sold by Multi-Metal Wire Cloth Company, New York

U = 30 ft./hr.) and to 0.200 cm²/sec. (filtration velocity = 5 ft./hr.; U = 10 ft./hr.). These differences do not show up in the compositions of the melts because of the large amount of wash water used.

A wash water distributor plate containing 0.06-inch holes on 1-1/2-inch center to center distance was used. The velocity of the wash water leaving the ports of this plate was about 60% of that produced by the previous plate. The dispersion coefficient was about twice as high and the salt content of the melt was about four times higher than in previous experiments. Apparently, the pressure drop across the holes was insufficient to produce an even distribution of wash water to the holes.

The same plate was also used to wash hydrate which was formed at a thermal driving force of 3°C. As in previous cases when hydrate produced at the higher driving force was washed, the salt content of the bed remained very high (more than 2500 ppm).

A distributor plate containing 0.043-inch holes, on a center to center distance of 1", performed slightly better. Again there was a significant difference in the dispersion coefficient depending on whether or not the bed remained in contact with the distributor plate throughout washing. (Dispersion coefficients of 0.400 cm²/sec. without - and 0.150 cm²/sec. with a void space; with U = 10 ft./sec. and melts of approximately 130 ppm.)

5.4 Five-Inch Column

Little work has been done in the filter press using beds deeper than 12 inches because the production rate of the 10-gallon reactor has not been sufficient to permit the charging of deeper beds within a reasonable period of time. Further, because of the relatively low production rate, the filtration rates in the 12-inch filter are only one-sixth of the minimum rate planned for the pilot plant filter-washer.

In order to wash deep hydrate beds which had been formed using higher filtration velocities, a washing column 5 inches I.D. by 66 inches long was fabricated and put into operation with the bench-scale unit. A piece of stainless steel wire cloth 28 x 500 mesh was used as the filter medium. The wash water distribution plate contained seventy 0.043-inch holes/sq. ft. (center to center distance - 1-1/2").

Washing tests were carried out using 15-inch, 30-inch and 66-inch chambers in order to obtain data which could be used to evaluate the effect of filtration velocity on bed density, the effect of the higher bed densities on the washing characteristics and the effect of bed length on the washing characteristics of the hydrate.

The average dispersion coefficient was about 0.360 cm²/sec. for the 66-inch beds (U = 10 ft./hr.). The average dispersion coefficients from the tests made in the 15-in. and 30-in. chambers were 0.125 and 0.170 cm²/sec., respectively

The dispersion coefficient from the runs at a wash water velocity of 26 ft./hr. was $0.420 \text{ cm}^2/\text{sec}$. and the salt content of the melts from these tests was 240 ppm. The increase of the dispersion coefficient with bed-depth was unexpected and it made the use of very deep beds rather unattractive.

The amount of solids in the bed formed in the 66-inch chamber, 40 volume per cent, was about the same as was obtained in the 15-inch chamber and slightly greater than that which resulted from the tests in the 30-inch chamber (37%).

5.5 Development of the Wash-Water Distributor

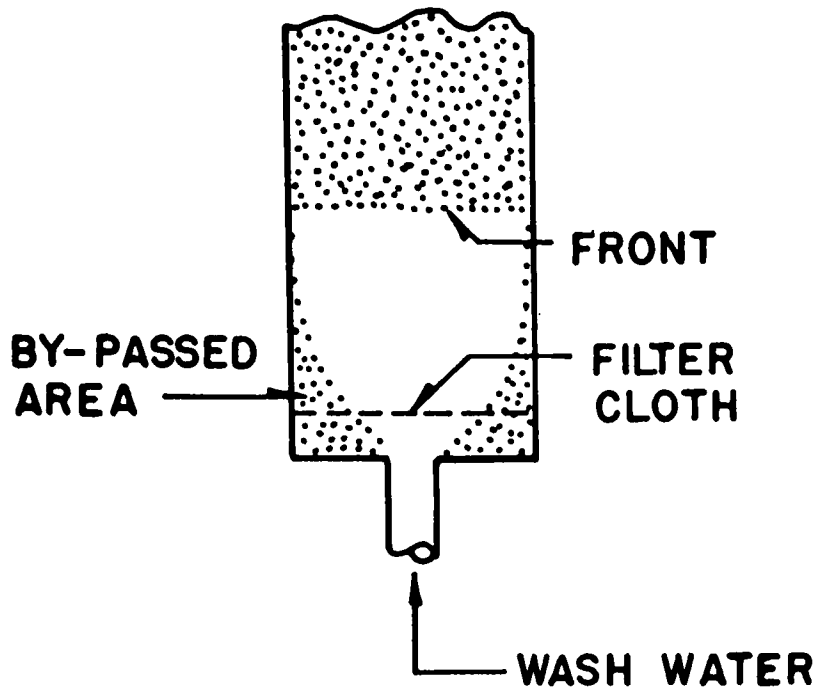
The experimental work showed that there were differences between actual data on hydrate and expectations based on data presented in the literature on washing of packed beds. The dispersion coefficient increased as the height of the hydrate beds was increased. The degree of plug flow through the bed should not be altered by the length of flow if the characteristics of the bed do not change. This could be caused either by the characteristics of the hydrate particles and/or of the bed which they form, or by the characteristics of the test equipment such as the means of introducing the wash water to the packed bed.

Proper wash water distribution appeared to be critical. If the wash water does not enter the bed with a horizontally flat front, it will be difficult to evaluate the true characteristics of the bed since the value for the dispersion coefficient will be distorted. For example: consider the apparatus shown in Sketch A, Figure 17, which consists of a column with an open filter cloth used as the water distributor device. The bed of particles rests on the filter cloth. Wash water admitted to the bed through the filter cloth does not enter the bed with a flat front, and because of the relatively low pressure drop across the cloth (and the bed), the front of wash water at the bottom of the bed has the profile of a cone. Thus, a portion of the bed is by-passed by the wash water. We obtain a washing curve like BB¹ in Sketch B of Figure 17. A filter cloth or perforated plate with higher resistance and sufficient openings will change the performance to one with more limited by-passing as shown in Sketch C. If the wash water had entered the bed in a flat front, the dotted curve having the slope AA¹ would have resulted. Another solution is presented in Sketch D. It is not difficult to design distributor arrangements which will perform even better. These devices will be more complicated and more costly. A compromise had to be found between cost of the device and effective distribution.

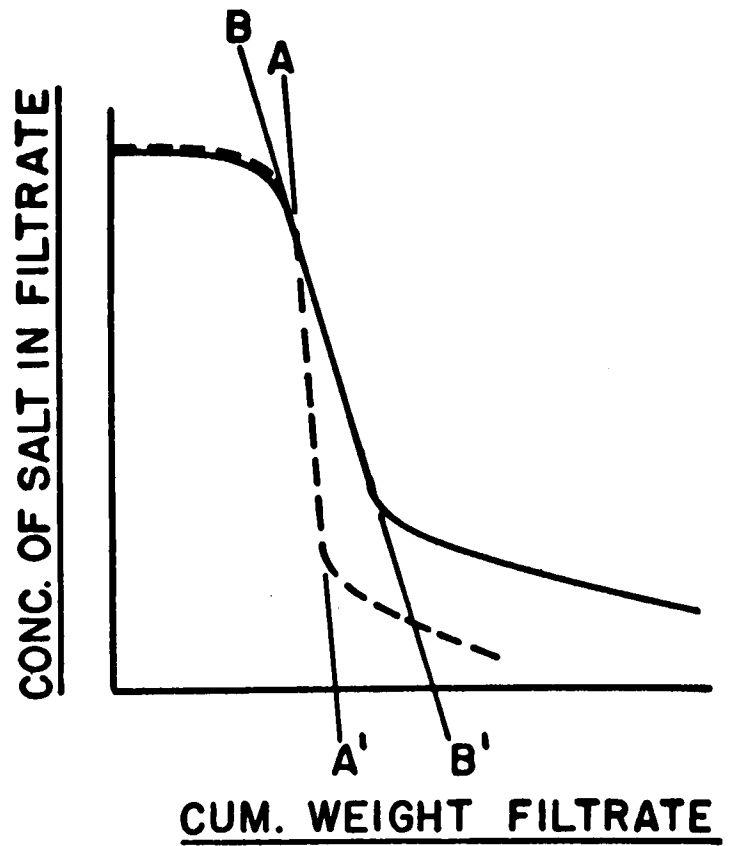
5.5.1 Experimental Work - Sand Washing Tests

Tests were made in which dyed water was washed from beds of sized sand.* Sand was used because the characteristics of the bed, such as particle

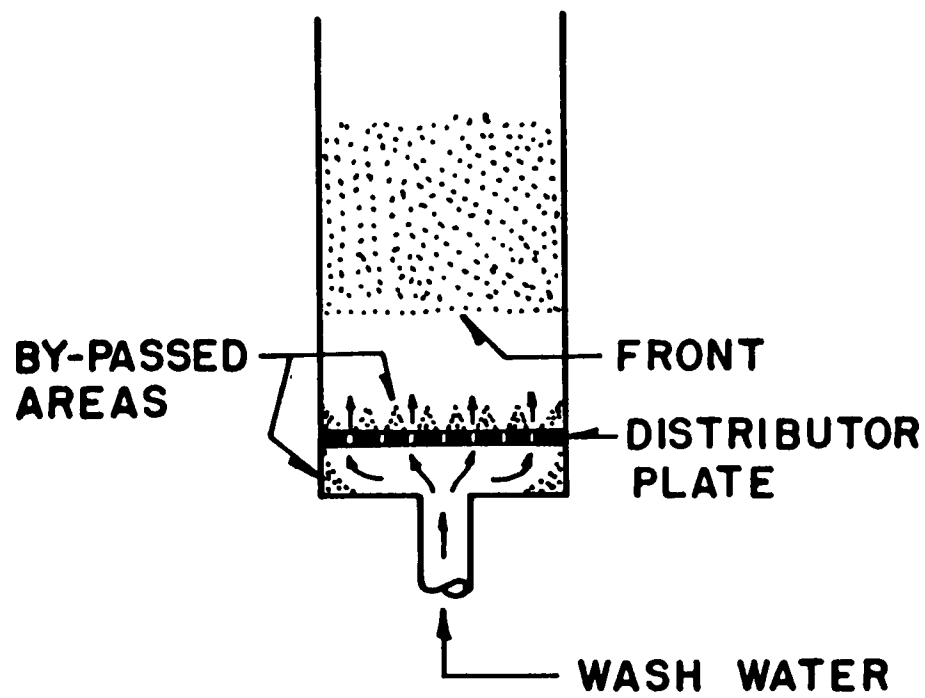
* Ottawa sand, 20-30 mesh. Fisher Scientific Co. Catalog No. 4-958.



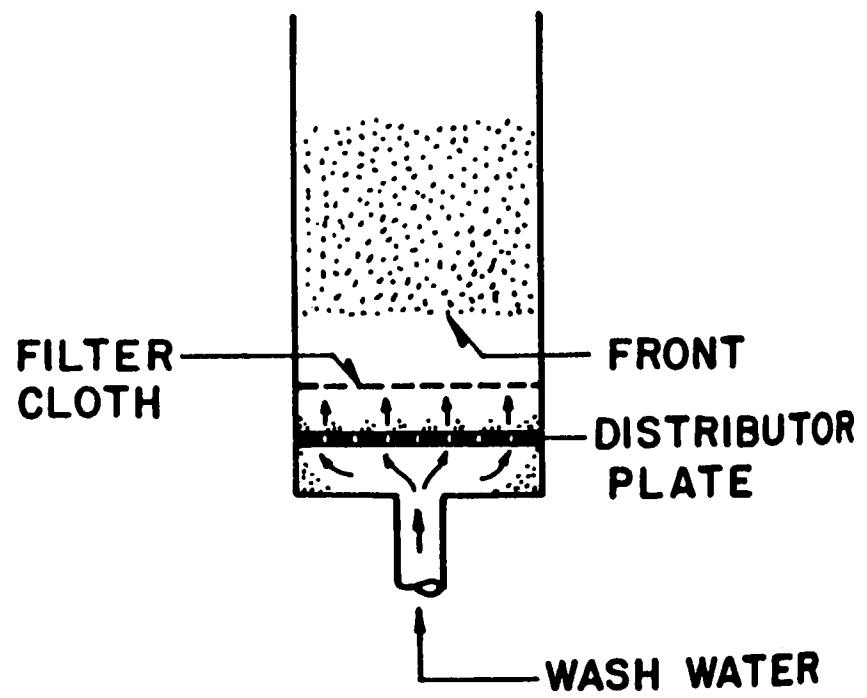
SKETCH A



SKETCH B



SKETCH C



SKETCH D

FIGURE 17
 SCHEMATIC SKETCHES OF WASH WATER
 DISTRIBUTION DEVICES

size and void fraction, could easily be determined and reproduced. The dye solution was used in the first series of tests to simplify the analytical part of the test. A photometric colorimeter was used to determine the change in the dye content of the effluent from the bed. Dispersion coefficients were calculated and used to compare different distributors.

5.5.1.1 Removing Dye Solutions Using Up-Flow

The sand was first washed in a 2-inch diameter tube to establish a base value of the dispersion coefficient. The two-inch tube was chosen since at this size water distribution problems and piping problems are greatly reduced. The obtained value for the dispersion coefficient, 0.027 cm² per second, agreed well with previous tests on small beads in the two-inch tube and also agrees well with values presented in the literature.

Having established a reference value for the dispersion coefficient for sand (average particle diameter 0.823 mm.), the investigation of distributing devices was initiated using a larger diameter column. A glass pipe 6 inches in diameter by 18 inches long was used to examine a water distributor based on the concept presented in Sketch D, Figure 17. The distributing device consisted of a plate containing twenty evenly spaced 0.062-inch holes and a 28 x 250 mesh Dutch Twill wire cloth located 0.3-inch downstream from the plate. The dispersion coefficient for two tests on sand using a velocity of 10 ft./hr. averaged 0.028 cm²/sec. which indicated that the device consisting of the perforated plate and wire cloth had functioned well. Beds containing polystyrene beads of approximately the same size had a dispersion coefficient of 0.039 cm²/sec. These beds were 18" deep.

A sintered metal porous plate was expected to be a very expensive but nearly ideal distributor. Therefore, a sintered metal plate was installed in the 5-inch column as the distributor. A dispersion coefficient of 0.031 was obtained from the 36-inch bed. The plate-wire cloth combination as used before produced a dispersion coefficient of 0.047. It was believed that the difference between these numbers was significant since duplicate tests give values which differed in most cases by not more than 0.005 cm²/sec.

5.5.1.2 Removing Salt Solutions Using Up-Flow

If salt solutions were removed in experiments that were otherwise identical to the dyed-water experiments, dispersion coefficients were obtained which were approximately three times higher than expected.

An explanation for this behavior could be that the sand selectivity adsorbed salt ions. If, however, a mixture containing dye and salt water were washed from the beds and the dye and salt contents of the effluent were determined separately, the results derived from the dye analysis also showed high dispersion coefficients, which meant that the salt was not retained on the surface of the sand particles.

5.5.1.3 Removing Fluid from the Bed Using Down-Flow

A more likely explanation for the high value of the dispersion coefficient produced when salt solution is washed from a bed of hydrate using up-flow of wash water was the difference in the specific gravities of pure water and the salt solution (sp. gr. 1.04). Figure 18 shows a comparison of the washing curves produced by up-flow and down-flow using sand.

Down-flow washing gave much better results than obtained before. Washing salt from sand via the porous plate gave $E = 0.025 \text{ cm}^2/\text{sec.}$ ($U = 10 \text{ ft./sec.}$); via a single plate, as mentioned in 5.5.1.1, $E = 0.021 \text{ cm}^2/\text{sec.}$ was obtained.

There is little difference in the values for the dispersion coefficient when dye is washed out using down-flow. Apparently gravity helps to prevent back-mixing of the heavier salt solution. This observation was not apparent from wash test data on hydrate in the 12-inch filter press. It was concluded that down-flow of wash water should be used.

5.5.2 Filter Press - Sand Washing Tests

Sand washing tests were carried out in the filter press using a 12-inch chamber. The purpose of this work was to: (a) determine the ability of the plate-screen type device to distribute the wash water over a larger area; (b) establish a base value for the dispersion coefficient on sand in this apparatus for comparison with values determined by washing hydrate in the filter press.

The wash water distributing system used for the first six tests consisted of a plate containing eighty-five 0.063-inch diameter holes/sq.ft. combined with a stainless steel cloth located 0.3-inch downstream from the plate. This plate contained the same fraction of open area as the plate used in the 5-inch column (see 5.5.1.1). Salt water was removed from the sand bed using down-flow of wash water at a velocity of 10 feet per hour. The wash water entrance ports in the top plate and the effluent ports in the bottom plate were varied during this series of tests to determine the effect of the piping arrangement. Each plate on the press was provided with two nozzles located on opposite sides of the frame at diagonal corners, as were the inlet ports of the top plate, which were located above the outlet ports of the bottom plate.

This series of tests showed that the method of distributing the water to the bed distributor can be important and suggests that with larger beds, such as the 5.5-foot diameter pilot-plate washer, the arrangement of the piping to the wash water distributor might be the controlling factor, not the distributor itself. A low dispersion coefficient ($0.025 \text{ cm}^2/\text{sec.}$) was produced only when both inlets and both outlets were employed. All other port combinations produced higher values for the dispersion coefficient. When only one inlet and one outlet was used, values of $0.075 \text{ cm}^2/\text{sec.}$ were obtained. Other tests which were carried out in a similar manner, except that no stainless

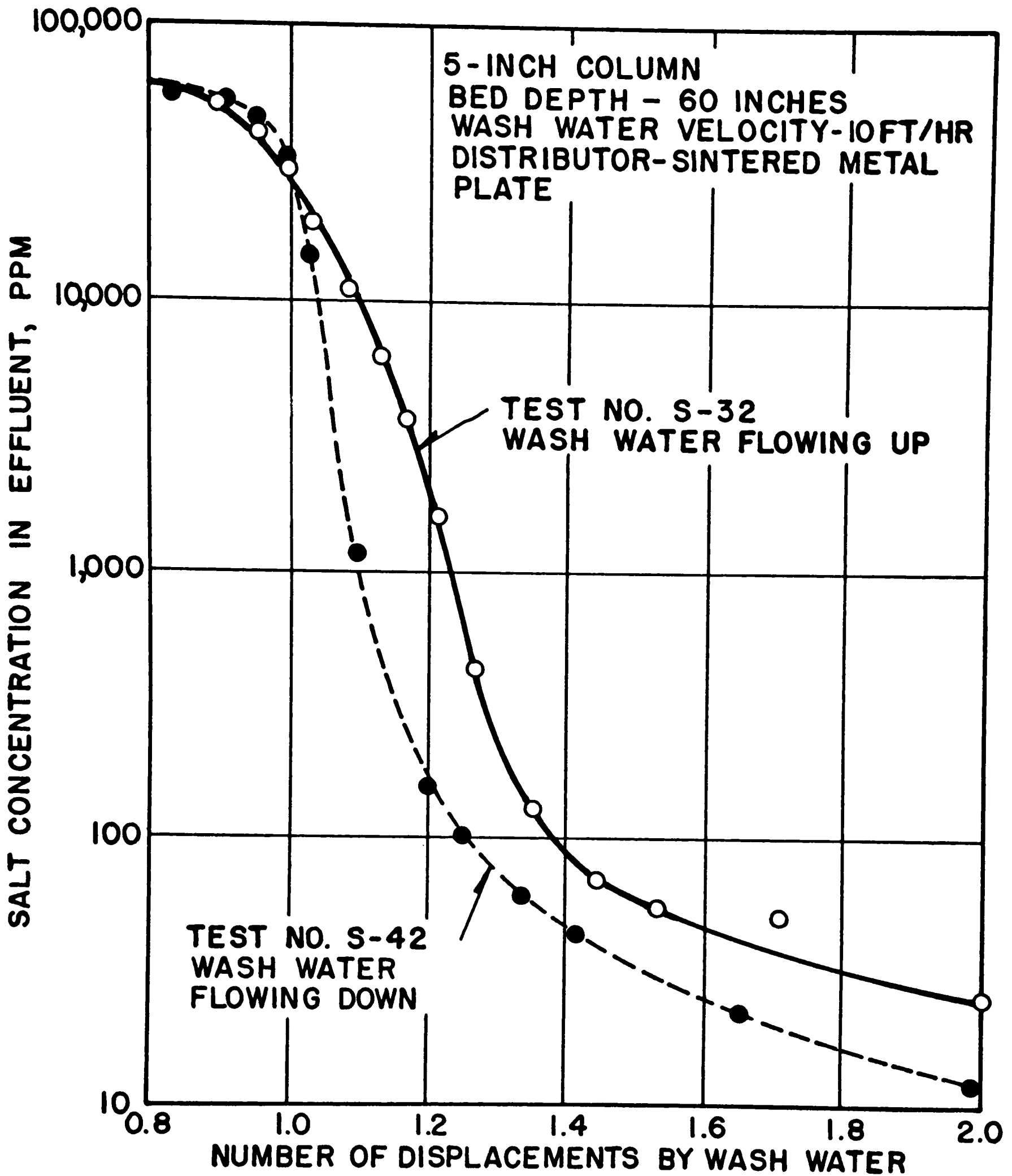


FIGURE 18
WASHING TESTS ON SAND

steel cloth was used in combination with the perforated plate, produced high dispersion coefficients regardless of the port combination (0.050-0.075 cm²/sec.).

5.5.3 Washing Tests on Propane Hydrate

The work done in the 5-inch column using sand was followed by washing tests on propane hydrate. Down-flow of wash water was used because of the tests on sand. A sintered metal plate was used for the wash water distributor as well as for the filter medium.

The results from these tests show that the physical components of the washing system together with down-flow of wash water are extremely important factors. The dispersion coefficients averaged at about 0.040 cm²/sec. and the salt content in the melt averaged the low value of 41 ppm. When the weight per cent of hydrate in the slurry was about 6%, the volume per cent hydrate in the bed was about 50. This is about a 25% increase in solids content over that which was obtained in this series when the slurry contained about 9% hydrate.

Some washing tests were made on 50-inch beds of propane hydrate in the 5-inch column. The dispersion coefficients for these tests were 0.050 cm²/sec. (U = 10 ft./hr.) and the melts were very low: 29 ppm.

5.5.4 Distributor Evaluation Tests

Previous tests have shown the importance of an even distribution across the bed. To achieve this condition, it is necessary to use a distributing device which offers resistance to the flow of water. However, a cheaper wash water distributor was needed. A pressure drop in excess of about 0.3 psi at a water velocity of 10 ft./hr. appears to be desirable in order to obtain good primary distribution across the wash water distributing device. Distributing devices which gave less favorable results had lower resistances. In an effort to incorporate this in a cheap distributor, it was decided to use a high resistance filter cloth in combination with two perforated metal plates containing 3/8-inch holes on 1/2-inch centers on each side of the cloth for protection against mechanical damage.

Twenty samples of filter cloth from various vendors were tested for permeability by measuring the pressure drop across the material at several water flow rates and some were found to have reasonable characteristics.

5.5.4.1 Sand Washing Tests - Filter Press

Tests were made in the 12-inch filter press in which salt water was washed from sand using a filter cloth having the desired permeability between

the perforated plates as the wash water distributor. The wash water entrance ports in the top plate and the effluent ports in the bottom plate were varied to determine the effect of the piping arrangement. Each plate on the press was provided with two nozzles located on opposite sides at diagonal corners. The press was set up so that the inlet ports in the top plate were located above the outlet ports in the bottom plate.

The results from these tests were used to calculate dispersion coefficients, which are given in the following table:

Wash-Water Distributor Evaluation Tests

Shriver 12-inch Filter Press; Bed Depth 12-inches
Salt Water Washed from Sand - Down-Flow of Water at
a Velocity of 10 ft./hr.

<u>Distributor Description</u>	<u>Average Dispersion Coefficient</u> <u>cm² per sec. x 10⁻³</u>		
	<u>1 Inlet,</u> <u>1 Outlet</u>	<u>1 Inlet,</u> <u>2 Outlets</u>	<u>2 Inlets,</u> <u>2 Outlets</u>
Plate perforated with 85 1/16-inch diameter holes in combination with stainless steel wire cloth 1/4-inch downstream from plate	40	41	24
Same distributor plate as above but without stainless steel wire cloth	67	-	60
Porous, stainless steel plate Grade D (65 micron mean pore opening)	60	-	52
Neva-Clog, Close Pattern	-	-	36
Filter cloth between two perforated plates having 3/8-inch holes on 1/2-inch staggered centers	37	33	29

The low values for the dispersion coefficients obtained by using the filter cloth between perforated plates were encouraging and indicated that this system should be suitable for use in the pilot plant washing chamber.

5.5.4.2 Hydrate Washing Tests - Filter Press

Washing tests on propane hydrate were carried out in the 12-inch filter press using the perforated-plate-filter-cloth system for the wash water distributor. The salt remaining in the melt averaged 33 ppm and the average value for the dispersion coefficients from the test data was 0.037 cm²/sec.

These values show again that a very close approach to plug flow through 1-foot hydrate beds can be obtained with a bed area of one square foot.

If a distributing device is used having the resistance mentioned, it is apparently possible to obtain similar results with sand as with hydrate. This made it worthwhile to build a filtration compartment which was much too large for the bench-scale reactor, but which could give indications from the washing experiments with sand about the expected behavior with hydrate.

5.5.4.3 Washing Chamber Mock-Up

As the final step in the experimental evaluation of the wash water distributor, sand washing tests were performed in a mock-up of the filter-washer-decomposer chamber proposed for the pilot plant. This unit consisted of a closed tank 5.5 feet in diameter containing a wash water distributor under the cover and a filter medium supported on the bottom of the vessel two feet beneath the distributor. The wash water distributor plate was patterned after the perforated-plate-filter-cloth system successfully used in the filter press on sand and hydrate. The distributor was located one-half inch below the top cover. Part of this space was occupied by a one-quarter-inch piece of sheet metal so that a V-shaped trough one-half inch deep by twenty inches wide at the wash-water inlet end extended across the center of the distributor plate. The trough and remaining one-quarter-inch space between the cover and the distributor plate was considered to be sufficient to bring about an even distribution of the incoming wash water before it passed through the distributor plate.

