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Aluminum Chloride Hexahydrate Crystallization by HCl Gas Sparging

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CONTENTS

ILLUSTRATIONS

TABLES

ALUMINUM CHLORIDE HEXAHYDRATE CRYSTALLIZATION BY HCl GAS SPARGING

by

J. H. Maysilles,[1] D. E. Traut,[2] and D. L. Sawyer, Jr.[3]

ABSTRACT

The Bureau of Mines is conducting research on various technologies to recover alumina from domestic resources for feedstock to existing aluminum smelting capacity as a means to reduce dependence on imported bauxite, which represents 93 pct of U.S. aluminum requirements. One of the more promising technologies being investigated is the hydrochloric acid leaching of kaolinitic clay. In the hydrochloric acid leaching technology, alumina is recovered from iron-free aluminum chloride leach liquor and separated from impurity elements by sparging the liquor with HCl gas to crystallize aluminum chloride hexahydrate (ACH).

A large-scale crystallizer with a 336-gallon usable volume was constructed and operated to obtain engineering and design data for potential scale up and to demonstrate the ability of the technology to produce specification grade alumina. Test campaigns involving about 1,400 hours of operation were completed. ACH meeting all chemical purity requirements could not be produced by a single crystallization, but was produced by recrystallizing the product from the calcined kaolin clay leach liquor. Product crystals with a size distribution of more than 80 pct plus 100 mesh and 65 pct plus 65 mesh were made at a rate of 10 pounds of ACH/(hr)(ft^3). The zirconium tube heat exchanger used to maintain constant process temperature operated with an overall heat transfer coefficient of 420 to 500 BTU/(hr)(ft^2)(°F).

INTRODUCTION

The United States is the world's largest producer and consumer of aluminum, an economically and strategically vital commodity (<u>23</u>).[4] At present, the

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

country's source for 93 pct of its aluminum raw material is imported bauxite. Domestic raw material resources are adequate to supply the Nation's projected demands; however, most known resources are in the form of clay, alunite, anorthosite, dawsonite, and shale, none of which can be treated by methods used to process bauxite. Thus, to fulfill its mission of serving the Nation's economic, social, strategic, and environmental needs as they relate to minerals, the Bureau of Mines is conducting research to evaluate methods for recovering alumina from domestic sources. The goal of the research is to decrease the dependence of the United States on foreign raw material supplies by producing alumina from domestic resources as feedstock to existing aluminum smelters.

Kaolinitic clay is one of the more promising domestic aluminous raw materials (4). It is found in relatively pure form in several known reserves and can be mined and crushed easily without hazard. The alumina is readily separable from unwanted constituents. The residue is mostly silica, which has little adverse environmental effect (1). Therefore, the production of alumina from clay has been the subject of intensive investigation by the Bureau of Mines. Alumina recovery methods studied include leaching with hydrochloric, nitric, sulfurous, and sulfuric acids, and lime sintering followed by sodium carbonate leaching (2, 12-13, 16-21). Of these methods, hydrochloric acid leaching is currently projected to be less costly and to consume less energy than the alternatives (4-5).

The clay-hydrochloric acid process for alumina production is illustrated in figure 1 (5). Kaolin clay is calcined at 725° to 750° C to chemically alter the hydrous aluminum silicate $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, its major constituent, to a form in which the alumina is amenable to acid leaching. Hydrochloric acid solution dissolves the alumina and some impurities, mostly iron. After the resulting aluminum chloride liquor is separated from the solid leach residue, the iron is eliminated from solution by oxidizing any ferrous iron present to Fe^{3+} with chlorine, then quantitatively removing all iron by solvent extraction. Unreacted HCl and excess water are evaporated to produce a relatively pure solution that is nearly saturated in $AlCl_3$. Dissolved alumina is separated from impurity elements and most of the remaining water by adding HCl gas to precipitate aluminum chloride hexahydrate (ACH), $AlCl_3 \cdot 6H_2O$, and simultaneously regenerate acid solution for recycle to the leaching step. Finally, after separation from the hydrochloric acid mother liquor, the ACH is decomposed in stages at 250° and 1,000° C to produce anhydrous alumina and an HCl-H_2O gas mixture from which HCl is recovered for process recycle.