The filter medium consisted of a piece of filter cloth supported between two perforated plates. The cake side plate contained 1/8-inch holes on 3/16-inch centers and the other plate was the same as those used in the distributor assembly, that is, 3/8-inch holes on 1/2-inch staggered centers. The space between the filter medium and the bottom had the same configuration as that between the cover and the distributor plate. The wash-water inlet port was located on the top cover at the edge of the vessel and the filtrate outlet was located on the side of the filter at the bottom 180° from the inlet port. Supporting equipment included flow meters, a 400-gallon tank for the preparation of salt water and a pump to charge salt water to the sand bed.

5.5.4.3.1 Method of Testing

A two-foot bed of washed and sized (20 x 50 mesh) white sand was formed in the vessel. This particle size is 10-100 times larger than propane hydrate particles. A 4% solution of salt water was prepared in the tank and about 1-1/2 displacements of the solution were passed through the bed to drain. The salt solution was then pumped through the bed in up-flow.

Fresh water containing about 120 ppm dissolved salts was used for the washing fluid. The wash water was passed through the bed using down-flow

at a superficial velocity of 10 ft./hr. Samples of the filtrate leaving the outlet port were taken throughout the washing procedure. Additional samples of filtrate were withdrawn through the bottom of the vessel at various points. All samples of filtrate were taken at the same time. Section A-A in Figure 19 shows the location of the sampling points (A through G).

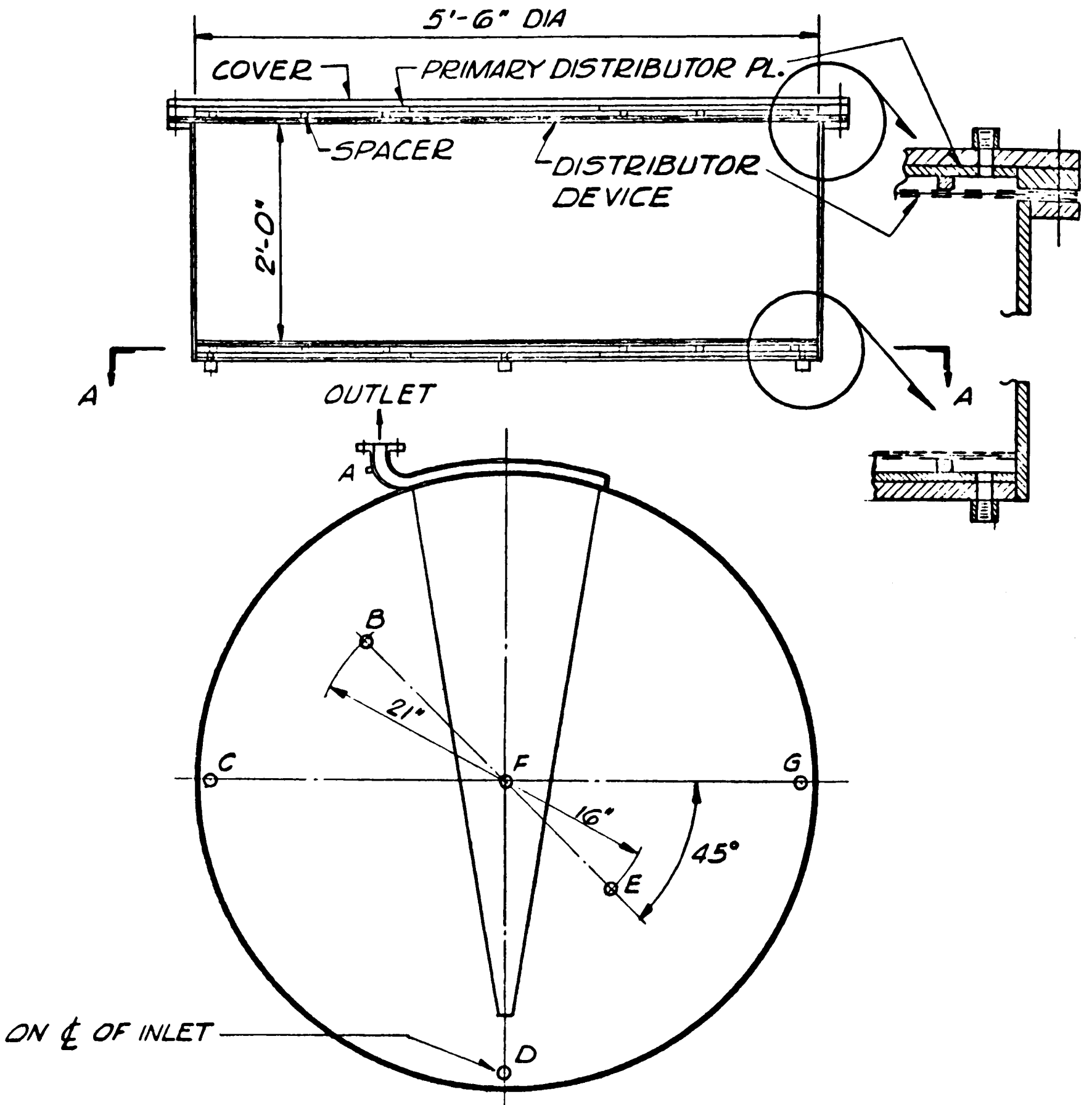
5.5.4.3.2 Results of Tests

Four sand washing tests were made in the washing chamber mock-up using a wash water velocity of 10 ft./hr. (feed rate of 30 gal./min.). Samples of filtrate were taken from the main effluent stream (sample point A) and from other points (see Figure 19). Dispersion coefficients calculated from the test data are given in the following table:

Dispersion Coefficients Obtained From
Washing Tests in Mock-Up

Run Number, S-	81	82	83	84
Dispersion Coefficient, $\text{cm}^2/\text{sec.} \times 10^3$				
Sample Point A	33	30	37	41
Sample Point B	-	-	34	38
Sample Point C	-	-	46	37
Sample Point D	24	29	33	25
Sample Point E	-	-	32	36
Sample Point F	37	35	17	16
Sample Point G	-	-	20	17

There was good agreement between the values developed from the samples taken from the main effluent stream (Sample A). Figure 20 shows the relationship between the salt content of the effluent and the cumulative effluent leaving the bed for the four tests. The dispersion coefficient based upon the curve in this figure is $0.030 \text{ cm}^2/\text{sec.}$, a value which demonstrated that good distribution of wash water across the sand bed was obtained. Figure 21 shows the salt concentration in the filtrate taken at the various sampling points as a function of time throughout Test No. S-84. It takes Sample C approximately 2 minutes longer to arrive at a concentration of 1000 ppm. It is remarkable that this does not have a stronger influence on the results.



SECTION AA
 (SHOWS PRIMARY DISTRIBUTOR
 PLATE AND SAMPLE POINTS)

FIGURE 19
 WASHING CHAMBER MOCK-UP

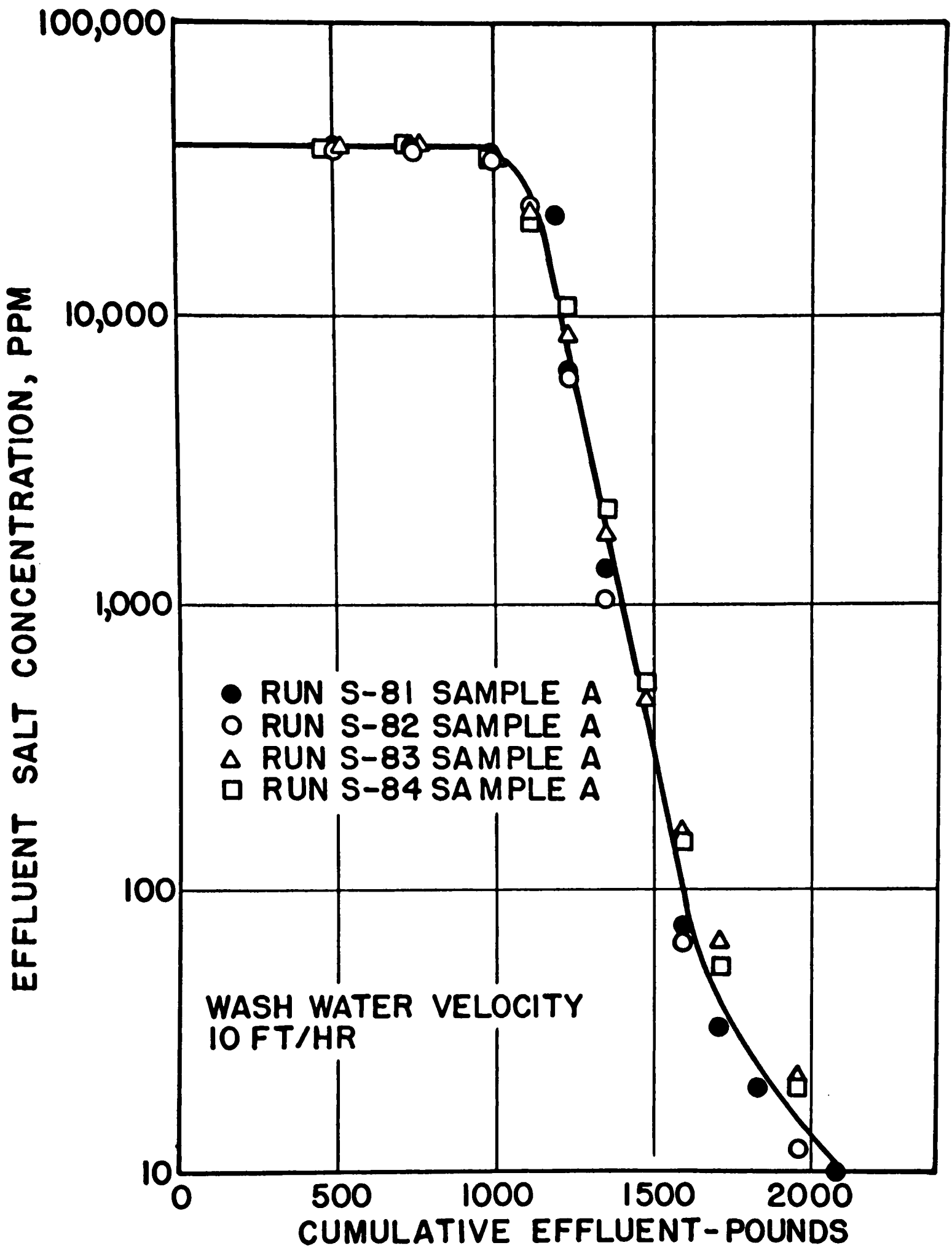


FIGURE 20
WASHING CHAMBER MOCK-UP
SAND WASHING TESTS

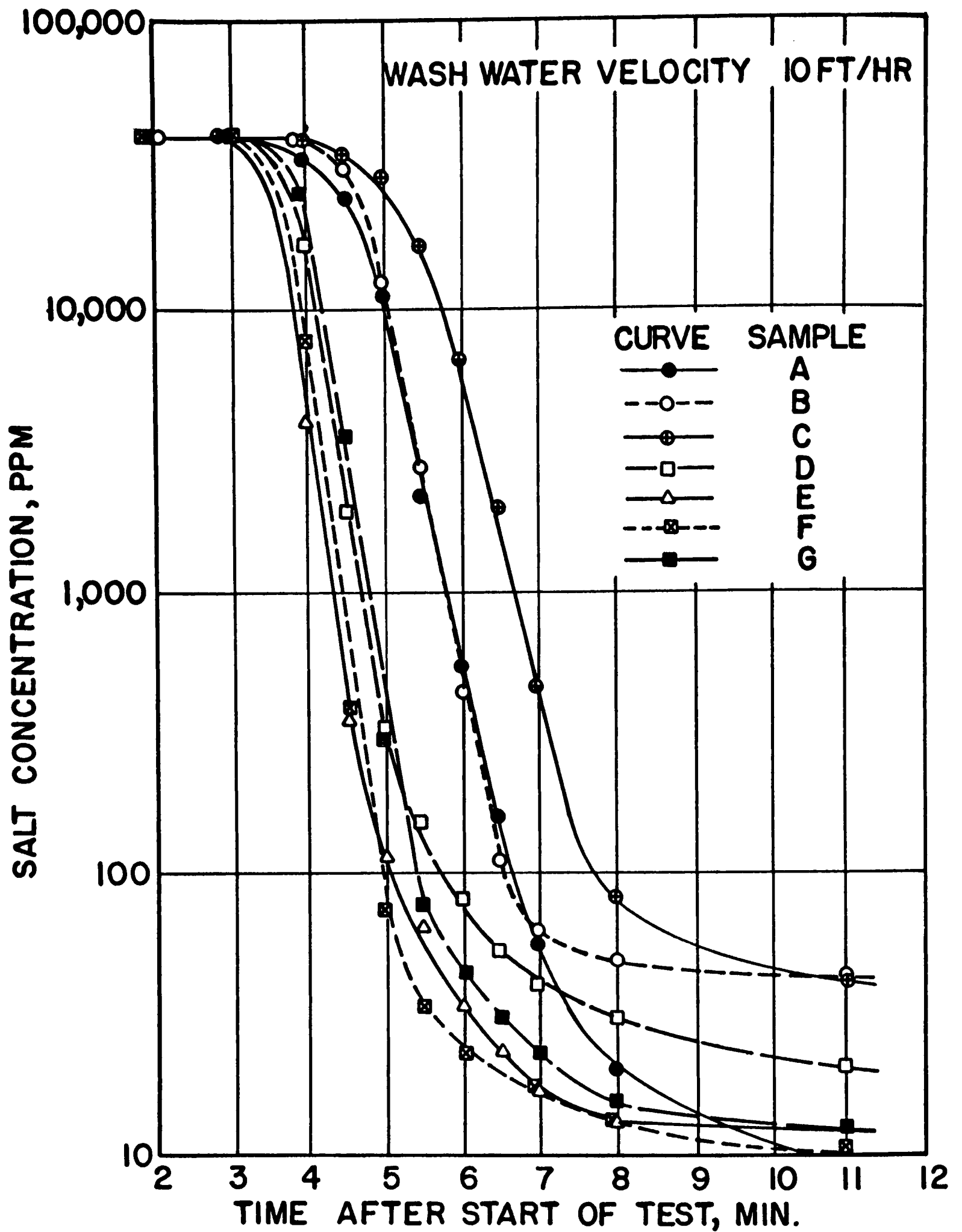


FIGURE 21
WASHING CHAMBER MOCK-UP
SAND WASHING TEST NO. S-84

6. HYDRATE DECOMPOSITION STUDIES

Experiments were performed to investigate various factors involved in the decomposition step of the hydrate process. Two different approaches were explored: decomposition of the hydrate as it remained in cake form in the filter and decomposition of hydrate suspended in an agitated slurry.

6.1 Decomposition Tests - Filter Press

Following the washing tests in the filter press, the washed hydrate was allowed to remain in the frame so that decomposition tests using condensing propane could be performed. An excess of gas at constant pressure was passed through the hydrate beds. The condensed propane and water from the decomposed hydrate were collected in calibrated melt receivers (see Figure 15). The heat transfer coefficients calculated for each test were based upon the condensation rate of propane as measured in the calibrated receivers, the temperature difference between the condensation temperature of the propane and the critical decomposition temperature of the hydrate and the superficial area of the bed at the start of the test (0.82 ft.²).

In general, the propane condensation rate varied throughout each test. During the first 2-3 minutes of the test, the condensation rate increased rapidly. After this initial period, a steady-state condition was reached and the condensation rate remained relatively constant. Near the end of the test, the condensation rate decreased with time until it reached zero. The maximum heat transfer coefficient was calculated from data taken during the steady-state period of the test and the average coefficient was based on the total amount of propane condensed and the total time during which the condensation took place.

Most of the fixed-bed decomposition tests in the filter press were made using a 12-inch deep chamber. The few tests carried out in a 6-inch deep chamber resulted in maximum and average heat transfer coefficients of 450 and 250 BTU/(hr.)(°F) for a cake of one square foot cross section and 10 inches deep, respectively. Experiments were also made in the 6-inch chamber to determine the decomposition rate using warm water as the source of heat rather than condensing propane. Warm water at 60 psig was passed into the bed at a constant rate. The temperature of the water leaving the bed was determined. Heat transfer coefficients during steady-state conditions averaged 525 BTU/(hr.)(°F).

The heat transfer rates obtained from the first eight runs carried out on 12-inch beds averaged 290 BTU/(hr.)(°F) for one square foot of bed.

In an attempt to improve the decomposition rate, a sparger pipe for the addition of the propane gas was installed inside the filter frame on top of the bottom filter cloth. The sparger consisted of a square formed from 1/2-inch copper pipe. The heat transfer increased to 570 BTU/(hr.)(°F) for one square foot of bed. There was also considerable improvement in the maximum heat transfer. The time required to decompose the hydrate was reduced to about half of that required when the propane was admitted through the filter cloth

(35 instead of 70 minutes). The maximum rate of heat transfer was increased by about 20%. A comparison of the maximum and average rates indicates that the distribution of the propane might be more important than the increased turbulence in the bed. Through the use of the sparger, the hydrate in the corners and along the outside wall of the frame was also decomposed by the condensing propane.

It was found that for a given propane gas distributor and bed depth, the fastest decomposition rates are obtained when the gas was introduced at the bottom of the bed and was permitted to flow up through the bed.

The decomposition tests were repeated after replacing the sparger by a plate with 0.063-inch holes on a 2-inch center to center distance, which gave apparently a good propane distribution. The average heat transfer coefficient was found to be 740 BTU/(hr.)(°F). Other plates with a larger number of holes gave varying results, the best being 10-20% higher than the first plate.

It would be desirable to design the distributor for a commercial installation so that it would function equally well as a filter medium and as a gas distributor. Therefore, a filter medium similar to that used successfully in the mock-up experiments was installed in the filter press to investigate the behavior of this device as a gas distributor. This assembly consisted of a highly permeable filter cloth supported between two perforated plates. The cake-side plate contained 1/8-inch holes on 3/16-inch centers. This arrangement resulted in about 9% exposed cloth area.

Three tests were made using this system. The decomposition rate during the first test was very low, approximately 350 BTU/(hr.)(°F) for a cake of one square foot. Increasing the excess of gaseous agent causes additional stirring which increases the heat transfer to about 700 BTU/(hr.)(°F) for one square foot of filter cake.

6.1.1 Decomposition Tests Combined with Flushing

Experiments were carried out in the filter press to determine if the washed hydrate cake could be removed by flushing the chamber with water. The washed hydrate bed was partially decomposed using condensing propane for various periods of time. The decomposition cycle was followed by admitting water to the chamber through various nozzles at different flow rates. The hydrate and sluicing water were removed from the chamber through the 1-inch charging nozzle. Following the sluicing cycle, the chamber was blown as dry as possible and then isolated from the receivers. The amount of material not removed from the chamber by decomposition and by flushing with water was reported as a per cent of the total melt.

The results of these tests were disappointing since some hydrate always remained in the chamber after flushing. The best situation was obtained when ninety per cent of the melt was removed by decomposing for 8 minutes with propane at 80 psig followed by a 4-minute flushing period with 6°C water at 3.6 gpm.

6.2 Decomposition Tests - 5-inch Column

Decomposition tests were made in the 5-inch column after the washing was complete. Considerably higher coefficients were obtained in the 5-inch column than were obtained in the 12-inch filter press. The height of the bed in the 5-inch column also affected the value of the coefficient. The average coefficient had an average value of about 1600 BTU/(hr.)(ft.²)(°F) for the 15-inch beds, 2350 BTU/(hr.)(ft.²)(°F) for the 30-inch beds and 5100 BTU/(hr.)(ft.²)(°F) for the 66-inch beds. The distributing plate was the same as used before (0.063-inch holes). It is possible that the decomposition goes more slowly in larger equipment. If this is true, it can be expected that the design of gas distributors for commercial installations will require special attention.

6.3 Slurry Decomposition Tests

Tests were carried out in the 10-gallon bench-scale reactor in which hydrate was decomposed while suspended in an agitated slurry. Heat for decomposition was supplied by circulating warm water through the reactor jacket and in other tests by condensing the hydrate-forming gas in the slurry. The rate at which the hydrate decomposed seemed to be limited only by the rate at which the heat could be supplied to the main body of the slurry. A study of the decomposition data obtained from tests in fixed chambers showed that decomposition rates ranging from 5 to 15 lbs. hydrate per hour per gallon were obtained in the 5-inch column and rates averaging about 5 lbs. hydrate per hour per gallon were obtained in the 12-inch filter press. Although these rates are similar to those obtained during the tests in the 10-gallon reactor, the thermal driving force in the fixed-bed tests was about 50 to 100 times larger than those existing in the slurry decomposition tests. It was concluded that agitation during decomposition increased the heat transfer rate from the water to the hydrate particle.

Several slurry decomposition tests were made in which the rate of propane condensation was very low. Samples of brine were removed from the reactor during the test to determine the hydrate concentration in the slurry. The slurry temperature was also recorded throughout the test. Figure 22 shows the relationship between the hydrate content of the slurry, the slurry temperature and the reactor pressure. As expected, a sharp break occurred in the curve representing the slurry temperature at the same time the hydrate content of the slurry reached zero.

Three decomposition tests were made using 4.8% artificial sea water and one using 3.6% artificial sea water. A decomposition curve in pure water was also determined in the bench-unit reactor. The break points obtained during these tests have been plotted against the dissolved salts in the brine on a graph shown in Figure 23. The curve representing the bench-unit data was used to determine the thermal driving forces during this investigation.

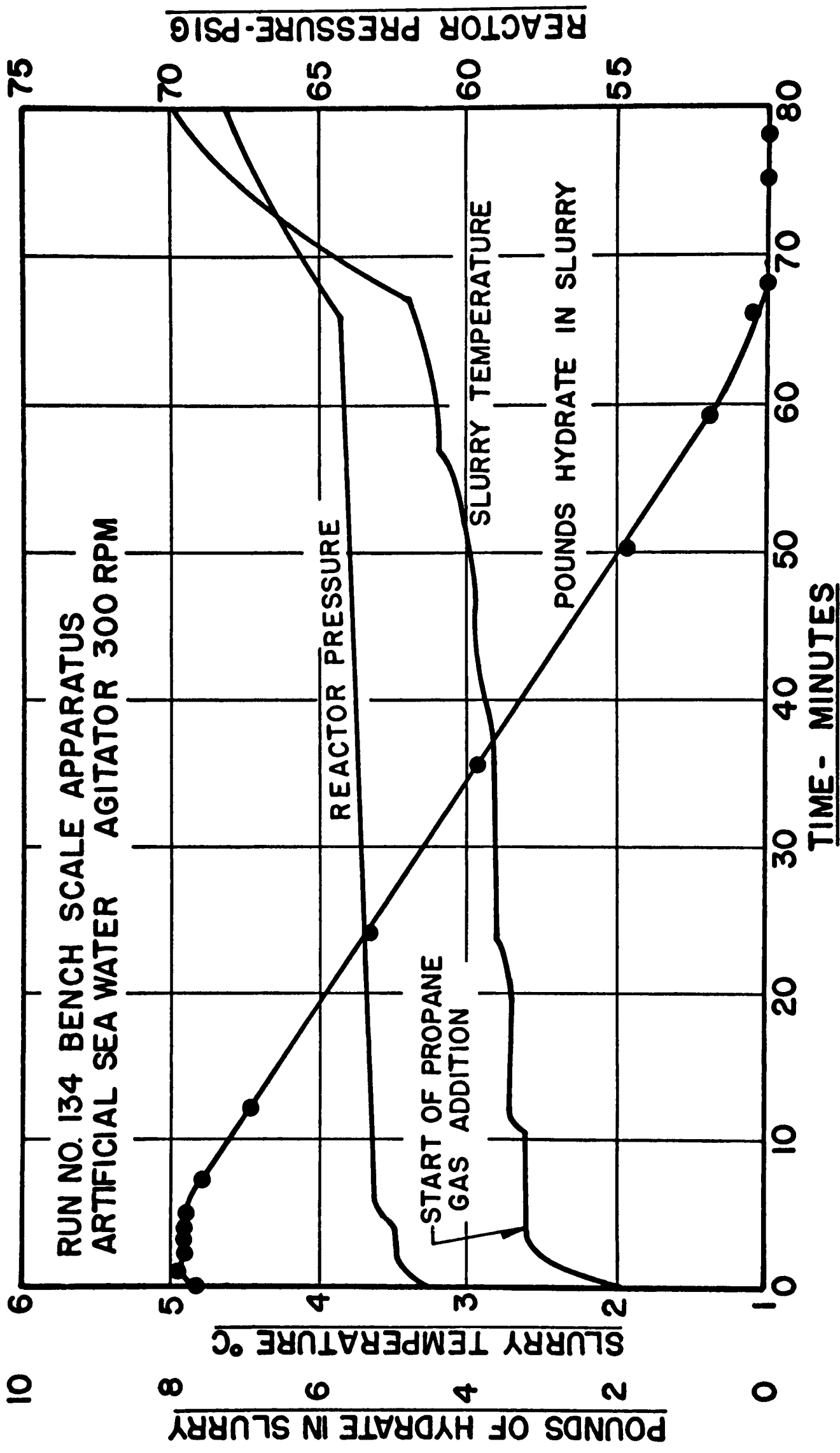


FIGURE 22
DECOMPOSITION OF PROPANE HYDRATE

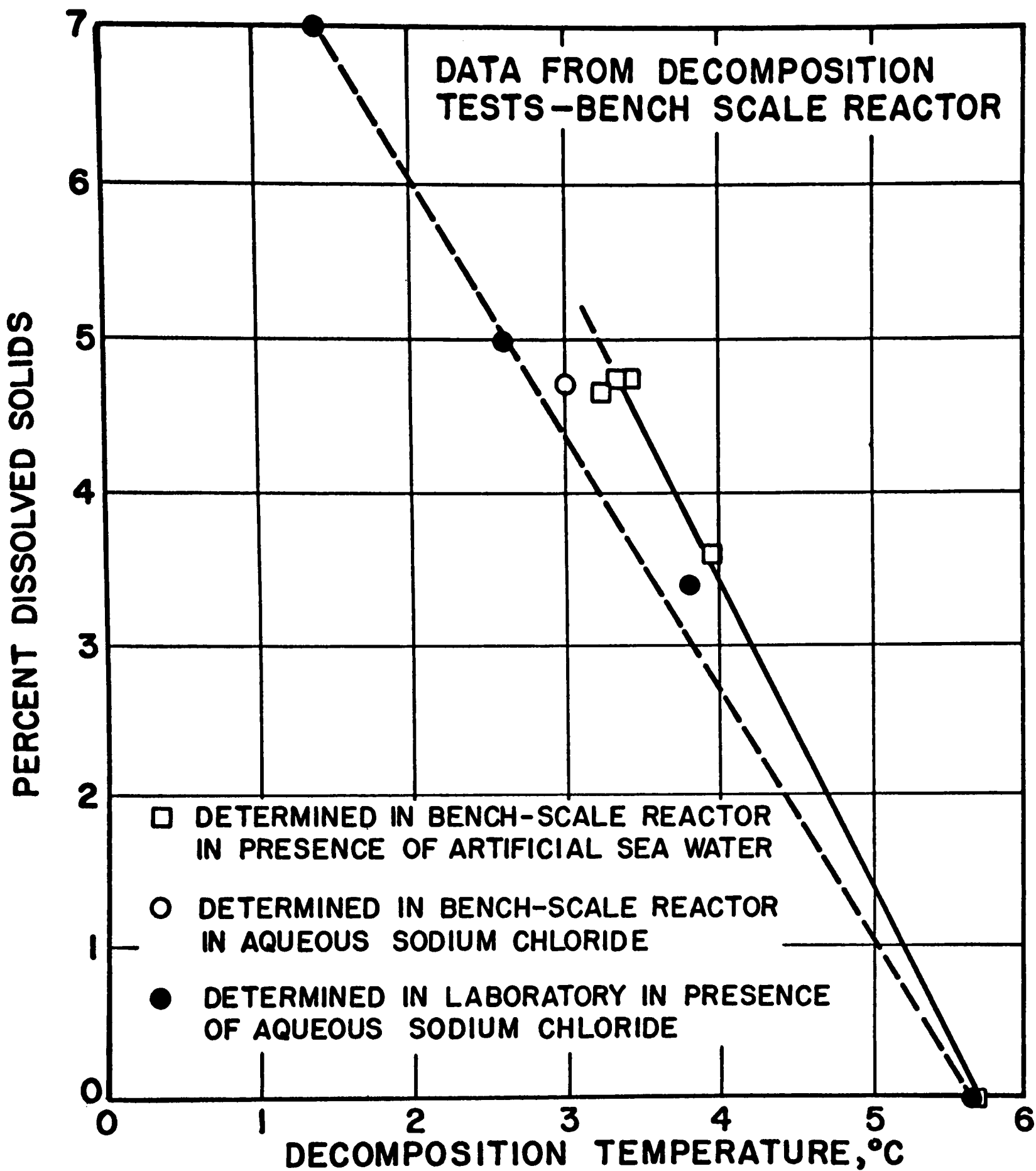


FIGURE 23
EFFECT OF DISSOLVED SOLIDS ON THE DECOMPOSITION TEMPERATURE OF PROPANE HYDRATE

7. LABORATORY STUDY OF PROPANE HYDRATE

Propane hydrate was formed and examined in the laboratory in order to obtain information which could be used to supplement the bench-scale studies. One phase of this work was devoted to the development of an optical system whereby the hydrate could be studied using a microscope and photomicrographs.

7.1 Micro-Visual Examination of Propane Hydrate

Hydrate for microscopic studies was formed in a small jacketed reactor fabricated from four-inch stainless steel pipe and a pipe cap with a four-inch sight-glass forming the top cover. The reactor was fitted with connections for a thermocouple, and the entry of gas and liquid propane. Two stuffing boxes were provided: one for an agitator shaft seal and the other for a 3/8" O.D. transparent plastic ("Lucite") rod. The agitator was turned by an air motor. A sight port containing a 3/4-inch O.D. x 0.068-inch thick glass window was installed on the side of the reactor directly opposite the rod-packing assembly. Figure 24 shows a sketch of the laboratory hydrate reactor and the optical system used in this work.

The Lucite rod was used to transmit light from the source to the inside surface of the viewing window. When the light-rod packing gland was loosened, the distance of the end of the rod from the window could be adjusted to vary the intensity of the illumination by moving the rod. The rod contained an eighth-inch dog-leg about two inches from its internal end so that by turning the rod about its own axis, the location of the light in reference to the axis of the microscope could be adjusted. The light-source end of the rod was square cut and polished. The internal end of the rod had a concave surface which was polished and contained a one-eighth-inch diameter opaque spot at its center. This configuration produced oblique lighting. Condensation of moisture on the outside surface of the viewing window was prevented by passing a small stream of nitrogen across the glass surface. A rubber bellows extending from the window to the microscope tube assisted in keeping the moisture from reaching the window.

Propane hydrate was formed in pure water in the laboratory reactor in the following manner: water in the reactor was brought to hydrate formation temperature and then pressured with propane gas to the condensation pressure of propane. Additional liquid propane was then added and the mixture of liquids was agitated rapidly for about five minutes. With little or no agitation, the pressure was reduced suddenly to cause some of the liquid propane to boil. The rapid evaporation of the propane caused the water to become sub-cooled at the liquid propane-water interface. The sub-cooling brought about the formation of a small amount of ice crystals and/or hydrate crystals which, in turn, would cause the hydrate to nucleate. On several occasions when ice particles were added to the reactor, sub-cooling by flashing the liquid propane was not necessary to start the formation of hydrate. Nucleation could also be initiated through the use of the agitator when the liquid agent was present. It was believed that cavitation behind the impeller blades caused some of the droplets of liquid propane to flash which resulted in nucleation.

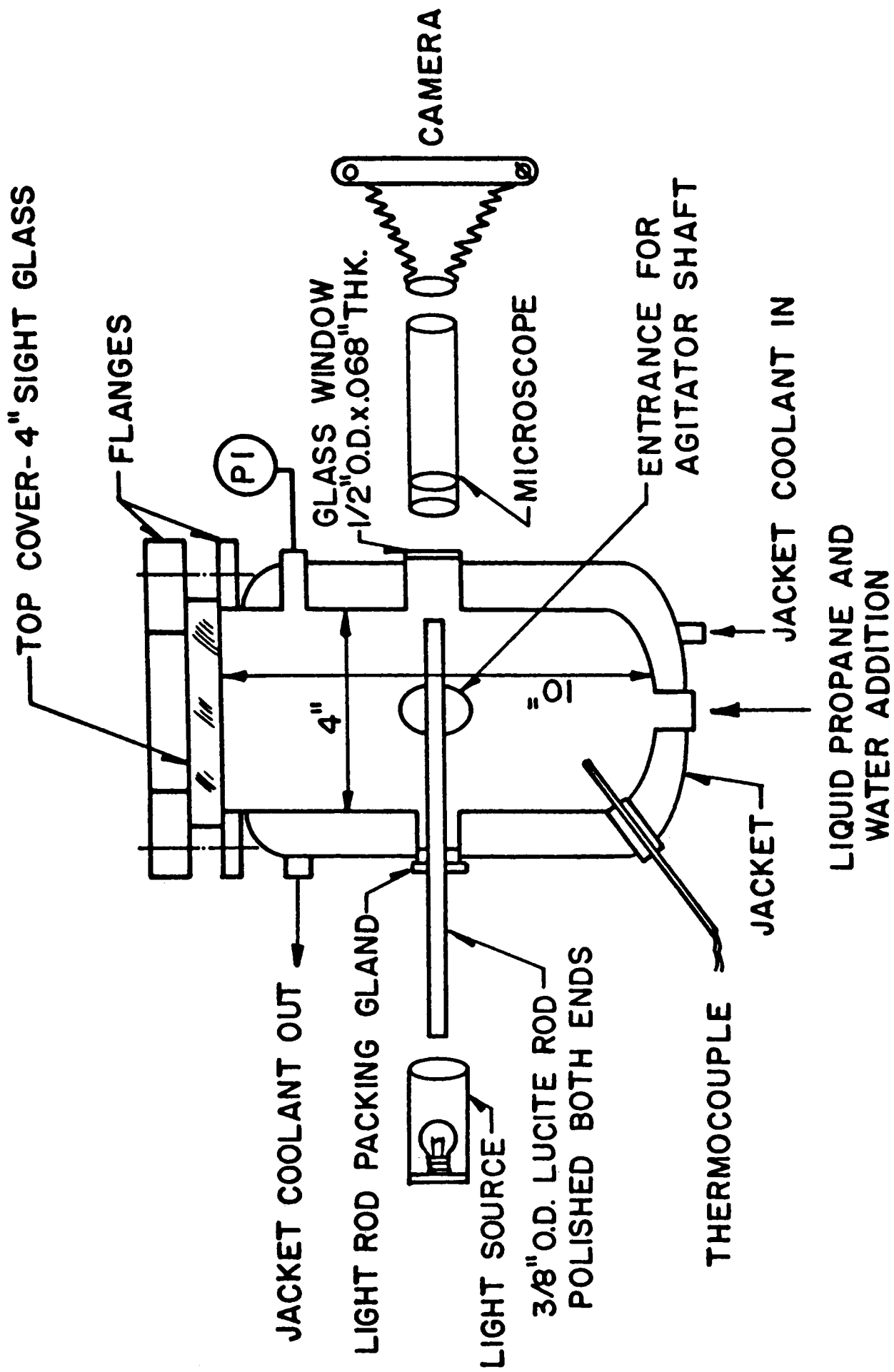


FIGURE 24
HYDRATE LABORATORY REACTOR SHOWING
PHOTOMICROGRAPHIC ASSEMBLY

An examination of propane hydrate grown in the aqueous phase indicated that hydrate crystals form on the surface of bubbles of propane gas. No growth of propane hydrate was ever seen in a region where the gas was not present. When a system containing liquid propane and water saturated with propane was allowed to stand with no agitation at temperature and pressure conditions favoring hydrate formation, no growth of hydrate would occur in the liquid phase even if seed crystals were present. Under these conditions, a slow growth of hydrate would take place on the inner surface of the reactor above the liquid propane level. Upon standing, the growth would cover the inside wall of the vessel, but under no circumstances did the growth of hydrate progress into the liquid propane layer. In the absence of liquid agent, the growth of propane hydrate could not be induced to take place under the surface of the water. It was concluded that the presence of the gas phase is necessary for the growth of hydrate to take place. Figures 25-29 show photomicrographs of propane hydrate crystals.

7.2 Rate of Propane Hydrate Formation in the Vapor Phase

The rate of hydrate formation on the inner surface of the laboratory reactor above the aqueous phase was determined at pressures below the propane saturation pressure. The growth rate was measured by determining the volume of propane gas absorbed in the reaction at constant pressure. The apparatus consisted of a propane gas reservoir, a water reservoir and a graduated sight glass containing water hooked in series with the reactor. The whole system was regulated to the test pressure and then isolated from the propane gas supply cylinder. As the propane was used in the reactor, an unbalance in pressure between the reactor and the gas reservoir caused water to flow from the water reservoir into the sight glass. The rate of volume displacement in the sight glass was taken as the rate of propane consumption. Figure 30 presents the growth rates as a function of thermal driving force. Note that the addition of 20 ppm of Aerosol MA caused about a 10-fold increase in the growth rate. There seemed to be little difference between the growth rate from diluted natural sea water and artificial sea water at a salt level of about 2.5%.

7.3 Adhesion of Hydrate to Surfaces

Experiments were made to determine if hydrate would adhere to various surfaces which were exposed to water and gaseous hydrate former. If this could be brought about, certain other systems of hydrate formation and hydrate-brine separation could be considered. A disk of the material to be tested was half submerged in water held at hydrate formation temperature. The disk was revolved at 6 RPM. Many surfaces were tested: wood, glazed and unglazed ceramic, Teflon, ZnO and MnO, stainless steel and carbon steel. In all cases, the adhesion was very poor. A small rod easily removed the hydrate mass from the surface of the rotating disk.

Cooled surfaces did not show better adhesion.

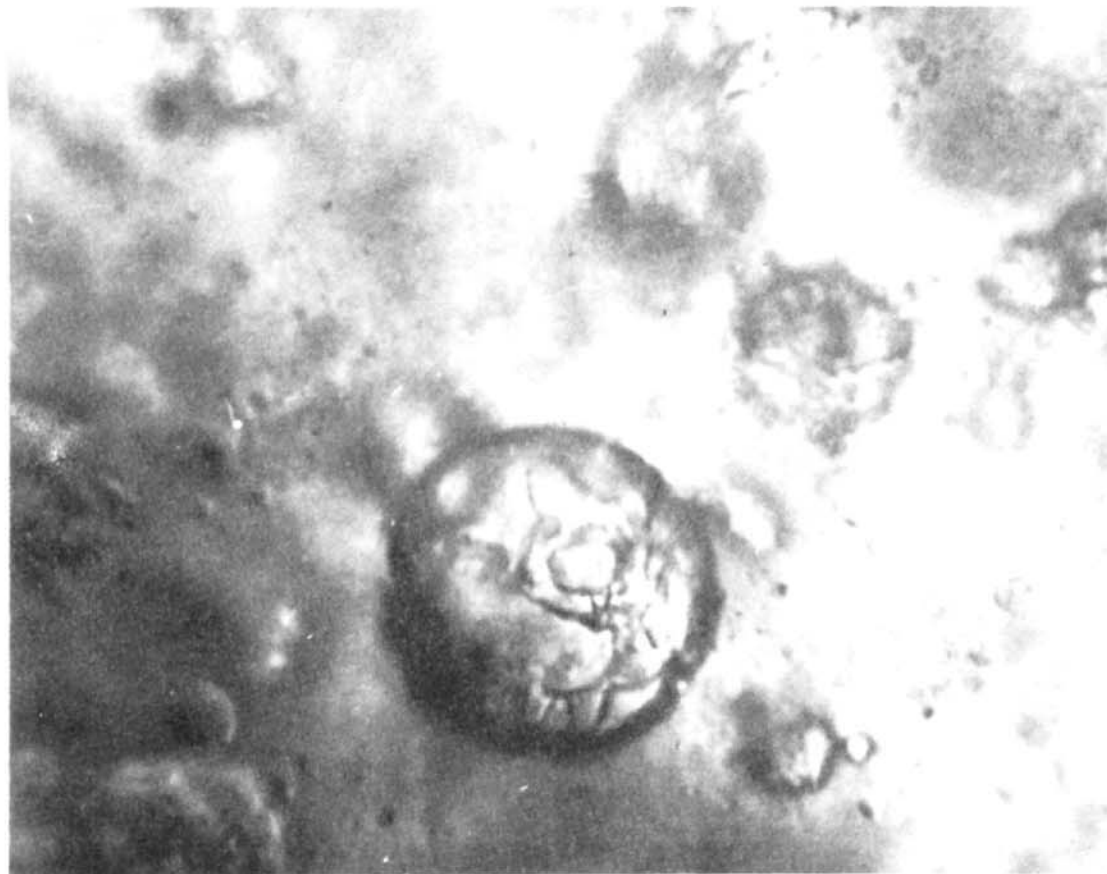
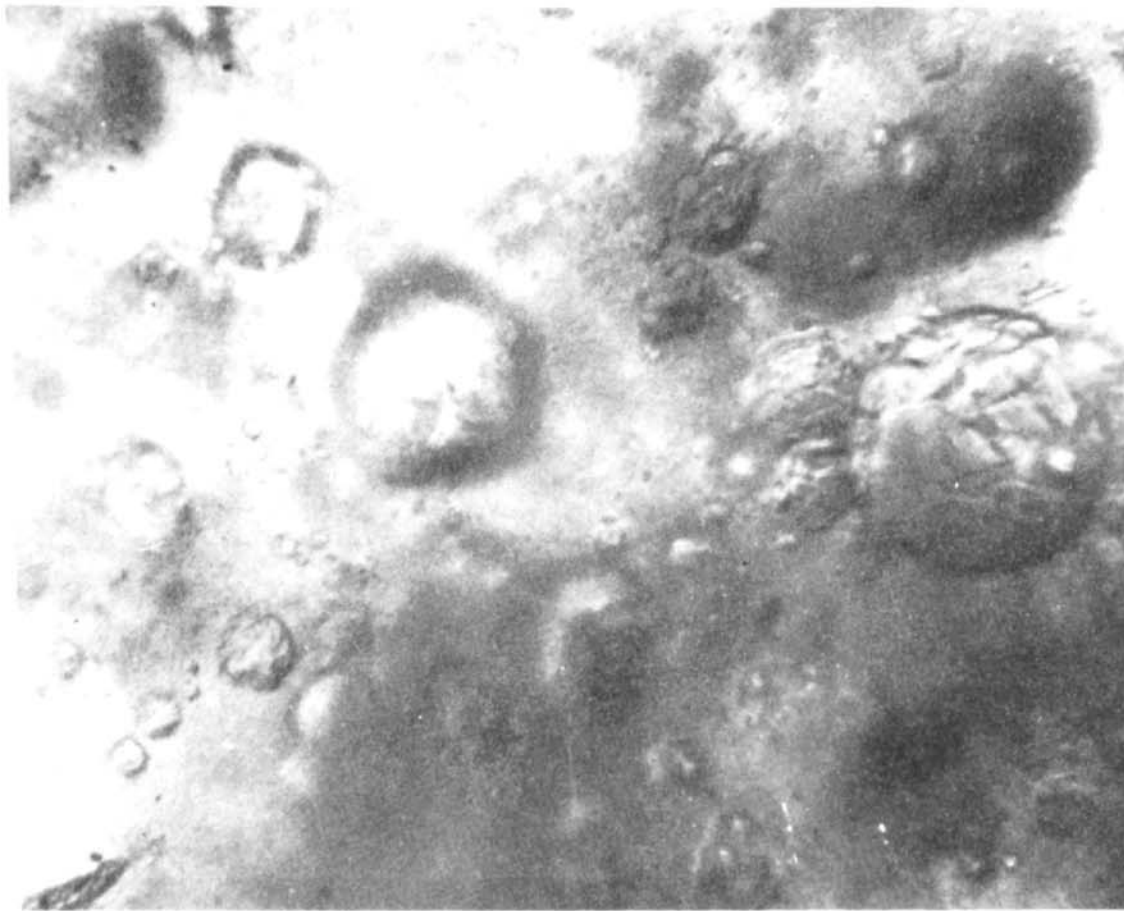


FIGURE 25 - PHOTOMICROGRAPHS OF PROPANE HYDRATE CRYSTALS FORMED ON THE SURFACE OF PROPANE GAS BUBBLES SUSPENDED IN PURE WATER. MAGNIFIED 150X.



FIGURE 26 - PROPANE HYDRATE CRYSTALS GROWN ON THE SURFACE OF A PIPE CLEANER SATURATED IN WATER CONTAINING 0.2% AEROSOL MA. PROPANE GAS WAS THE CONTINUOUS PHASE. MAGNIFIED 65X.

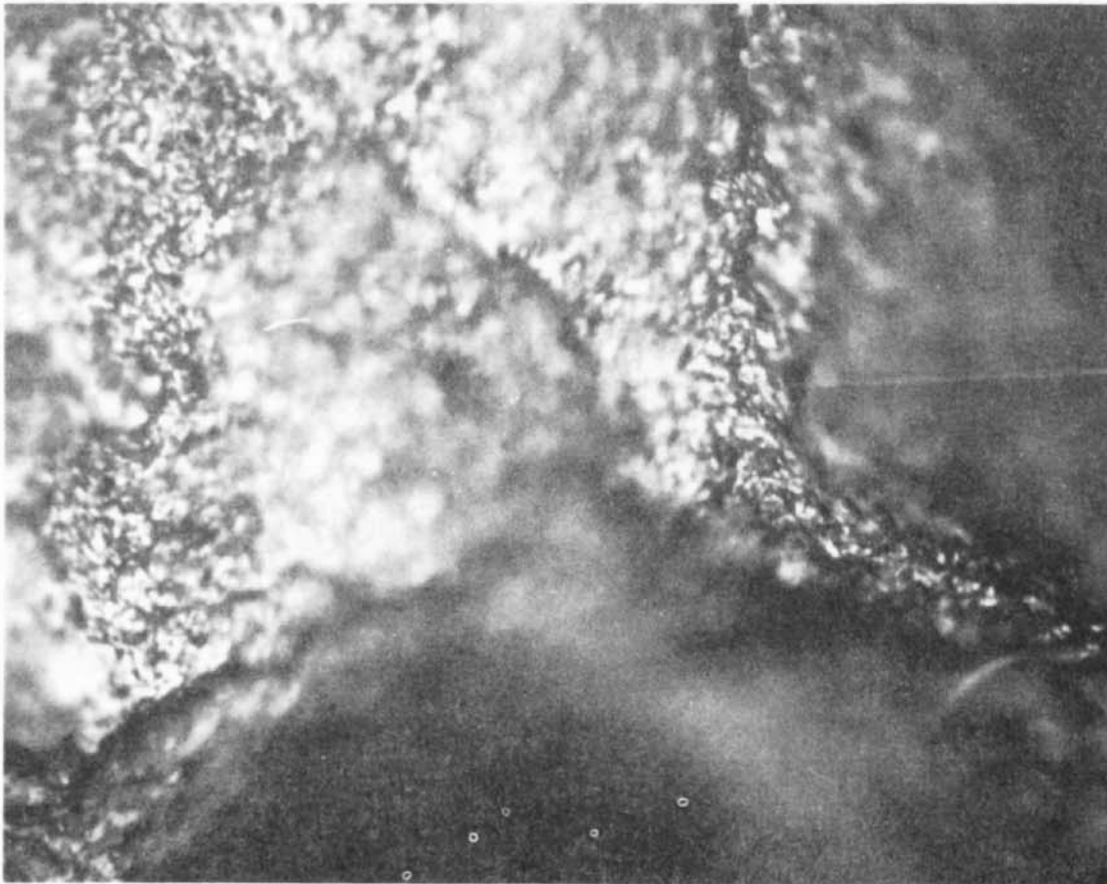


FIGURE 27 - APPROXIMATELY SAME FIELD AS FIGURE 26 AFTER PROPANE HAD BEEN CONDENSED ON SURFACE OF CRYSTAL MASS.

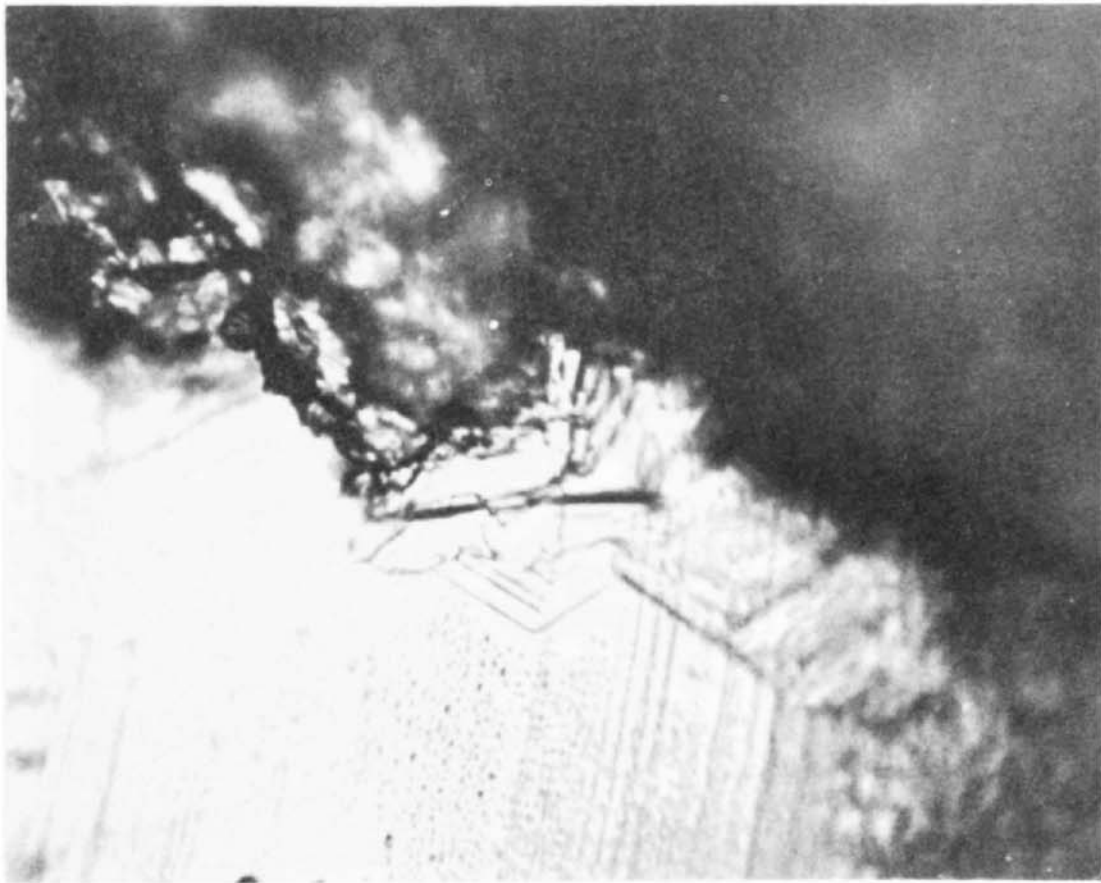
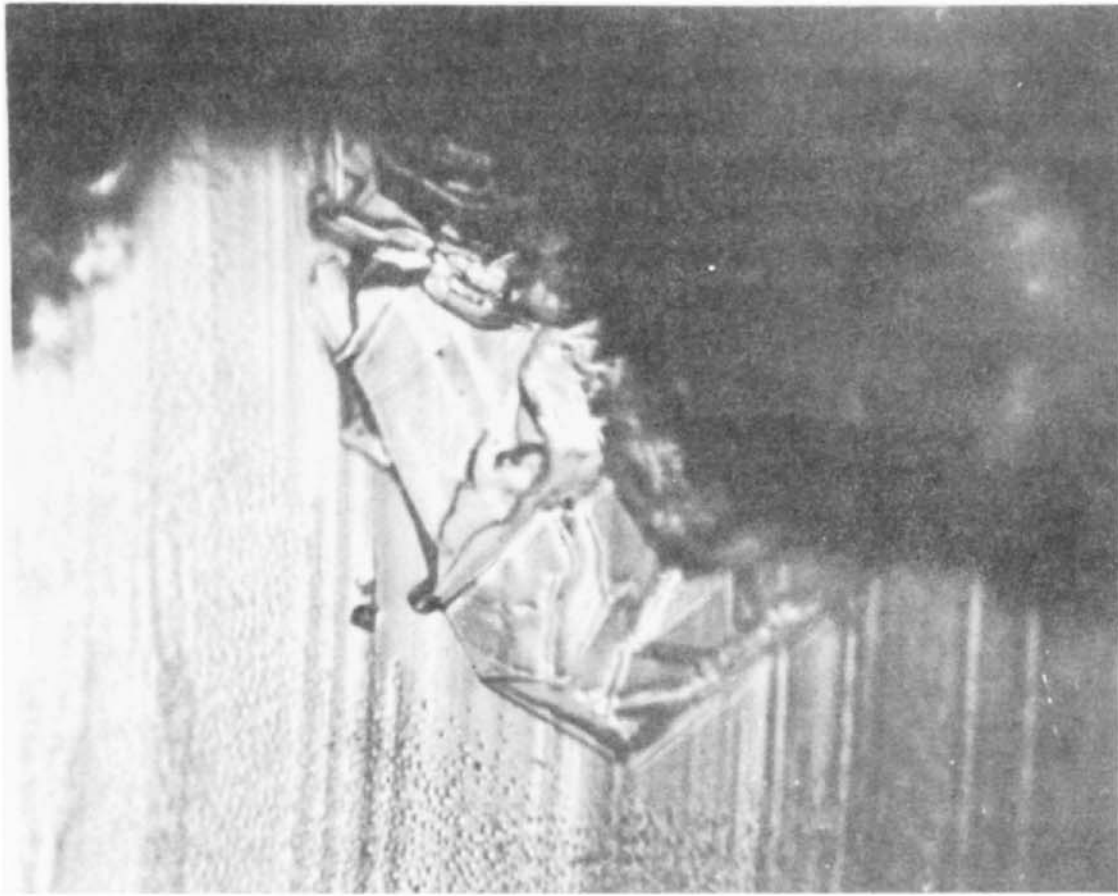


FIGURE 28 - PROPANE HYDRATE CRYSTALS GROWN ON THE END OF THE LIGHT ROD (SEE TEXT) WITH PROPANE GAS AS THE CONTINUOUS PHASE. NO WETTING AGENT PRESENT. MAGNIFIED 175X.

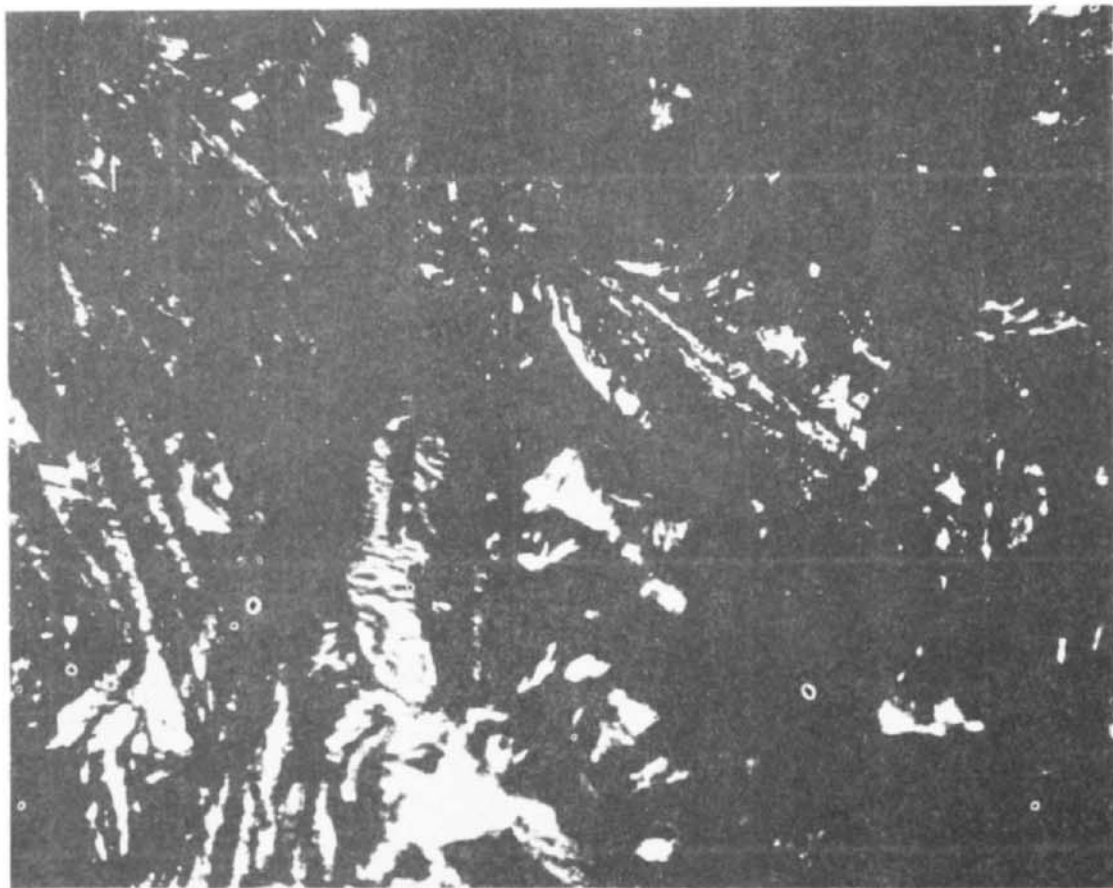
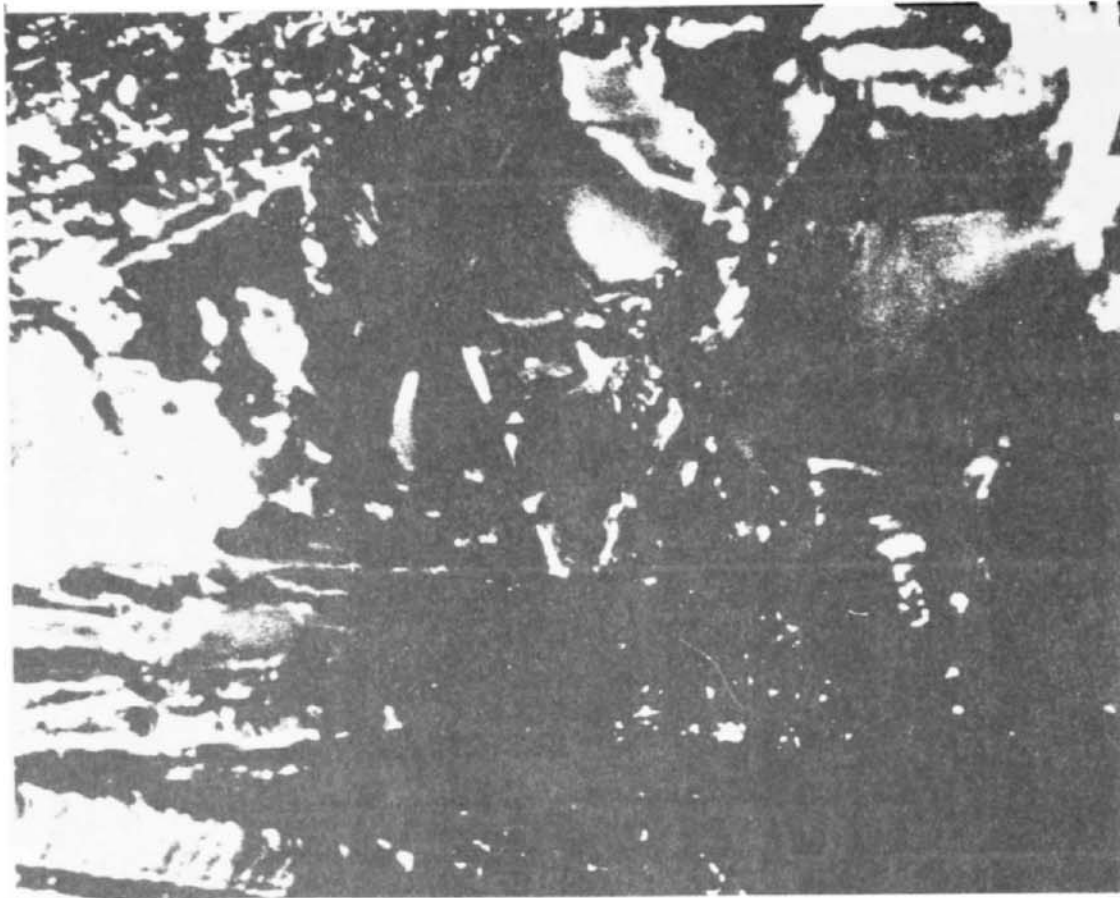


FIGURE 29 - PROPANE HYDRATE CRYSTALS GROWN ON THE END OF THE LIGHT ROD (SEE TEXT) WITH PROPANE GAS AS THE CONTINUOUS PHASE. WATER CONTAINED 0.1% AEROSOL MA. MAGNIFIED 45X.

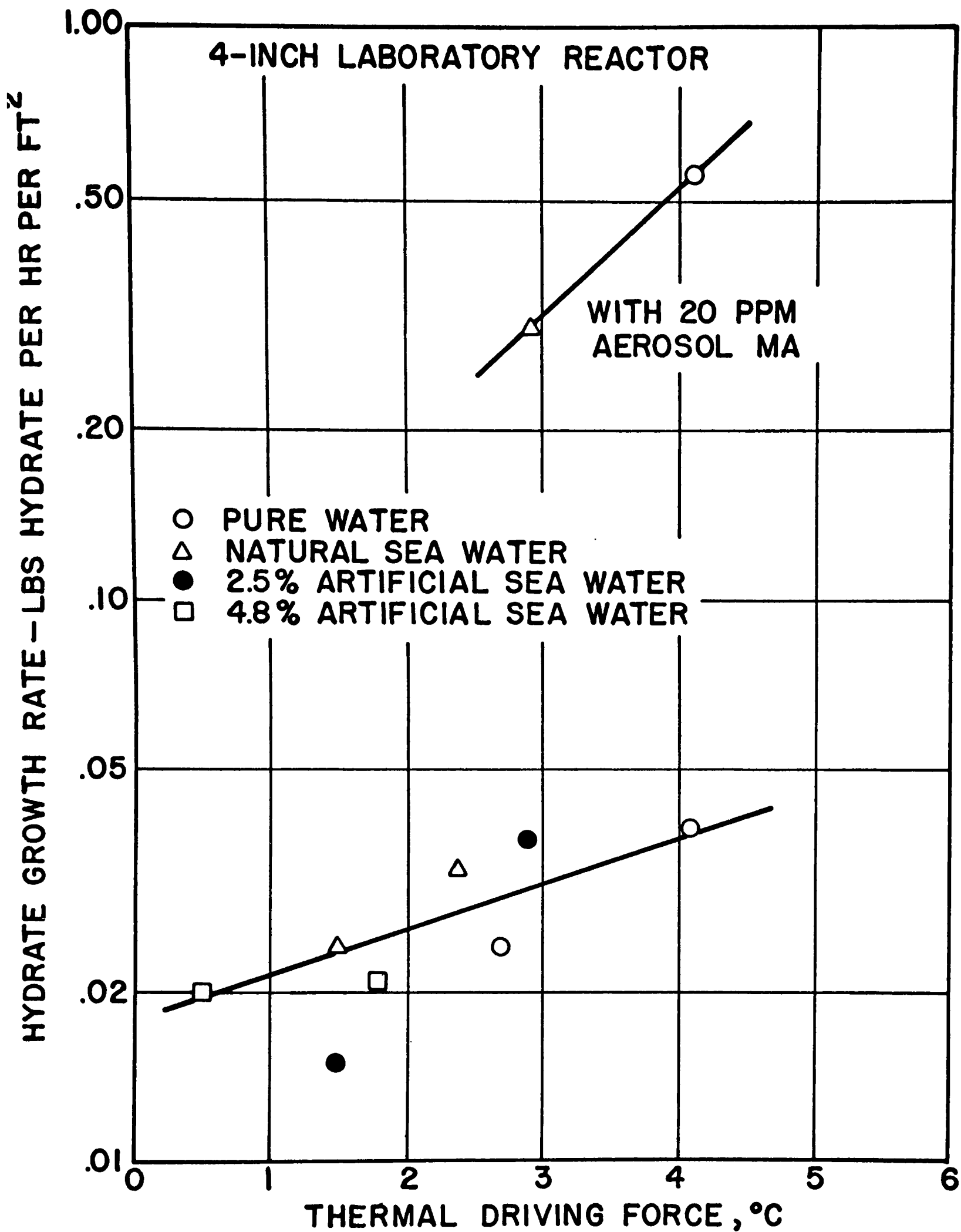


FIGURE 30
EFFECT OF THERMAL DRIVING FORCE ON THE SURFACE GROWTH RATE OF PROPANE HYDRATE

7.4 Nucleation Studies

Experiments were carried out using a 2-inch glass tube to study hydrate nucleation and growth. Propane hydrate was formed on the surface of pure water held in an ice bath by flashing a small quantity of liquid propane on the surface of the water. Growth of hydrate was allowed to take place at a pressure slightly lower than saturation pressure (48 psig) for about one-half hour by bubbling propane gas through the column of water. The pressure was then reduced to atmospheric and the hydrate was allowed to decompose. The system was allowed to stand for 2 hours in the ice bath at atmospheric pressure. When the propane pressure in the tube was again elevated to 48 psig, hydrate growth started on the surface of the water without sub-cooling.

This experiment was repeated. However, before the system was repressured to 48 psig, nitrogen at atmospheric pressure was passed through the column of water for about 10 minutes. The nitrogen flush was followed by a 2-minute flush using propane gas to purge the system. Spontaneous growth of hydrate did not take place after the system was repressured to 48 psig. Another experiment in this series showed that spontaneous nucleation of the hydrate will not take place if the water is heated to 10°C following the decomposition step at atmospheric pressure.

8. HYDRATING AGENTS OTHER THAN PROPANE

Propane was chosen initially for use in the hydrate process because it is an inexpensive and non-toxic agent with a low solubility in water. The experimental work involving the use of this agent demonstrated that a hydrate process using propane as the hydrate agent is technically feasible. However, it was decided to examine other hydrate agents to determine their potential usefulness as the agent in the process. Experimental work was carried out in the bench-scale unit and/or the laboratory reactor using six different halogenated hydrocarbons. The table on the following page lists some properties of these agents and their hydrates.

8.1 Laboratory Investigations

Five different halogenated hydrocarbons were examined in the laboratory reactor which was used in the work with propane hydrate. Photomicrographs of the hydrates of several of these agents are reproduced in Figures 31 through 36. With the exception of F-142b, the hydrates of these compounds formed with much greater ease than did propane hydrate. The size of the crystals varied from 200 to 1000 microns. The appearance of F-152a hydrate was quite similar to that of F-31 hydrate; both are type I transition hydrate.

Freon-21 was used in crystallization studies carried out in a continuously operating unit fabricated mostly from laboratory glassware. This hydrating agent was chosen because its critical pressure is very close to atmospheric pressure and thus no pressure equipment was required. The unit shown in Figure 37 was designed to provide a flexible system for hydrate crystallization studies based on the general principles of crystal growth which utilize elutriation and changes in the concentration of the solute to bring about growth of large and uniform crystals.

Hydrate crystals were formed in the glass crystallizer. Water was saturated with the hydrating agent at conditions of temperature and pressure which favor the growth of hydrate into the bottom of the crystallizer. The velocity of the water through the crystallizer changed from a maximum at the bottom to a minimum near the top of the vessel. By adjusting the velocity through the crystallizer, small crystals and nuclei were removed. Larger crystals remained suspended in the crystallizer at various levels depending upon their size and the velocity of the mother liquor through the vessel. The largest crystals stayed at the bottom level.

The small crystals which were swept from the crystallizer were decomposed by heating and by decreasing the concentration of the hydrating agent by dilution with agent-free water. The diluted mother liquor was held at pressure and temperature conditions which favor decomposition for a relatively long period of time in a hold tank before recycling back to the crystallizer.

The mother liquor containing no hydrate was returned to the crystallizer after it was cooled and resaturated with the hydrating agent.

Some Physical Properties of Freon Hydrates

Hydrated Agent	Freon-11*	Freon-12	Freon-21*	Freon-31*	Freon-142b*	Freon-152a*	Propane
Formula of Agent	CCl ₃ F	CF ₂ Cl ₂	CHFCl ₂	CH ₂ FCl	CH ₃ CClF ₂	CH ₃ CHF ₂	C ₃ H ₈
Molecular Weight of Agent	137	121	103	69	100	66	44
Hydrate Composition	M•17H ₂ O	M•17H ₂ O	M•17H ₂ O	M•8H ₂ O	M•17H ₂ O	M•7.7H ₂ O	M•17H ₂ O
Molecular Weight of Hydrate	443	427	409	213	406	205	350
Wt. Per Cent Water in Hydrate	69.1	71.6	74.9	67.5	75.3	67.7	87.4
Specific Gravity of Hydrate	1.14	1.10	1.05	1.18	1.04	1.18	0.88
Critical Decomposition Temp. (T _c)--°F							
In Pure Water	46.4	53.8	47.7	64.3	55.6	59.6	42.3
In 6% Sodium Chloride**	41.0	48.4	41.5	58.7	50.0	54.0	36.9
Critical Decomposition Pressure (P _c)--psia							
In Pure Water	8.1	65.4	14.7	41.6	48.5	80.3	80.1
In 6% Sodium Chloride**	7.2	59.7	12.8	36.9	44.8	68.7	73.5
Cost of Agent--cents per pound	20 ¹ /	27 ¹ /	150 ² /	-	82 ¹ /	53 ¹ /	1.53/

* See Reference (20).

** Koppers data in artificial sea water.

1/ Present cost in tank car quantities.

2/ Cost in cylinders - no tank car quantities available at present.

3/ Commercial grade. 10 cents/lb. for pure grade in tank cars.

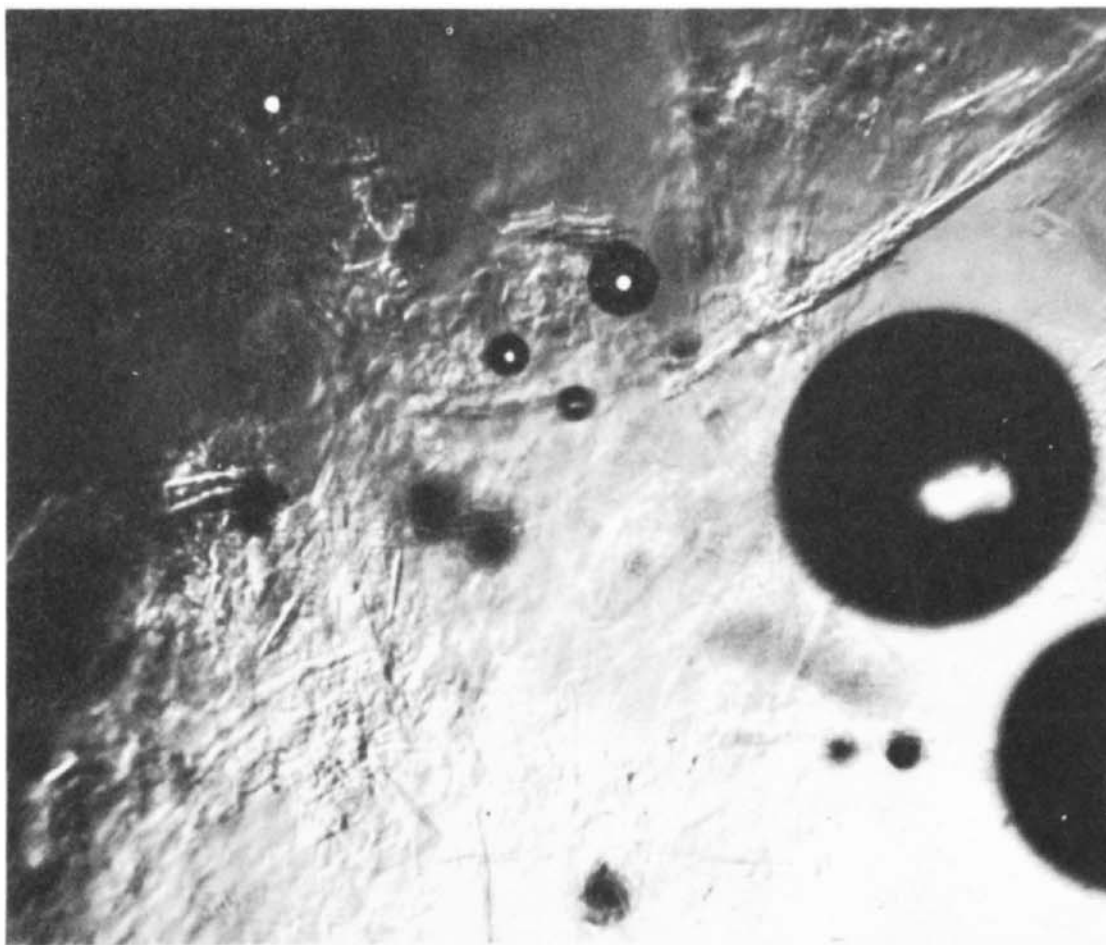
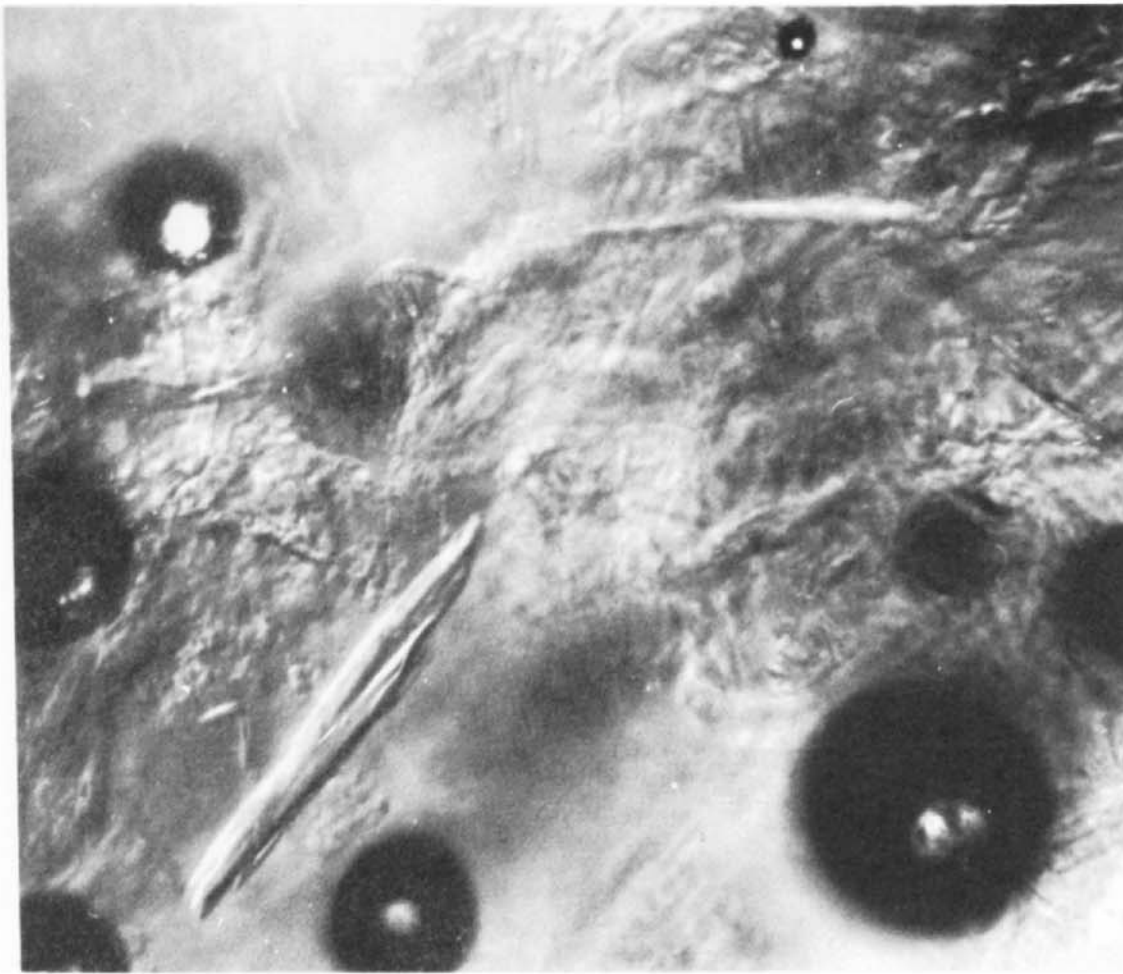


FIGURE 31 - FREON-12 HYDRATE FORMED IN DISTILLED WATER AT A THERMAL DRIVING FORCE OF 2.8°C. MAGNIFIED 35X.

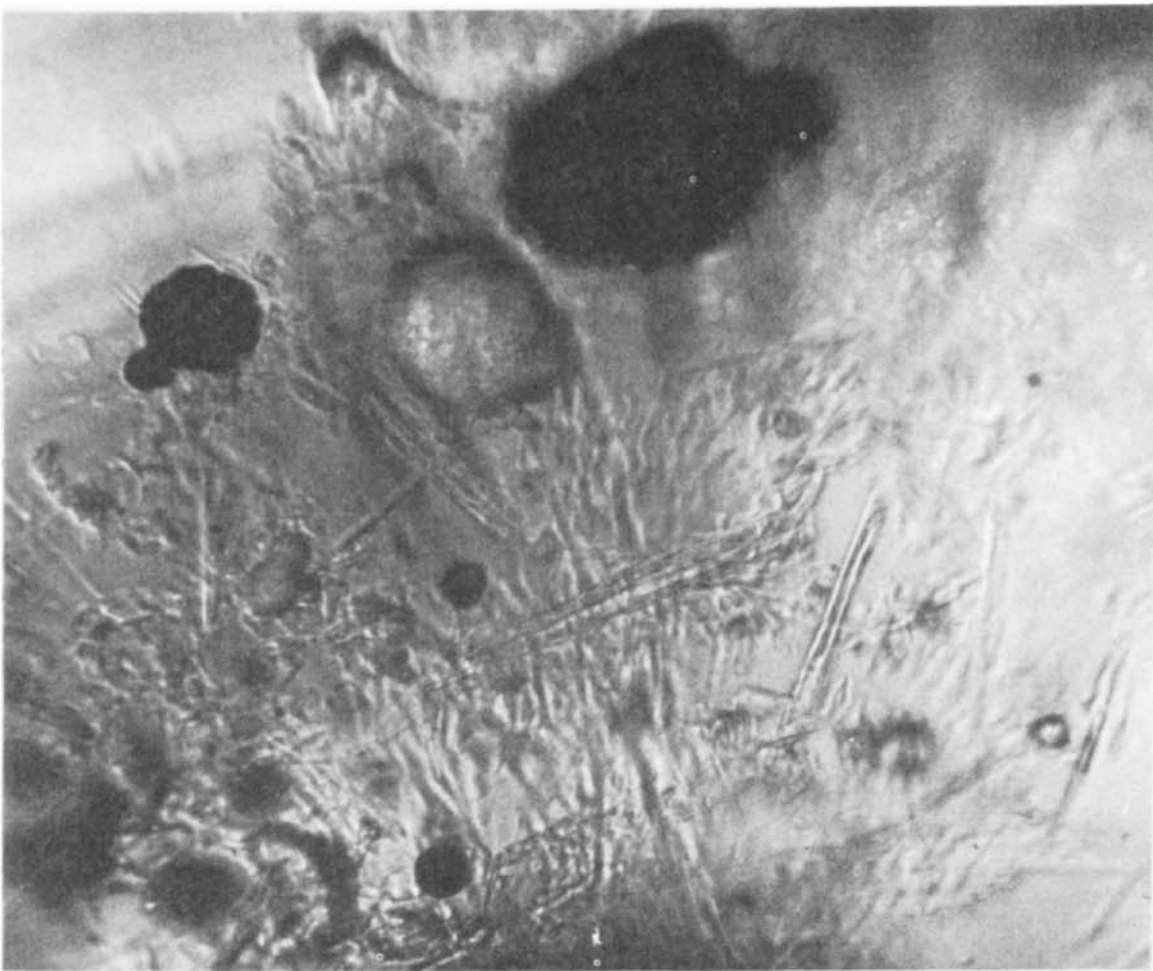


FIGURE 32 - FREON-21 HYDRATE FORMED IN DISTILLED WATER AT A THERMAL DRIVING FORCE OF 2.9°C . MAGNIFIED 35X.

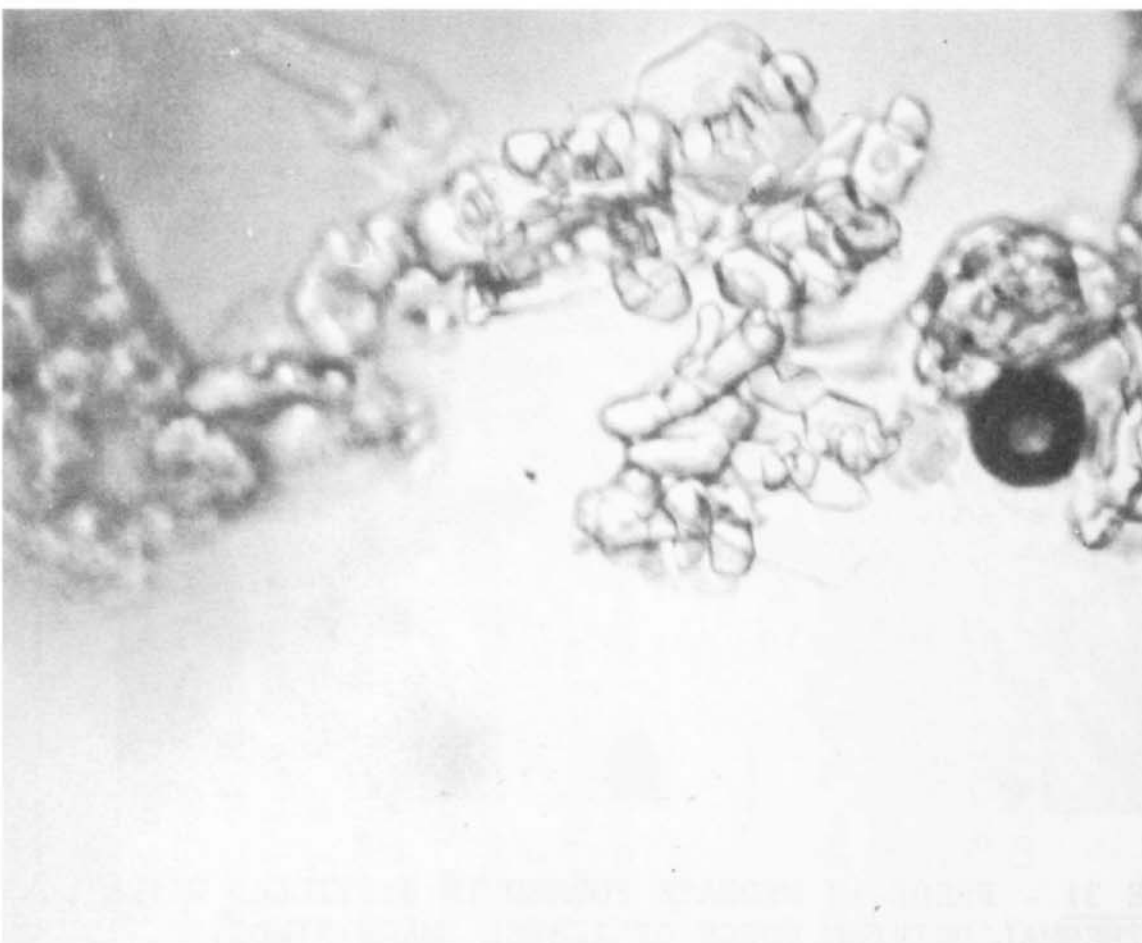


FIGURE 33 - FREON-31 HYDRATE FORMED IN DISTILLED WATER AT A THERMAL DRIVING FORCE OF 2.5°C . MAGNIFIED 165X.

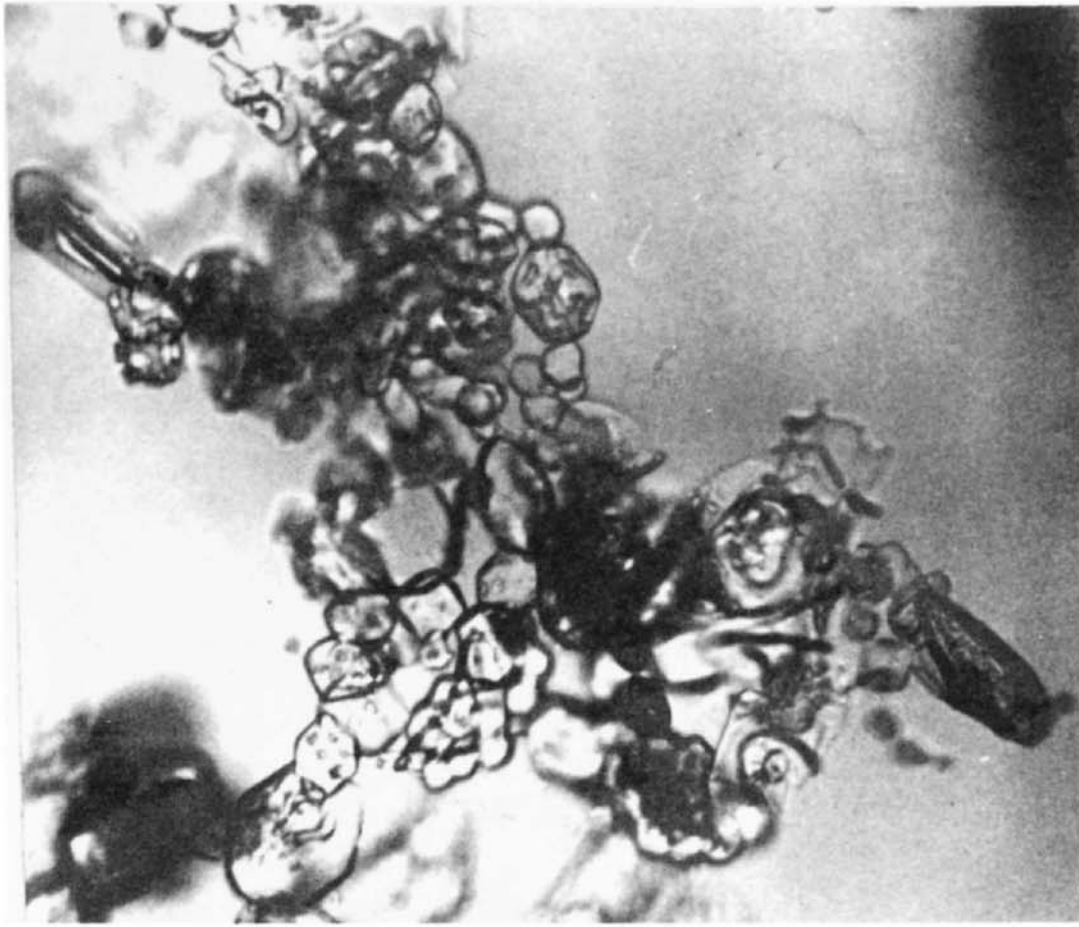


FIGURE 34 - FREON-152a HYDRATE FORMED IN DISTILLED WATER AT A THERMAL DRIVING FORCE OF 2.0°C. MAGNIFIED 110X.

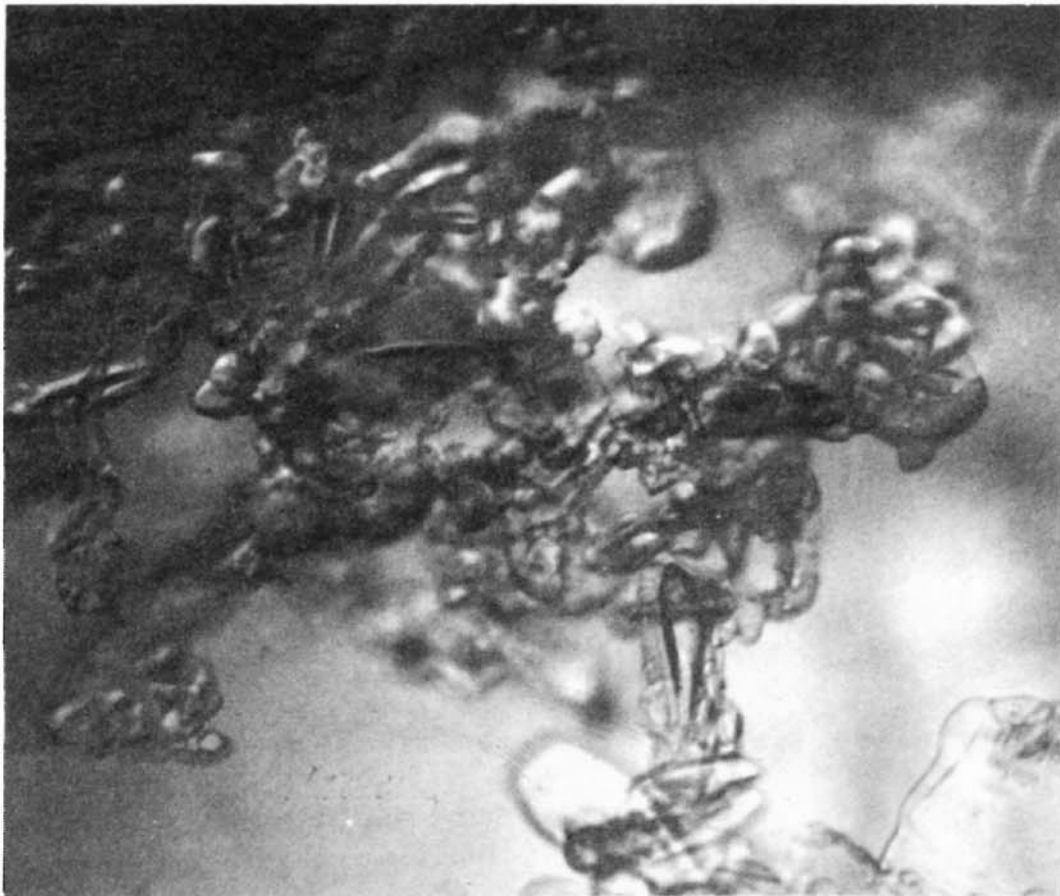


FIGURE 35 - FREON-152a HYDRATE FORMED IN DISTILLED WATER AT A THERMAL DRIVING FORCE OF 4.4°C. MAGNIFIED 75X.

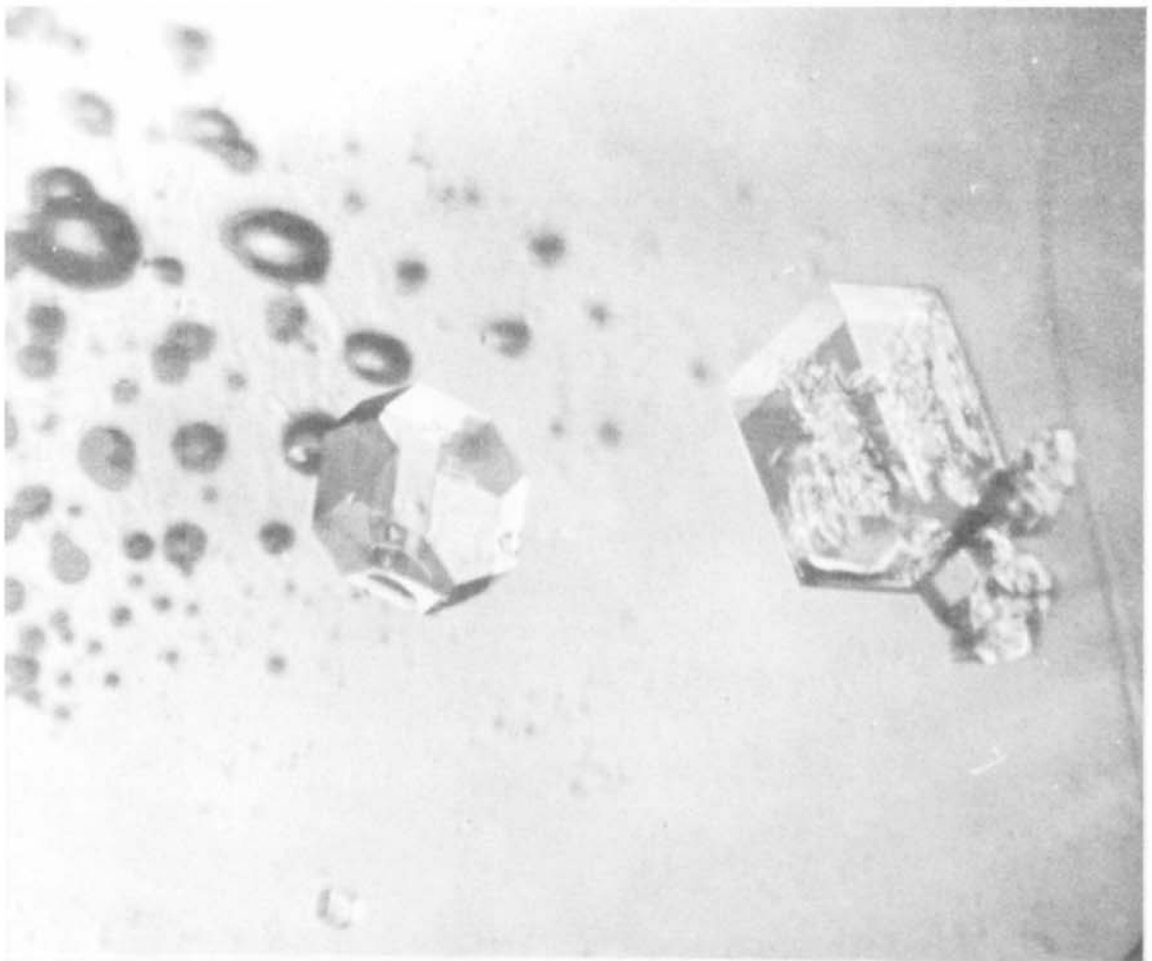
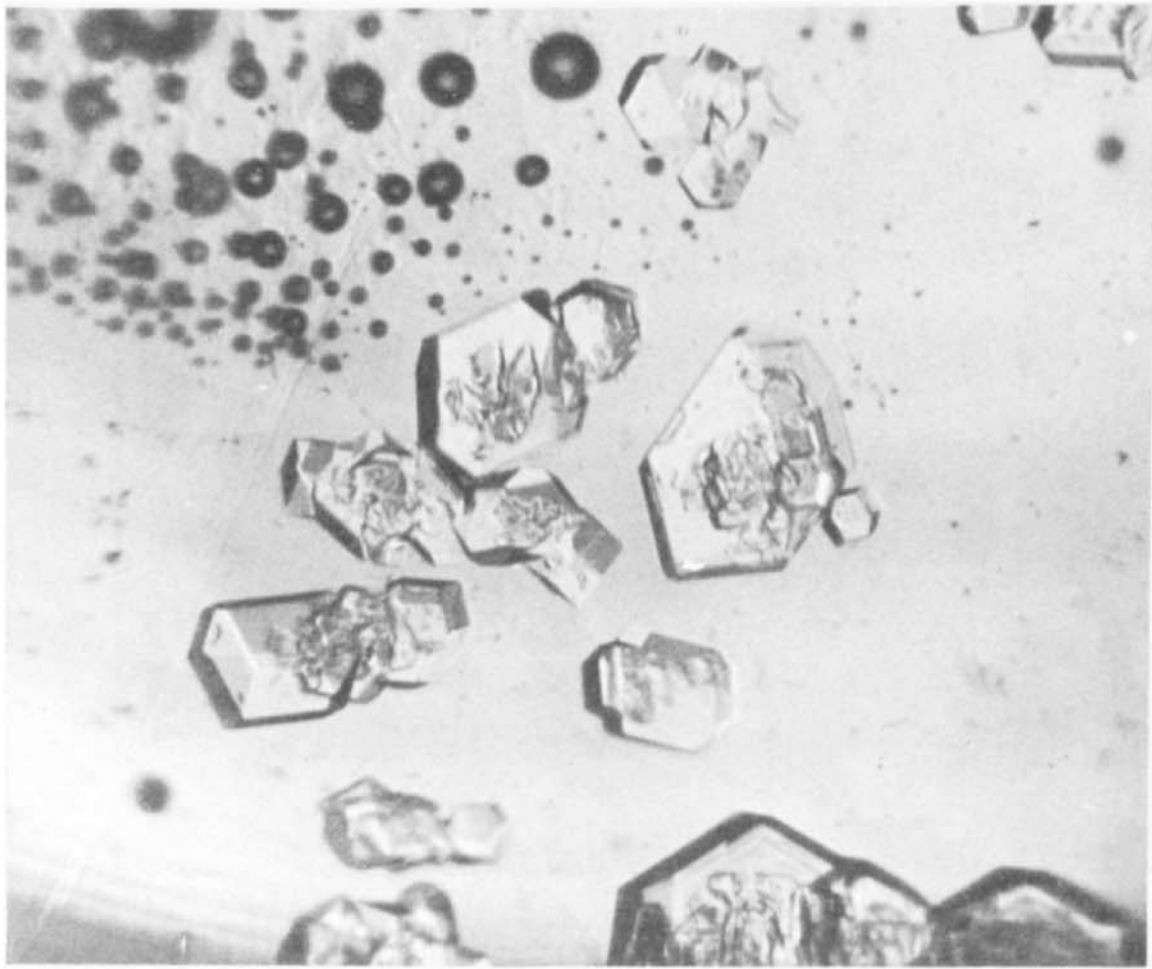


FIGURE 36 - FREON-31 HYDRATE FORMED IN DISTILLED WATER AT A THERMAL DRIVING FORCE OF 6°C WITH NO AGITATION. MAGNIFIED 35X.

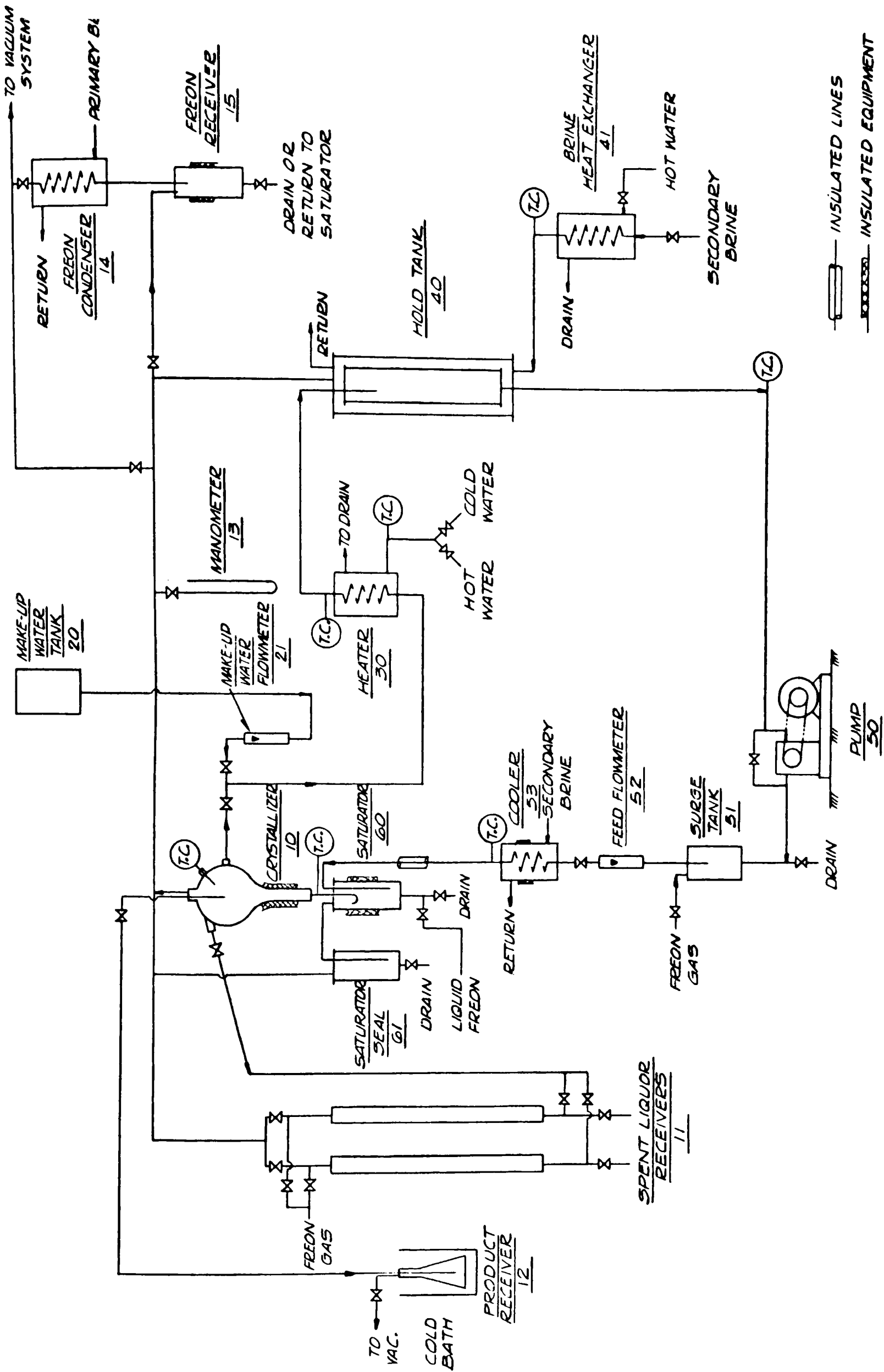


FIGURE 37

FLOW DIAGRAM-LABORATORY APPARATUS FOR HYDRATE CRYSTALLIZATION STUDIES

Excess water in the system (added to dilute the mother liquor) was removed by over-flow from the top of the crystallizer.

Experiments varying in duration from 1 to 6 hours were made. Variables investigated were: thermal driving force, 0.2°C to 4.5°C; circulation rate, 0.13 to 1.6 liters per minute; method of saturation; and number of phases present under growth conditions (gaseous agent, liquid agent, or both). Although some long, slender, hair-like crystals of F-21 hydrate were produced, the rate of crystal growth was very slow. The amount of solids produced was also small. The fastest production rate occurred when gaseous agent was present, however the crystal size was very small. The largest crystals, about 0.5 to 1 mm in cross section by about 20 mm long, were produced in the water phase. Because of the low formation rate, this technique of hydrate crystal growth was not carried to a larger scale of operation.

8.2 Bench-Scale Experiments - Refrigerant-12 Hydrate

Experiments were carried out in the 10-gallon stirred reactor to determine the rate of formation of F-12 hydrate at thermal driving forces of about 1° and 2° at average residence times of from 5 to 15 minutes. Figure 38 shows the results graphically. Comparable data from experiments using propane as the hydrating agent are also shown on this chart. Note that at a thermal driving force of 1°C, the rate of formation of F-12 hydrate is generally higher than that of propane hydrate.

The critical decomposition temperature of F-12 hydrate in pure water and in artificial salt water was determined in the laboratory reactor and in the 10-gallon bench-scale reactor. The results of these tests are presented graphically in Figure 39. Similar data for propane hydrate are also shown on this chart. A phase diagram for the F-12-water system, based on the work of Wittstruck, et al^{31/} is shown in Figure 40.

The 10-gallon bench-unit reactor was operated at a 15-minute reaction time and various agitator speeds to determine the effect of agitative power input on the rate of F-12 hydrate formation at thermal driving forces of 1° and 2°C. The data obtained during these tests are shown graphically in Figure 41. The data from similar tests with propane are also shown on this chart. Note that at all agitator speeds investigated, the amount of water precipitated as F-12 hydrate was considerably greater than that precipitated as propane hydrate.

Washing experiments were carried out on F-12 hydrate in the 5-inch washing column using a 30-inch deep chamber. The dispersion coefficients developed from these tests averaged about 0.031 cm²/sec. and the salt content of the melt averaged about 40 ppm. These values are comparable to those obtained from washing tests in the 5-inch column on propane hydrate. When the filter was charged with a slurry containing less than 10% by weight F-12 hydrate, it was possible to form a bed containing 55% F-12 hydrate by volume. With propane hydrate under similar circumstances, the volume per cent solids in the bed was about 50%.

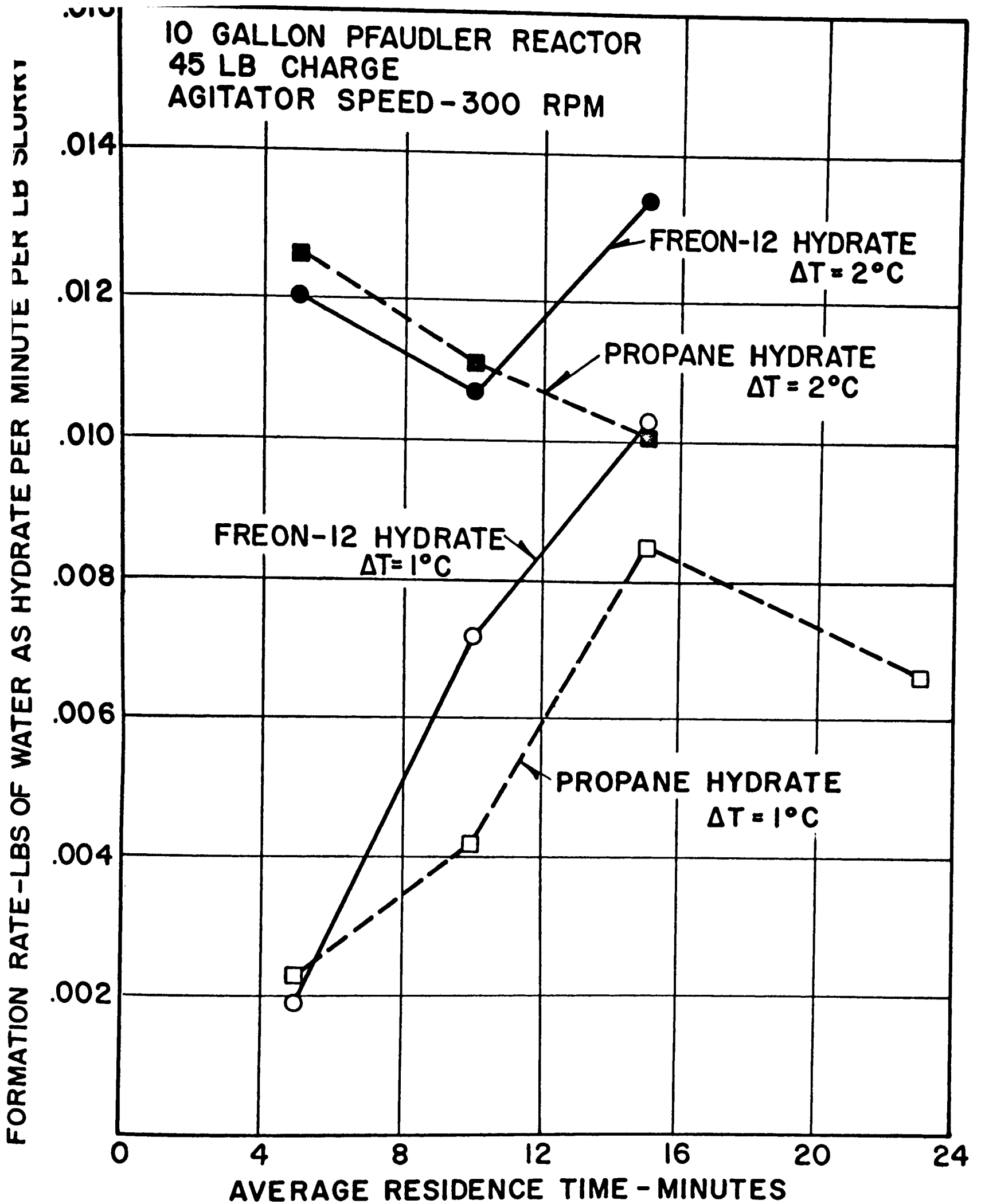


FIGURE 38
EFFECT OF RESIDENCE TIME AND THERMAL DRIVING FORCE ON THE RATE OF HYDRATE FORMATION

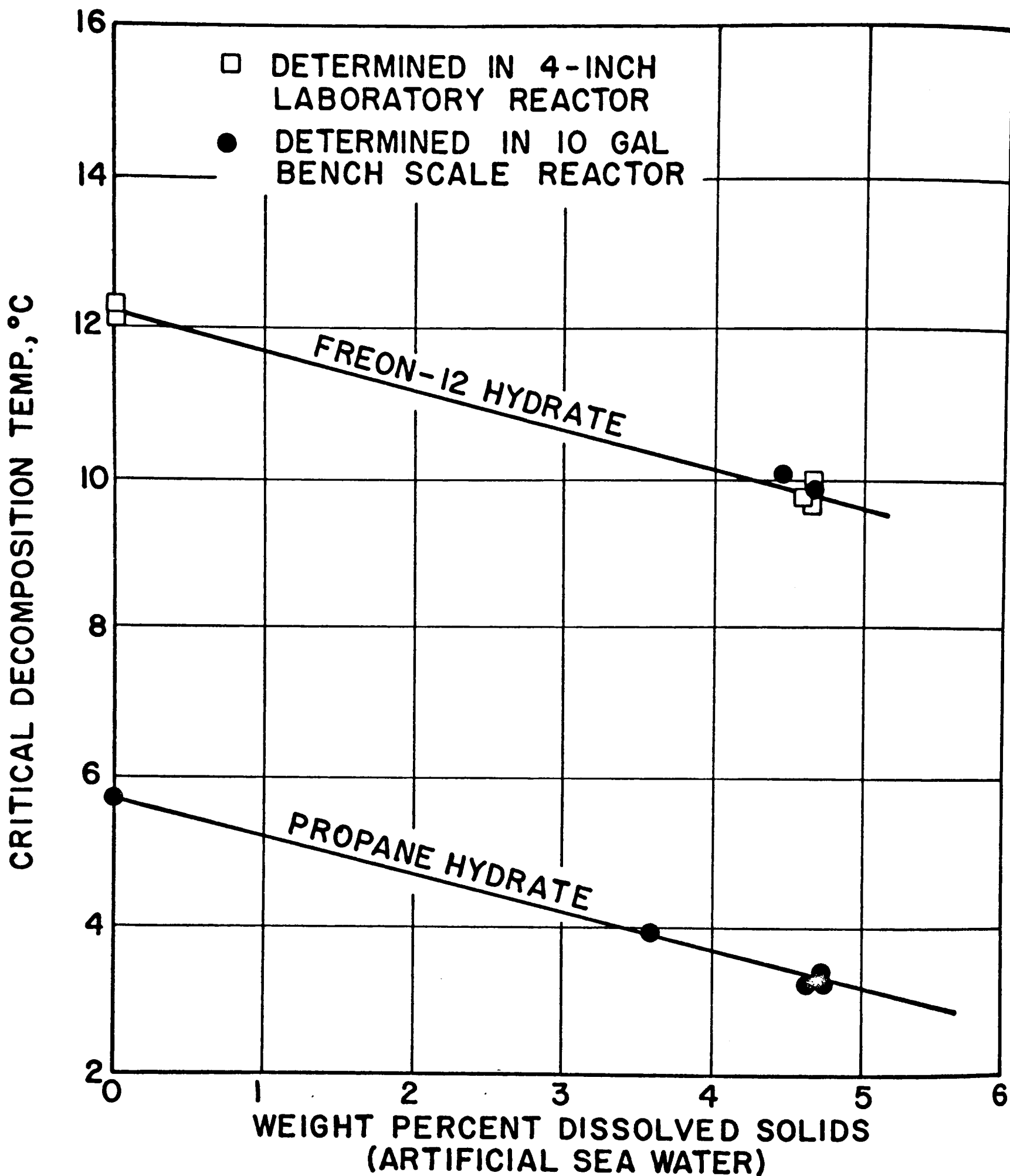


FIGURE 39
EFFECT OF DISSOLVED SALTS ON THE
CRITICAL DECOMPOSITION TEMPERATURE

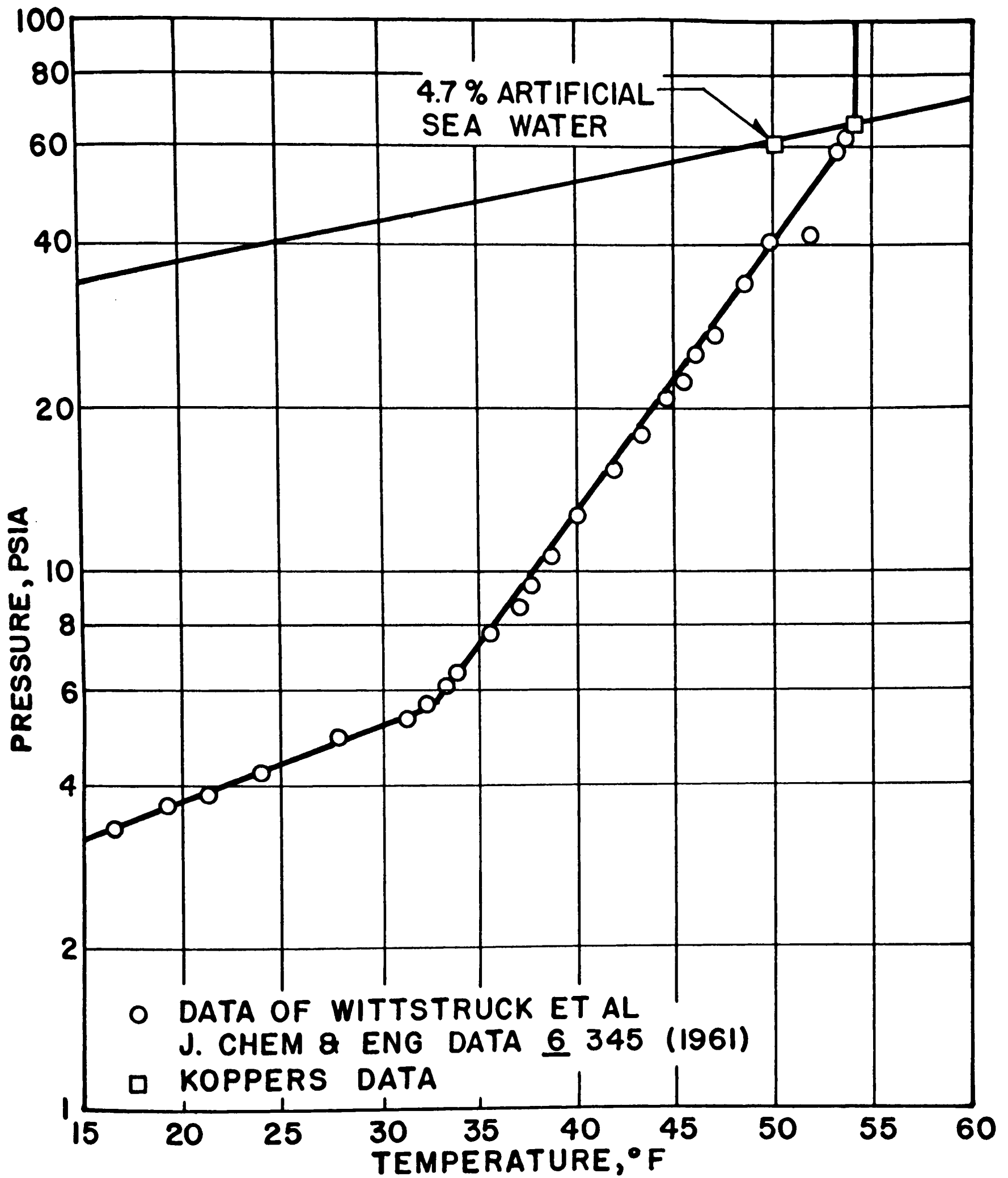


FIGURE 40
PHASE DIAGRAM
FREON-12 HYDRATE

FORMATION RATE- LBS OF WATER AS HYDRATE PER MIN PER LB OF AQUEOUS CHARGE

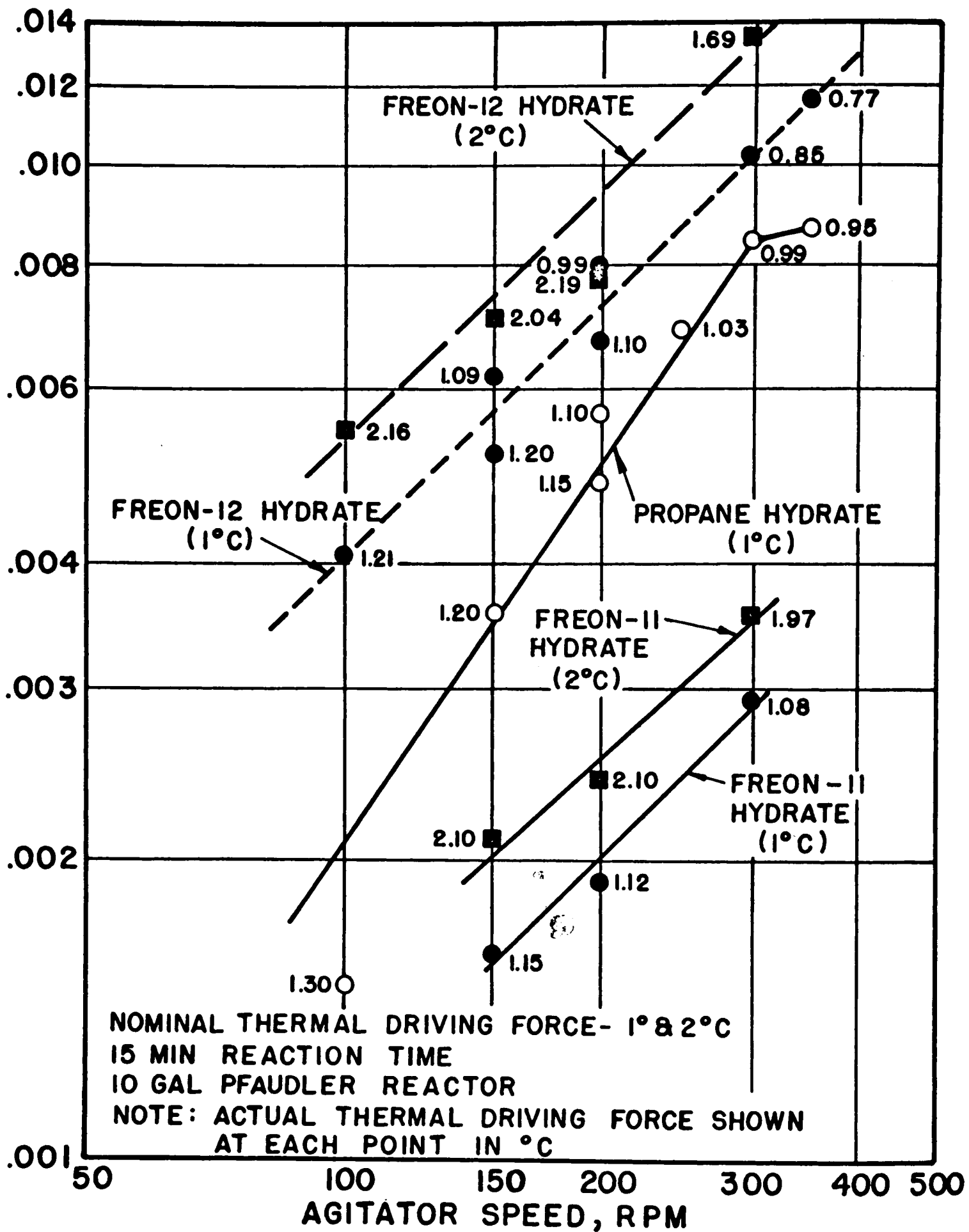


FIGURE 41
 EFFECT OF AGITATOR SPEED ON HYDRATE
 FORMATION RATE

The results of the bench-scale experiments with F-12 showed that the hydrate of this agent possesses several interesting characteristics. As with propane or other agents, a final evaluation of F-12 as the hydrate former can only be made after experimentation on a larger scale.

8.3 Bench-Scale Experiments - Refrigerant-11 Hydrate

F-11 hydrate formation tests were made in the 10-gallon stirred reactor at agitator speeds of 150, 200, and 300 rpm and at thermal driving forces of 1°C and 2°C. F-11 hydrate was formed continuously, using a reactor charge of 45 lbs. of artificial sea water and a sea water feed rate of 3 lbs./min. Operating pressure (about 7 psia) was maintained by means of a vacuum pump and control system. A comparison of the formation rates of F-11 hydrate, F-12 hydrate, and propane hydrate is shown in Figure 41. At 300 RPM and a driving force of 1°C, the conversion rate of F-11 was about one-fourth that of F-12, and about one-third that of propane. The only desirable characteristic seems to be its low formation pressure.

8.4 Losses of Hydrating Agent

An important factor which must be considered in the choice of the agent for the hydrate process is its cost. Factors which make the cost of the agent of prime importance are: (a) capital invested in the agent inventory; (b) mechanical losses: leaks, losses during repairs, transportation losses etc., and (c) solution losses in the potable water and the waste brine leaving the plant.

Estimates of mechanical losses in a continuously operating plant based upon a percentage of the total amount of agent circulated in the plant have been made. It was concluded that a loss as low as 0.001% of the circulating amount of agent can probably be realized. F-12 and F-152a would give a loss contributing about 9 cents to the cost of a thousand gallons of potable water produced. The cost of propane losses at this rate (0.001%) would be about one cent per thousand gallons. If the plant were operated at atmospheric or sub-atmospheric pressure, the mechanical losses would be reduced considerably. The use of F-12 would permit this type of operation (ca. 13 psig). However, because of the high cost of this agent, the loss rate would have to be about 0.0002% of the circulation in order to limit the cost of mechanical losses to ten cents per thousand gallons.

Techniques which have been established can be used to recover the dissolved agent. Four methods of F-12 recovery were subject to comparative engineering analysis: vacuum stripping, inert gas stripping plus solvent absorption and steam stripping, inert gas stripping followed by re-absorption in the sea-water feed stream, inert gas stripping followed by adsorption on activated carbon. Calculations showed that at a recovery cost of about four cents per thousand gallons, the cost of F-12 lost in effluent streams can be reduced to about two cents per thousand gallons.

8.5 Recovery of Hydrating Agents - Bench-Scale Experiments

A 4-inch stripping column was installed at the bench-scale site for investigation of the inert gas stripping step which is common to three of the recovery methods examined. The column was packed with 10 feet of 1/2-inch Berl saddles which was considered to be adequate for an evaluation. Saturated solutions of both F-12 and F-21 were prepared in the bench-scale equipment and stripped in the 4-inch column, using nitrogen as the stripping gas. A flow diagram is shown in Figure 42. The experimental data are presented in the table on page 88.

Solutions, which were saturated with hydrating agent at ambient conditions, were prepared in the following manner: Deionized water was charged to the 10-gallon reactor and 33-gallon feed tank, and was circulated between the vessels by means of a pump. The feed tank was vented to the atmosphere. The reactor was not vented. Water was brought in contact with liquid hydrating agent in the agitated kettle at room temperature and at the corresponding vapor pressure of the Freon being used. Circulation of the water between the contacting vessel and the vented feed tank was continued for one hour. Flow of water to and from the kettle was then stopped and the solution in the feed tank was circulated on itself, using the pump, in order to release any supersaturation which may have existed.

Sufficient saturated solution was prepared in this manner to operate the stripping column for one-half hour at a liquid rate of about 1 gpm. The solution was pumped to the top of the column where it entered a spray nozzle. Nitrogen was introduced at the bottom of the column, just below the packing support. Both nitrogen and liquid flows were indicated by means of rotameters. Samples of the feed and effluent from the column were taken after about 20 minutes of steady-state operation.

Five tests were made in the 4-inch stripping column in which F-21 was stripped from water with nitrogen at ambient conditions. The tests were made at a constant liquid rate of 9.2 lbs./min. and molar L/V values in the range 300-900. H.T.U. values of 1.5 to 1.8 feet were obtained in four tests in which L/V ratios of 300-400 were used. One test, at L/V = 885, gave an H.T.U. of 8 feet. The best run produced an effluent containing 220 ppm F-21. This test was made at L/V = 322 and gave an H.T.U. of 1.5 feet.

It was concluded from the experimental data that a saturated solution of F-21 (9700 ppm) can be stripped to 25 ppm in the test equipment by employing higher gas rates (L/V = 100). At these rates, an additional 3 feet of packing would be needed to produce an effluent containing 5 ppm of F-21. There is no reason to believe that the F-21 content of the effluent could not be reduced substantially below 5 ppm.

Two F-12 stripping tests were made using the same apparatus and procedure. H.T.U. values of 3.1 and 1.9 feet were obtained at L/V values of 4220 and 2870, respectively. The corresponding effluent contained 17 ppm and 2 ppm F-12, respectively.

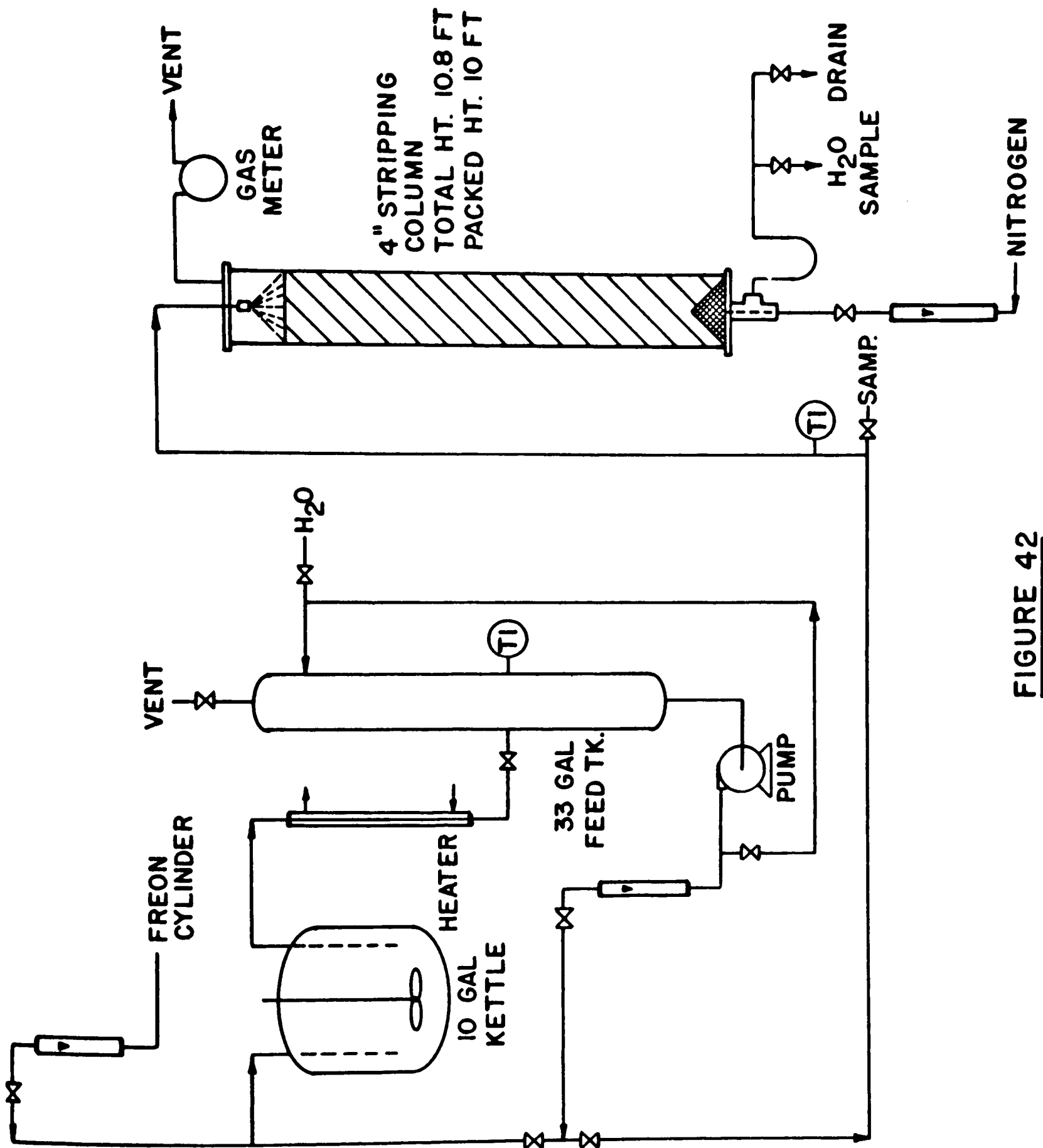


FIGURE 42
FLOW DIAGRAM, FREON RECOVERY APPARATUS

Freon Recovery Tests - Data Summary

Stripping of Freon-21 and Freon-12 from Aqueous Solution
 Apparatus: 4-inch Diameter Column Packed with 10 Feet of 1/2-inch Berl Saddles

Run Number	Freon-21						Freon-12	
	DF-1	DF-2	DF-3	DF-4	DF-6	DF-7	DF-8	
Liquid Rate, lbs./min.	9.2	9.2	9.2	9.2	9.2	9.2	9.2	
Nitrogen Rate, SCFM	0.207	0.422	0.422	0.422	0.677	0.044	0.064	
L/V, mols water/mols nitrogen	885	434	434	434	322	4220	2870	
Feed Temperature, °C	25	25	26	26.5	24	23	24	
Barometric Pressure, mm Hg	748	748	745	750	748	745	748	
Feed Analysis, ppm Freon	9890	14200	12250	10700	8675	286	218	
Product Analysis, ppm Freon	2660	1170	780	910	220	17	2	
Freon Stripped (calculated from analyses), SCFM	0.231	0.417	0.389	9.314	9.271	0.0074	0.0060	
Outlet Gas Concentration(calculated from analyses), Mol % Freon	52.7	49.8	47.9	42.7	32.4	14.4	8.6	
Packed Bed Height, ft.	10.2	9.8	9.8	9.9	9.9	10.0	10.0	
Number of Transfer Units	1.3	5.5	6.4	5.4	6.6	3.2	5.2	
Height of Transfer Unit, ft.	8.0	1.8	1.5	1.8	1.5	3.1	1.9	

9. ADDITIONAL BENCH-UNIT EXPERIMENTS

The hydrate process design is based on the use of a stirred-tank reactor which operates at constant pressure and temperature. Experimental studies using this type reactor showed that hydrate could be formed at a suitable rate. It was further shown that the hydrate could be transported in highly concentrated slurries and that filter cakes of the hydrate could be formed and freed of dissolved salts.

Although most of the experimental effort was directed towards the use of the stirred tank reactor operating at constant conditions, some test work was carried out to investigate other methods of reactor operation or to explore other reactor designs.

9.1 Hydrate Formation In Liquid Propane

The 10-gallon reactor was used to make a run in which liquid propane was the continuous phase. Salt water was sprayed into the reactor which contained about 6 gallons of liquid propane. The aqueous phase was fed to the reactor at 7 lbs./minute and withdrawn at the same rate. A 10 lb. heel of the aqueous phase was held in the reactor to prevent the discharge of liquid propane. The temperature of the liquid propane was adjusted to produce a 2°C thermal driving force. The agitator was run at a speed which kept the aqueous phase in motion but did not inter-mix the two phases. Less than 1% hydrate was formed. When the aqueous heel in the reactor was increased to 32 lbs., the amount of hydrate in the aqueous phase increased to about 4%. Apparently, the hydrate formation was taking place in the aqueous phase. The low formation rate of hydrate can be explained by assuming that the time of contact between the aqueous and organic phases was too short to saturate the droplets of salt water with propane. The use of a fogging nozzle and a very deep column of liquid propane might have produced more attractive results.

9.2 Precontacting Brine with Propane

Two runs were made to determine the effect of increasing the amount of propane in the aqueous phase on the rate of formation of propane hydrate. The bench-scale apparatus was operated at 1.95°C at an eleven-minute retention time in the usual manner except the mixture of liquid propane and salt water was compressed with a pump to 20 atmospheres before it entered the reactor. In both cases, the hydrate formation rate was increased by about 50% by the pre-treatment step.

9.3 Addition of Carbon Dioxide

It is known that a number of gases, among them carbon dioxide, stabilize the lattice of hydrates of type II. Mixed hydrates in which carbon dioxide

occupies some of the small voids in the type II lattice are reported to result.^{1/} In order to explore this phenomenon, three runs were made at different operating conditions during which carbon dioxide gas was admitted to the bench-unit reactor through the bottom nozzle. Liquid propane was added to the salt water feed in the usual manner. The partial pressure of carbon dioxide was 13 psi and the aqueous phase contained 0.2% by weight dissolved CO₂. The rate of hydrate formation increased by about 50% by the addition of CO₂ compared to the rate of formation with propane alone. The effect was not considered large enough to be important. The use of CO₂ in the refrigeration cycle would decrease the efficiency considerably.

9.4 Partial Decomposition of Hydrate

Experiments were made in the bench unit during which part of the slurry in the reactor was subjected to partial decomposition in a recirculated loop with the aim of thermally destroying the small crystals and nuclei. Conditions in the reactor which would favor crystal growth were maintained while partial decomposition was taking place in the recirculated stream. The amount of slurry recycled was varied from 3% to 50% of the reactor charge per minute and the amount of hydrate production which was decomposed was varied from 5% to 50%. It was found that this treatment had little effect on the characteristics of the hydrate particles.

9.5 Spray Reactor

Experiments were carried out to explore the feasibility of using a spray-tower type reactor for the formation of propane hydrate. Two schemes were investigated: the formation of hydrate on the surface of falling drops of chilled salt water; and, the formation of hydrate on a cooled metal surface over which a film of cold sea water was passed. Both systems were examined in a jacketed metal tower 1-foot in diameter by 5-feet long in an atmosphere of pressured propane gas. Although many variations in operating procedure were used, the production of hydrate by either method was low. At a thermal driving force of 3°C and a feed rate of 5 lbs. per minute, the spray tower produced 0.05 lb. of hydrate per minute. Under similar conditions of thermal drive, the 10-gallon kettle reactor would produce about 0.45 lb. of hydrate per minute.

9.6 Formation of Propane Hydrate in Concentrated Salt Water

One test was made in the 10-gallon reactor wherein hydrate was formed in 14.7% artificial sea water. A slurry containing 6% hydrate was made at a 22-minute residence time using a thermal driving force of 3.3°C. This is a production rate of 0.12 lb. of hydrate per minute. Under similar conditions of thermal drive in 6% salt water, the formation rate would have been about 9 times as fast. In all probability, the higher salt concentration reduced the solubility of propane in the aqueous phase and therefore the rate of formation was reduced.

9.7 Mechanical Compaction of Hydrate Cakes

An investigation was carried out to explore a method of separating salt from the hydrate particles without the use of wash water. The approach involved the mechanical compression of hydrate cakes.

Experiments were made in which propane hydrate beds were mechanically compacted using pressures up to 7000 psi. The purpose of these experiments was to establish the relationship between: (1) compacting pressures and volume per cent hydrate in the bed; and (2) compacting pressure and salt content of the bed.

The hydrate was compacted by forcing a piston down on a bed of hydrate contained in a 2-inch I.D. jacketed cylinder. A filter screen at the bottom of the cylinder retained the crystals and allowed the brine squeezed from the bed to pass from the cylinder. Pressure seals between the piston and cylinder wall were maintained using O-rings. The cylinder contained a charging port located between the two O-ring seals and a brine discharge port under the filter screen. The piston contained a gas bleed port and a depth indicator. The cylinder and piston were placed on a hand-operated hydraulic press. The force applied to the compacting piston was measured by using a gauge cell placed between the press platen and the compacting piston. The gauge cell consisted of a 2-inch I.D. cylinder one inch deep fitted with an O-ring sealed piston. A pressure gauge was connected to the cell using a 1/4-inch O.D. x 0.083-inch I.D. tube. The cell, gauge and gauge line were filled with water. The test apparatus is shown in Figure 43.

The compaction experiments demonstrated that filter cakes containing 90% hydrate by volume could be formed through the use of mechanical force. The relationship between the volume of hydrate in the compacted bed and the salt content of the decomposed cake and compacting pressure is given in Figure 44.

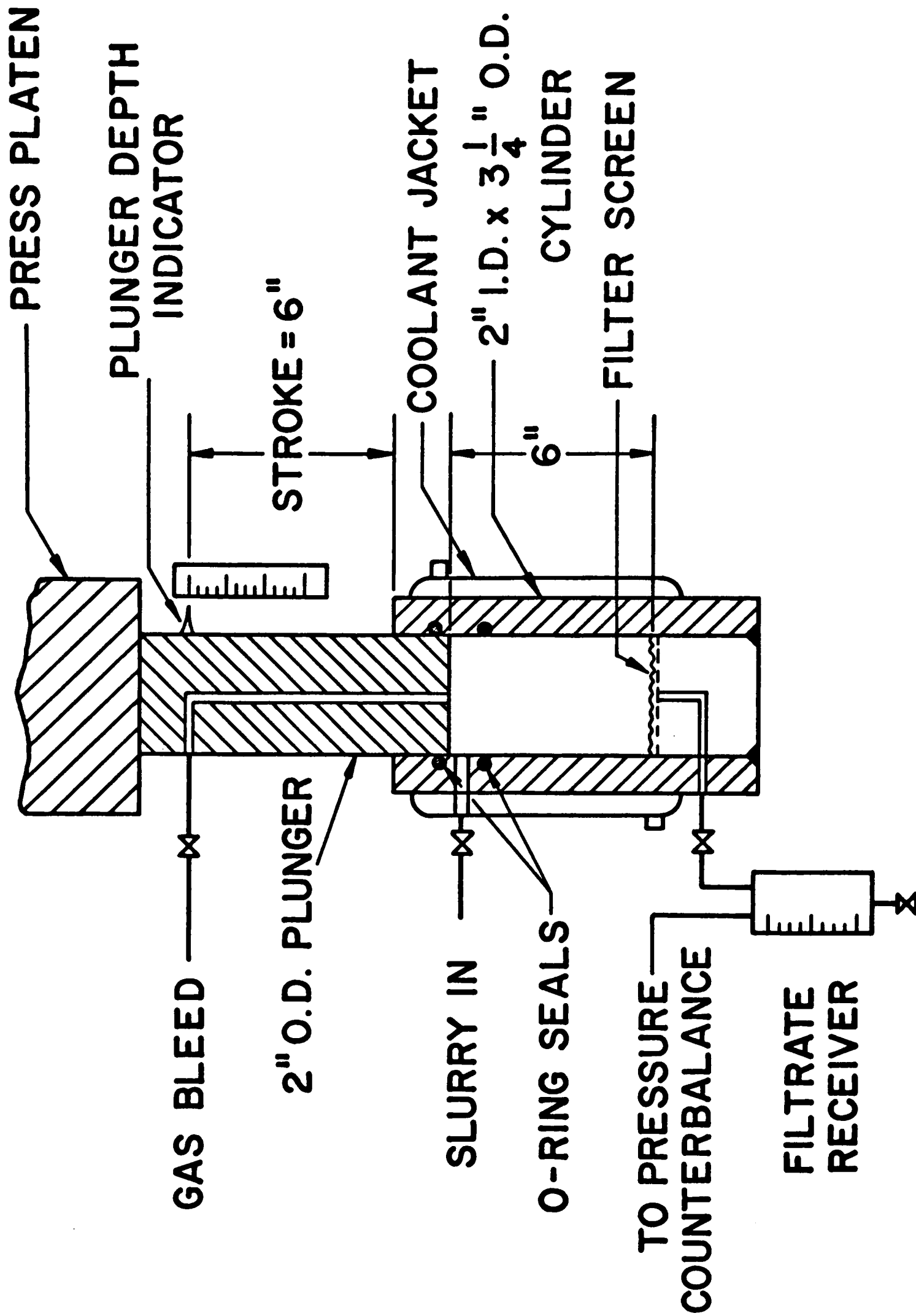


FIGURE 43
 HYDRATE CAKE COMPACTION APPARATUS

HYDRATE IN COMPACTING CYLINDER - PERCENT BY VOLUME

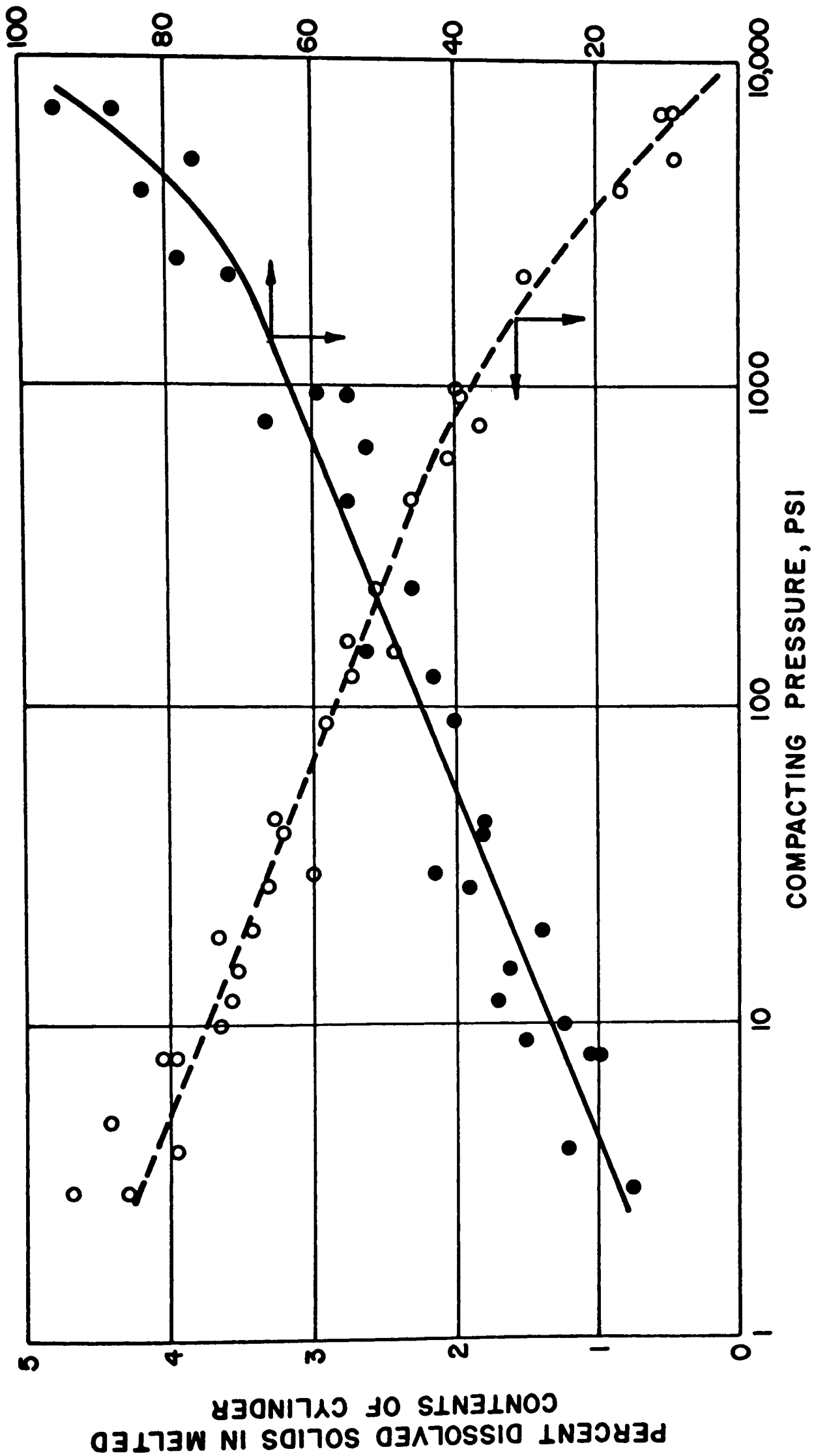


FIGURE 44
MECHANICAL COMPACTION OF PROPANE HYDRATE CAKES

10. HYDRATE PROCESS PILOT PLANT

10.1 Objectives

A pilot plant for the production of 10,000 GPD of potable water using the Koppers Hydrate Process was designed based on engineering data obtained from the bench-scale unit experimental work. The major objectives of the pilot plant are: (a) to demonstrate the feasibility of all areas of the hydrate process; (b) to produce sufficient data for an economic evaluation of the process on larger scale; and (c) to collect information for the design of larger and commercial installations.

10.2 Basis of Design

The pilot plant was designed to function over a range of operating conditions using propane as the hydrating agent. With minor modifications Freon-12 could be used in place of propane. In order to obtain this flexibility for experimental work, the auxiliaries were sized to water streams and propane streams associated with conversions ranging from twenty to sixty per cent of the sea water feed. Under average operating conditions, forty per cent of the inlet sea water containing 3.5% dissolved salts will be converted to potable water containing 500 ppm dissolved salts at a rate of 10,000 gallons per day using propane as the hydrating agent. It was assumed that an adequate supply of sea water free of flotsam will be available at a temperature ranging from 50 to 85°F. The product water and waste brine will be depropanized.

10.3 Description of Process Equipment

A general description of the process equipment and flow diagrams for the pilot plant are presented in the following discussion. For simplification, only the major process lines are shown in the figures. Cooling water lines and all valves and instruments have been omitted.

10.3.1 Feed Preparation (Figure 45)

Sea water which has been screened to remove large objects is fed to the plant by a vertical centrifugal pump rated at 300 gpm. This pump, P-100, provides sea water for the process and also for cooling purposes.

The process sea water is pumped into a clarifier, V-101. This unit, which is 10 feet in diameter by 8 feet high, is similar to an Eimco Type B clarifier and has a design feed rate of 800 gallons per day per square foot.

The clarified sea water is fed into a deaerator (V-104) which is an 18-inch diameter column that has a 10-foot high packed section of 1-inch pall

P- PUMP

V- VESSEL

M- COMPRESSOR

E- HEAT EXCH.

SEA WATER

IN

COOLING

WATER

TO

PRECOOLERS

P-100

V-101

V-104

M-105

P-106

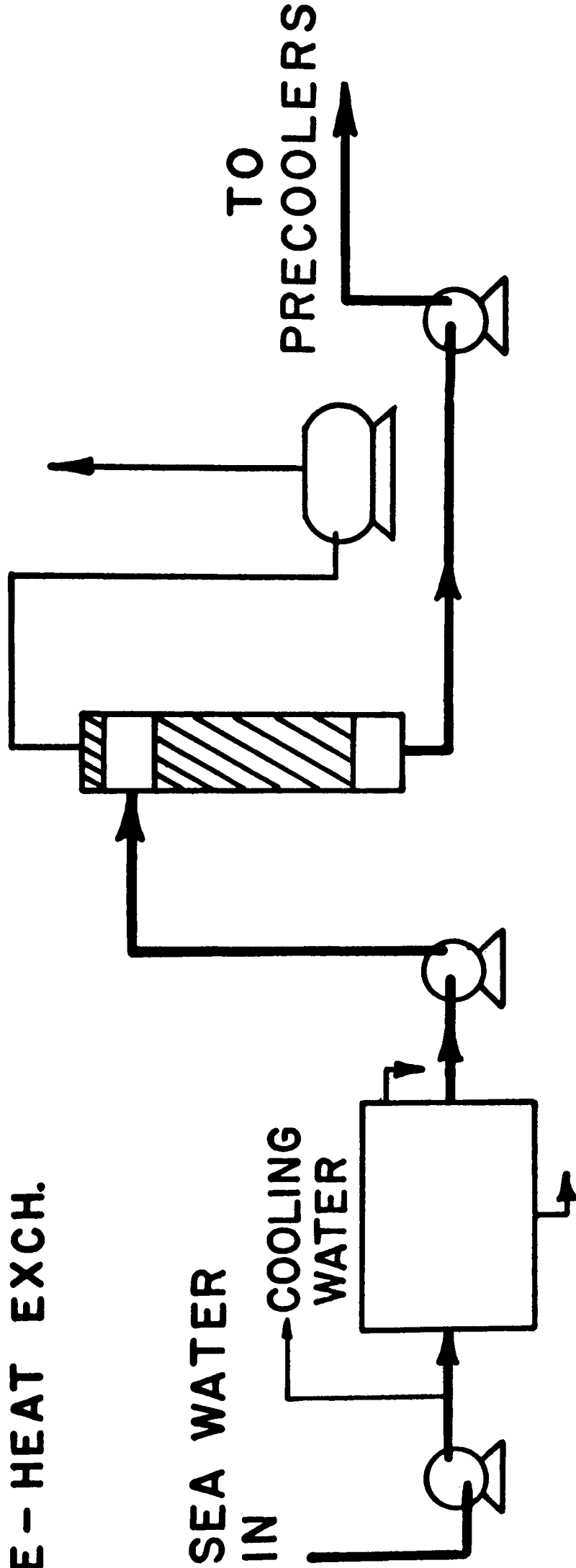


FIGURE 45
FEED PREPARATION

rings. The deaerator is designed to operate at a pressure of 24 mm. Hg absolute and to reduce the oxygen content of the sea water to less than 1 ppm.

A single-stage vacuum pump coupled with an air ejector provides the vacuum for the deaerator. The vacuum pump is of an all-bronze construction to permit the use of sea water as the internal liquid sealant.

A two-stage centrifugal pump, P-106, rated at 35 gpm at 300-foot head, is required to transfer the deaerated sea water through the precoolers and into the reactor.

10.3.2 Sea Water Cooling System (Figure 46)

The deaerated sea water is cooled by heat exchange with the cold potable water and the effluent brine streams leaving the plant.

Plate-type heat exchangers were chosen for this service. The plates for this installation are 90-10 copper-nickel alloy.

Sea water leaving exchanger E-202 can be cooled to the reactor temperature, 30-35°F, by heat exchange with vaporizing liquid propane in exchanger E-204. This unit consists of two sections of multi-tube exchangers, connected in series. Each section has two 15-foot long, 4-inch diameter U-tube shells containing twelve 1/4" tubes. A total of 150 square feet of heat transfer surface is provided in these units. Process sea water passes through the tubes and liquid propane is vaporized on the shell side of the exchangers. The cooled sea water from the exchanger is fed directly to the hydrate reactor.

The final precooler and its attendant refrigeration compressor (M-205) and condenser (E-204) have been added to provide an additional degree of flexibility and to aid in cooling the charge to reactor temperature during start-up operations.

The refrigeration compressor is a 20 HP horizontal non-lubricated reciprocating compressor. The unit is rated to compress 1400 lbs./hr. of gaseous propane at 25°F from 50 psig to a discharge pressure of 160 psig. This discharge pressure is required in order to attain a propane dew point temperature approximately 10°F higher than the maximum temperature of the cooling sea water.

The superheated compressed propane vapors are sub-cooled and condensed at 95°F in condenser E-204. A six-pass shell-and-tube type exchanger will be employed for this service. The unit, constructed with Admiralty tubes and a carbon steel shell, will provide approximately 220 square feet of heat transfer surface.

Liquid propane from the condenser will pass through a let-down valve, prior to entering exchanger E-204, thereby permitting some of the propane to flash and to sub-cool the remaining liquid to approximately 25°F.

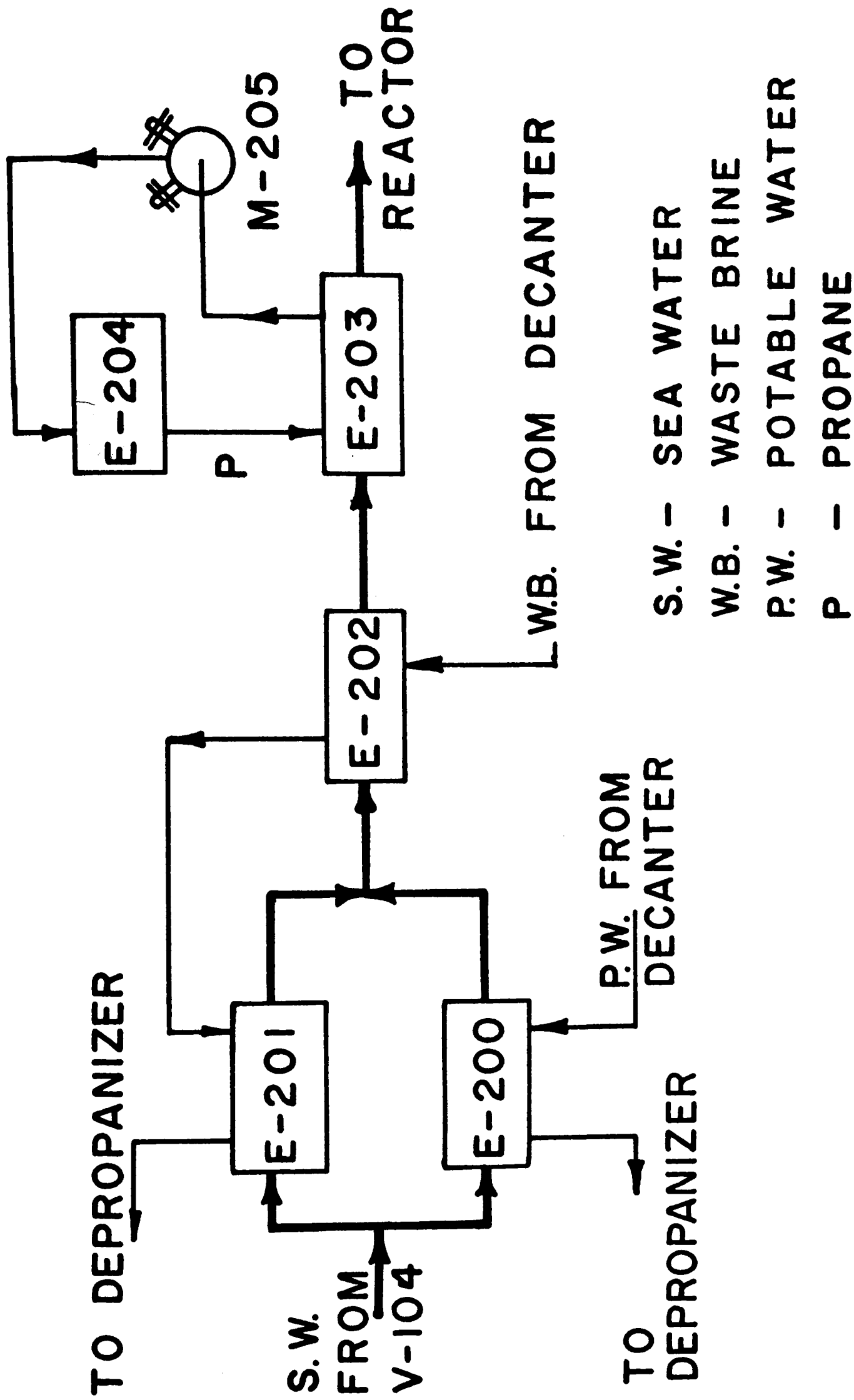


FIGURE 46
FEED PRECOOLING

10.3.3 Reactor and Filter-Washer-Decomposer Units (Figure 47)

Cold sea water from exchanger E-203 is fed into the reactor, V-300, where it combines with propane to form insoluble hydrate crystals. Liquid propane suspended in the reactor charge serves as a direct refrigerant as well as the hydrate forming agent. The heat of formation of the hydrate is removed by propane evaporation. The propane gas leaving the reactor is fed to the primary compressor.

The reactor is a 6000-gallon carbon steel vessel designed for a maximum working pressure of 75 psig. The vessel is equipped with baffles and a variable speed turbine agitator driven by a 50 HP motor.

The hydrate is pumped as a slurry to the filter-washer-decomposer units represented by items number V-400 through V-402 in Figure 47. The slurry transfer pump, P-301, is a single-stage 30 HP centrifugal pump which has a capacity of 200 gpm at a 300-foot head.

During the filtration step, the hydrate slurry is concentrated to form a cake containing from 35% to 55% solids by volume. About 80% of the filtrate is recycled to the reactor to maintain the desired slurry concentration. The remaining filtrate is sent to the decanter to remove any liquid propane present.

The hydrate cake is washed countercurrently with fresh water in a stagewise fashion previously discussed in the section, 5.1, on washing. The filter-washer-decomposer units will consist of a series of separate vessels similar in construction to the mock-up previously described, but for pressure operation. The cake chambers will have an I.D. of 5.5 feet and a depth which can be varied from 1 to 4 feet. The number of these units which are in use at any one time will depend upon the production rate at which the plant is being operated or other operating variables which will be explored. Each unit has been designed to permit easy changing of the wash-water and propane gas distributors and to permit flexibility of operation for experimental purposes.

The washed cake is decomposed to liquid propane and potable water by the heat provided from condensing propane gas. The liquid propane-water mixture flows to the decanter for separation.

10.3.4 Decanters and Primary Compressor (Figure 48)

Water and propane are separated by decantation in vessel V-502. This vessel is a 600-gallon carbon steel horizontal tank, approximately 3-1/2 feet in diameter by 9 feet long, designed for a maximum pressure of 100 psig. The tank is provided with a weir located 7 feet from the inlet end. Approximately 8 minutes residence time is provided for the liquid in the decantation chamber and 5 minutes hold-up time in the propane chamber.

Product water is pressured from the decanter through the sea water precooler to a depropanizer column. Wash water is also pumped from this tank through the washer.

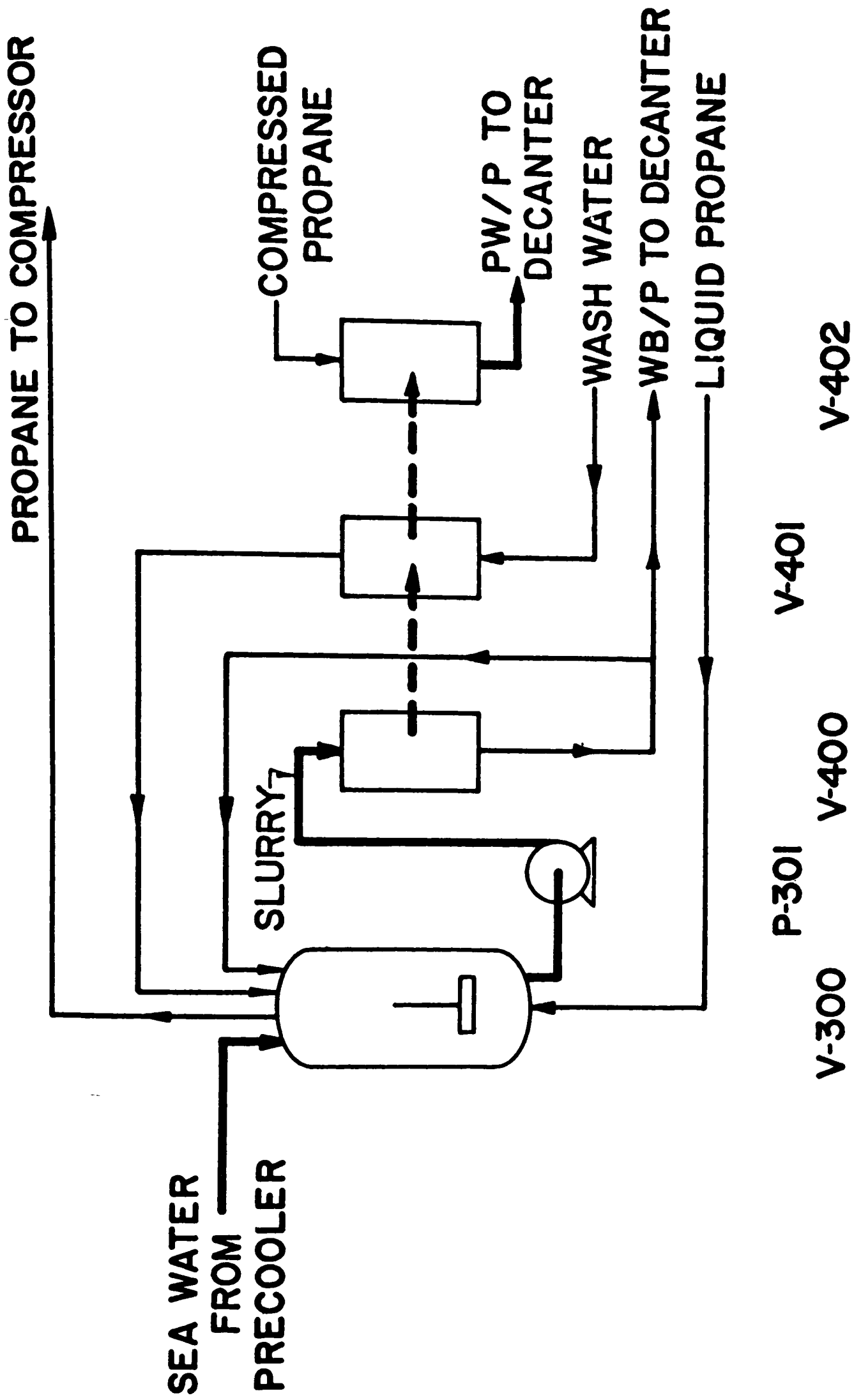


FIGURE 47
HYDRATE REACTOR AND
FILTER - WASHER - DECOMPOSER

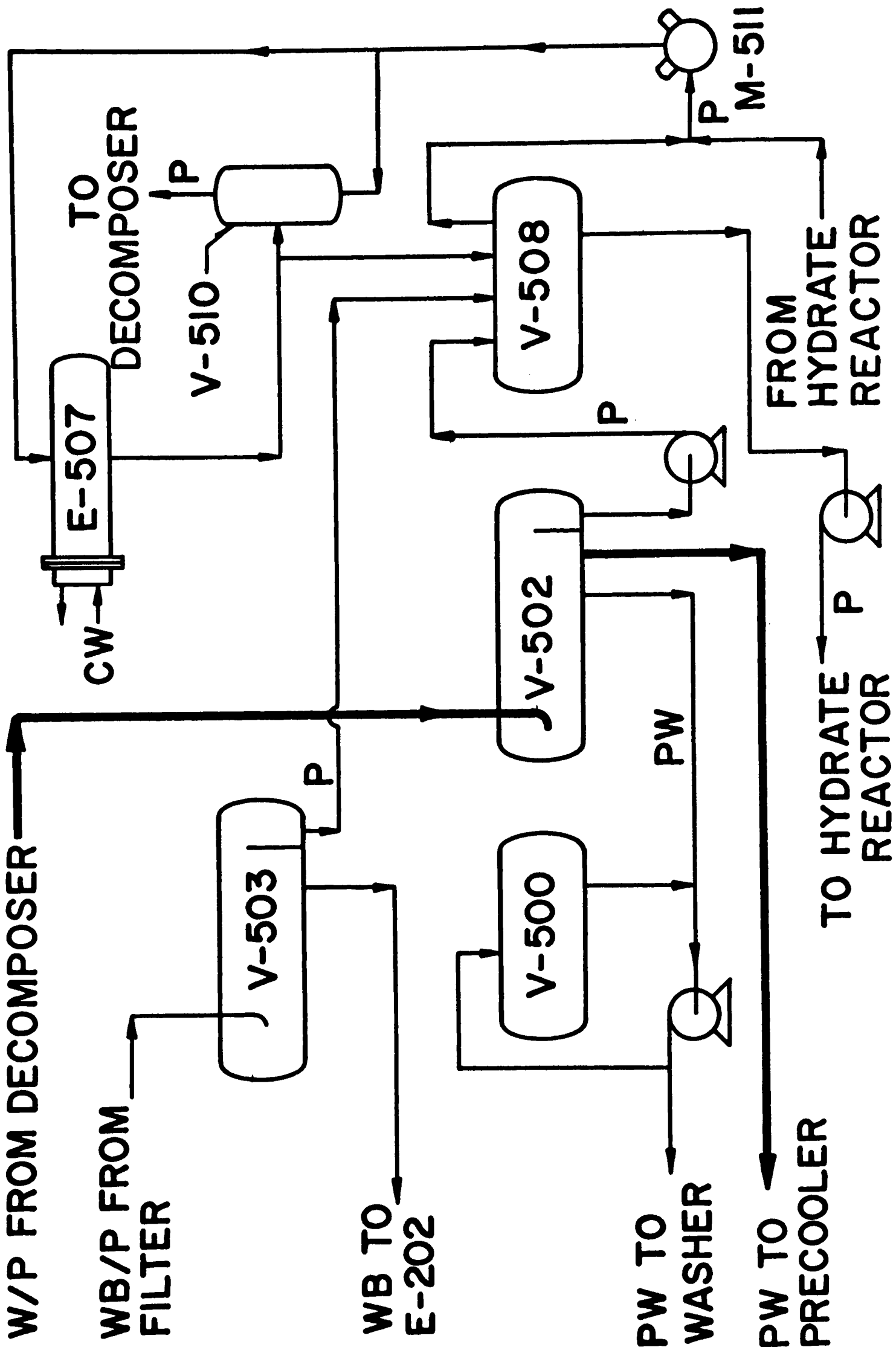


FIGURE 48
DECANTERS & PRIMARY COMPRESSORS

Liquid propane from the decanter is cooled from 42°F to reactor temperature (30-35°F) by flash evaporating a small portion of the stream in vessel V-508.

A 750-gallon carbon steel wash water hold tank V-500 has been provided to assure an adequate supply of fresh water for hydrate washing during start-up operations.

The waste brine and propane stream from the filter are separated by decantation in vessel V-503. This unit is similar in construction to the potable water-propane decanter, V-503, except that it is slightly smaller having a capacity of 400 gallons.

The decanted waste brine, which is at the reactor temperature is pressured from the decanter through the sea water precoolers E-201 and 202 and, after depropanizing, returned to the ocean.

The liquid propane decanted in vessel V-503 is returned to the running tank V-508, at reactor temperature, and is subsequently recycled to the hydrate maker.

Primary compressor, M-511, is required to elevate the propane gas from reactor pressure to a pressure at which the dew point is such that the gas can be condensed by direct contact with hydrate during decomposition and by indirect heat exchange with cooling water having a maximum temperature of 85°F. The heat of formation of the hydrate is thereby expelled from the system, and propane, in liquid form, is available for recycle to the hydrate reactor.

The combined propane vapor streams from the reactor and the running tank, V-508, are compressed from 50 psig and 30°F to approximately 160 psig by a 100 HP horizontal non-lubricated reciprocating compressor, M-511. This unit has a maximum capacity of about 200 CFM of propane at the suction conditions.

Approximately 40% of the compressed gas stream is condensed at 95°F in exchanger E-507 and then further flash-cooled to the reactor temperature in vessel V-508 for recycle to the reactor. The temperature and pressure of the remaining portion of the compressed propane are adjusted in the flash chamber V-510 by introducing a portion of the liquid propane stream from exchanger E-507. The gas leaving the flash chamber is fed directly to the decomposer units where it is condensed.

Condenser E-507 is a six-pass shell-and-tube heat exchanger, constructed with Admiralty tubes and a carbon steel shell. The unit has approximately 470 square feet of heat transfer surface.

The flash chamber, V-510, is a carbon steel vertical tank approximately 2 feet in diameter by 4 feet high and is designed for 200 psig.

Propane running tank, V-508, is a 1200-gallon carbon steel tank designed for a maximum pressure of 250 psig. This vessel has two functions:

(1) during plant operations, it serves as a flash chamber for cooling liquid propane down to the reactor temperature and (2) during shut-down periods, it provides sufficient storage capacity for all the propane.

10.3.5 Depropanizer (Figure 49)

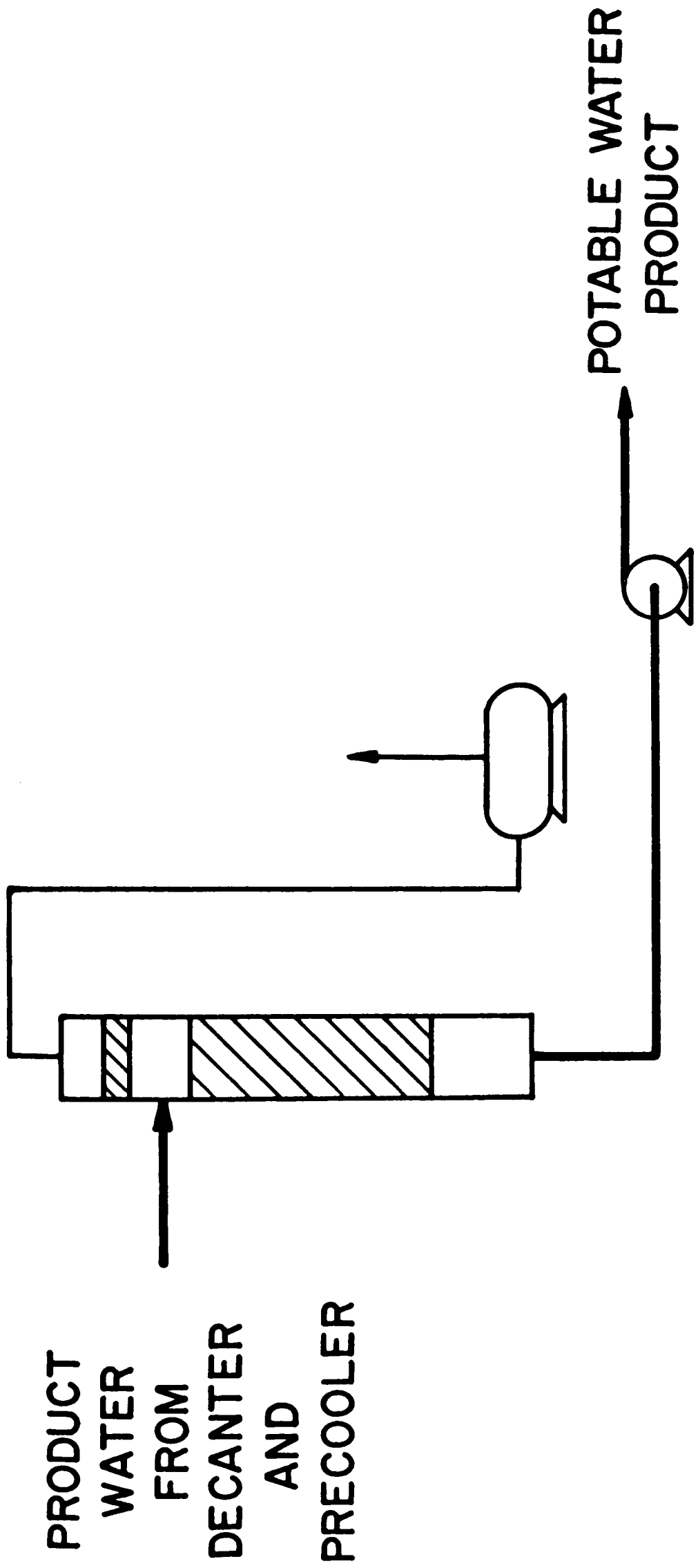
The product water which was pressured from the decanter through the sea water pre-cooler is fed to a depropanizer column, V-600. The depropanizer is an 8-inch diameter column with a 15-foot high packed section of 5/8-inch Raschig rings. The unit is designed to operate at 27 mm Hg absolute to reduce the residual propane content of the potable water to approximately 5 ppm. A single stage vacuum pump coupled with an air ejector provides the vacuum for the deaerator. The potable water product from the depropanizer is metered and sampled. The waste brine will be treated in a similar manner.

10.3.6 General

Auxiliary equipment such as chlorination equipment, miscellaneous transfer pumps, liquid propane receivers and an instrument air compressor will also be included in the pilot plant. A prefabricated control room building, approximately 14 feet wide x 30 feet long, will be provided for office space and for housing the instrument control panel.

The electrical system throughout the plant is designed to meet the code requirements for Class I, Group D explosion-proof installations. All motors rated at 1/2 HP and larger are designed for 440 volt, 3-phase operation. A 600-ampere, 440 volt, 3-phase main power feeder will be required by the plant. A step-down transformer will be provided to supply 220 and 110 voltage for single phase power and lighting requirements.

A scale model of the pilot plant was fabricated to assist in equipment and piping layout and also to serve as an aid during the fabrication of the pilot plant. All piping in the model was color-coded. Figure 50 shows a photograph of the model. The filter-washer-decomposer units, not shown in the photograph, will be located in the space between the reactor (large vertical vessel in the background) and the control room.



V-600 M-601 P-602

FIGURE 49
POTABLE WATER DEPROPANIZER

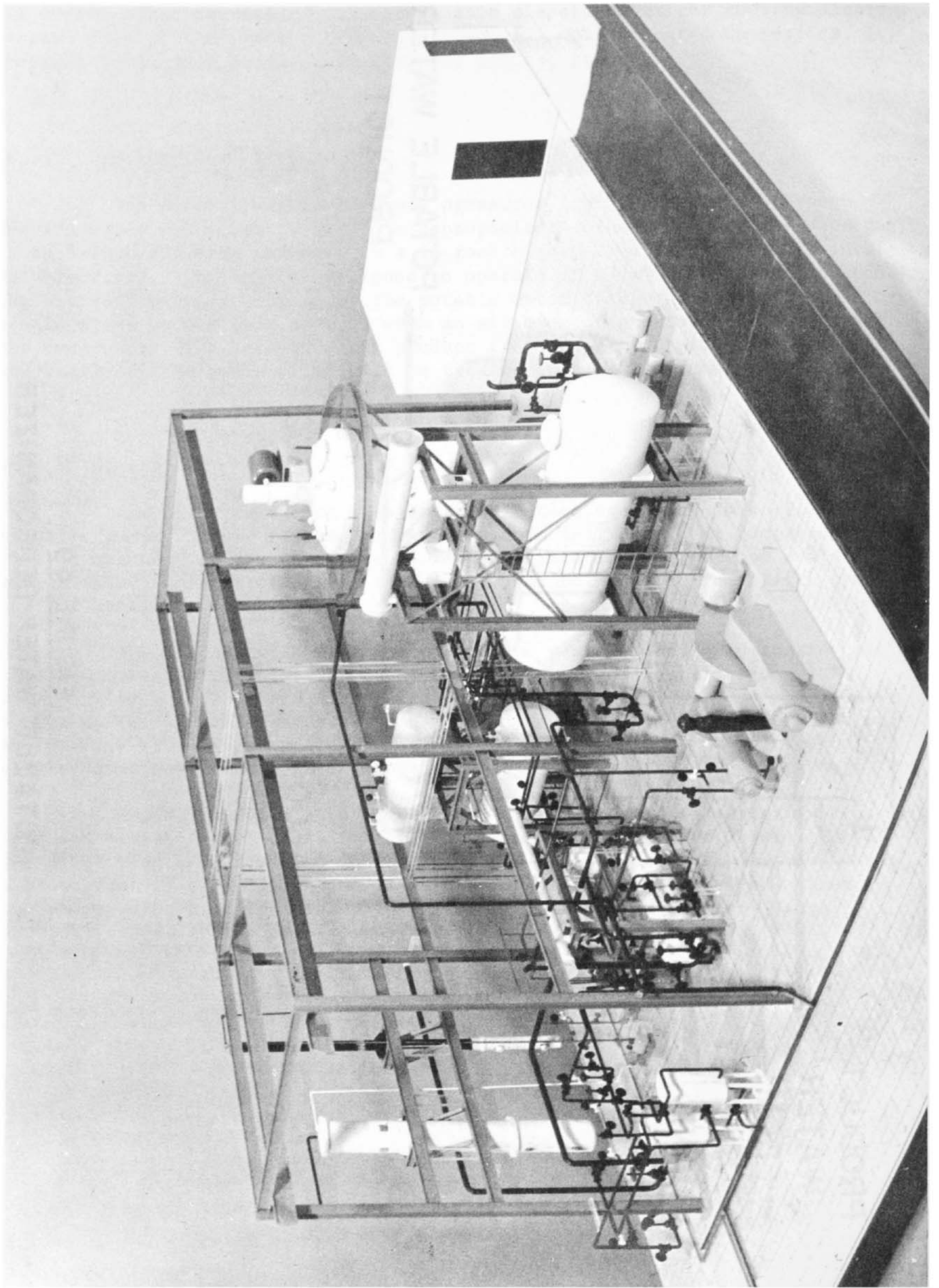


FIGURE 50 - PHOTOGRAPH OF SCALE MODEL OF KOPPERS HYDRATE PROCESS PILOT PLANT

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Immediate supervision of the bench-unit operations was carried out by Mr. E. D. Brennan.

Mr. M. Greco performed the many salt analyses required by this project.

REFERENCES

- 1/ Schroeder, W., "Die Geschichte der Gashydrate," F. Enke, Stuttgart, 1926.
- 2/ Stackelberg, M. von, and Mueller, H. R., Z. Electrochem., 58, 40 (1954).
- 3/ Claussen, W. F., J. Chem. Phys., 19, 1425 (1951).
- 4/ Powell, H. M., J. Chem. Soc. (London), 61 (1948).
- 5/ Allen, K. W. and Jeffrey, G. A., J. Chem. Phys., 38, 2304 (1963).
- 6/ Waals, J. H. van der, and Platteeuw, J. S., "Advances in Chemical Physics, Volume II," Interscience, New York City, 1959.
- 7/ Barduhn, A. J., O.S.W. R & D Report No. 44, PB171031, (1960).
- 8/ Barduhn, A. J.; Towlson, H. E. ; and Yee Chien Hu, A.I.Ch.E. J., 8, 172 (1962).
- 9/ Jeffrey, G. A., Dechema Monograph., 47, 849 (1962).
- 10/ Private Communication from C. M. Adams, Mass. Inst. Technol., Cambridge, Mass.
- 11/ Cleef, A. van, Dissertation, Delft, 1962.
- 12/ Cleef, A. van, and Diepen, G. A. M., Rec. Trav. Chim., 81, No. 5, (1962).
- 13/ Marshall, D. R., and Kobayaski, R., Paper submitted for publication in A.I.Ch.E. J., January 15, 1962.
- 14/ Frost, E. M., Jr., and Deaton, W. M., Oil Gas J., 45, No. 12, 170 (1946).
- 15/ Miller, B. and Strong, E. R., Jr., Proc. Am. Gas Assoc., 27, 80 (1945).
- 16/ Badger, W. L. and Associates, Inc., O.S.W. R & D Report No. 25, PB161399, (1959).
- 17/ Perry, J. H., Chemical Engineers Handbook, 3rd. Ed., McGraw-Hill, New York, 1950, p. 394.
- 18/ Perry, J. H., Chemical Engineers Handbook, 3rd. Ed., McGraw-Hill, New York, 1950, p. 1059.
- 19/ McMullin and Weber, Trans. A.I.Ch.E., 31, 409, (1935).

- 20/ Calderbank, P. H., Trans. Inst. Chem. Engrs. (London), 36, 443 (1958).
- 21/ Vermeulen, T.; Williams, G. M.; and Langlois, G. E., Chem. Eng. Progr., 51, 85F (1955).
- 22/ Wilke, C. R. and Chang, P., A.I.Ch.E. J., 1, 279 (1955).
- 23/ Reid, R. C., and Sherwood, T. K., "The Properties of Gases and Liquids," McGraw-Hill, New York, 1958.
- 24/ Batchelor, G. K., "Homogeneous Turbulence," Cambridge University Press, Cambridge, Mass., 1953.
- 25/ Beran, M. J., Dissertation, Harvard University, Cambridge, Mass., 1955.
- 26/ Cairns, E. J., and Prausnity, J. M., Chem. Eng. Sci., 12, 20 (1960).
- 27/ Cairns, E. J., Dissertation, University of California, Berkeley, 1959.
- 28/ Rifai, M., Dissertation, University of California, Berkeley, 1956.
- 29/ Danckwerts, P. V., Chem. Eng. Sci., 2, 1 (1953).
- 30/ Jahnke, E., and Emde, F., "Tables of Functions with Formulae and Curves," 4th. Ed., Dover Publications, New York, 1945.
- 31/ Wittstruck, T. A.; Brey, W. S., Jr.; Buswell, A. M.; Rodebuck, W. H., J. Chem. Eng. Data, 6, No. 3, 343 (1961).
- 32/ Heat Exchanger Cost Data by H. J. Lamater, Chemical Construction Corp., presented at the AACE Convention, June 10, 1958, Cleveland, Ohio.

APPEND IX

Mass and Heat Transfer Resistances

Resistance	Dispersion Coefficient	Driving Force*	Dispersion Rate	Area $\frac{\text{cm}^2}{\text{cm}^3}$	Diameter, microns	Driving Force Gradient	Number of Particles/cm ³	Calculated Film Thickness, microns
1. Propane Dispersion to Crystal	$D = 1.2 \times 10^{-5} \frac{\text{cm}^2}{\text{sec.}}$	$\Delta C = 7.3 \times 10^{-5} \frac{\text{g}}{\text{cm}^3}$	$1.82 \times 10^{-5} \frac{\text{g}}{\text{cm}^3 \text{ sec.}}$	375	(crystal) 24.8	$\frac{dc}{dx} = 4.05 \times 10^{-3} \frac{\text{g}}{\text{cm}^4}$	1.94×10^7	180
2. Heat Transfer to Crystal	$k = \frac{\text{BTU}}{\text{hr. ft. } ^\circ\text{F}}$ $\alpha = 1.42 \times 10^{-3} \frac{\text{cm}^2}{\text{sec.}}$	$\Delta T = 1.85^\circ\text{F}$	$.200 \frac{\text{BTU}}{\text{cm}^3 \text{ hr.}}$	375	24.8	$\frac{dT}{dx} = .0472 \frac{^\circ\text{F}}{\text{cm}}$	1.94×10^7	392,000
3. Salt Dispersion from Crystal	$D = 0.7 \times 10^{-5} \frac{\text{cm}^2}{\text{sec.}}$ at 0°C	$\Delta C = 7.6 \times 10^{-5} \frac{\text{g}}{\text{cm}^3}$	$6.3 \times 10^{-6} \frac{\text{g}}{\text{cm}^3 \text{ sec.}}$	375	24.8	$\frac{dc}{dx} = 2.4 \times 10^{-3} \frac{\text{g}}{\text{cm}^4}$	1.94×10^7	32,000
4. Propane Dispersion from Droplet	$D = 1.2 \times 10^{-5} \frac{\text{cm}^2}{\text{sec.}}$	$\Delta C = 7.3 \times 10^{-5} \frac{\text{g}}{\text{cm}^3}$	$1.82 \times 10^{-5} \frac{\text{g}}{\text{cm}^3 \text{ sec.}}$	30	(droplet) 200	$\frac{dc}{dx} = .0505 \frac{\text{g}}{\text{cm}^4}$	2.39×10^4	14
Heat Transfer from Droplet	$k = \frac{\text{BTU}}{\text{hr. ft. } ^\circ\text{F}}$	$\Delta T = 1.85^\circ\text{F}$	$.200 \frac{\text{BTU}}{\text{cm}^3 \text{ hr.}}$	30	200	$\frac{dT}{dx} = .594 \frac{^\circ\text{F}}{\text{cm}}$	2.39×10^4	31,200

Note: Hydrate formation conditions: Salt content in feed - 4.8%; Residence time - 15 minutes; Hydrate produced - 13.6% by weight; Power input - .04 HP/gallon.

* Assumes that each resistance to mass transfer is sole resistance.