The Bureau of Mines is presently acquiring engineering and design data in its miniplant-scale operation at Boulder City (Nev.) to confirm data used in the preliminary design of a 25-ton-per-day alumina pilot plant to demonstrate the clay-HCl process. Before the present study began, data at the necessary operating condition did not exist for the crystallization step. Specifically, the following information was required for equipment design and construction:

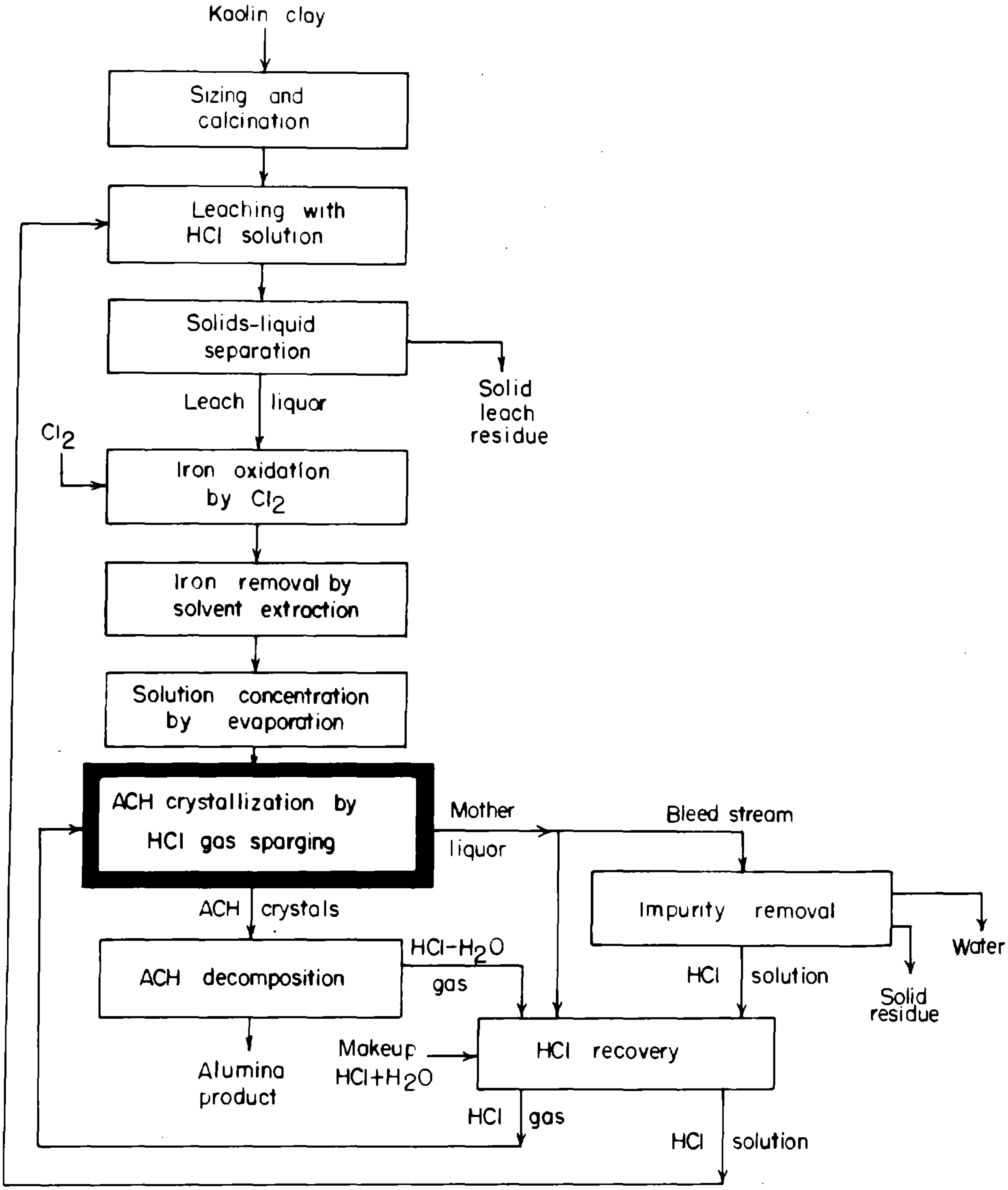

FIGURE 1. - Alumina production by the clay-HCl process, simplified flowsheet.

1. Aluminum chloride solubility in HCl solution, to determine the mass balance for the process when $AlCl_3$ solution is sparged to a specified concentration of HCl.

2. Reaction heat of crystallization, to determine the heat exchange requirement for maintaining constant process temperature.

3. Factors that affect the concentrations of impurities in the ACH, to determine conditions for which an alumina product can be made that meets chemical specifications.

4. Crystal growth rate, to determine the crystallizer capacity in pounds per hour per unit volume for producing crystals of a given size distribution. Larger crystals can be dewatered and washed more effectively, and fines production during subsequent decomposition to alumina is minimized.

5. Dewatering and washing efficiency for ACH/mother liquor separation, to determine degree of product and impurity separation, equipment requirements, and effect on process flow scheme.

6. Effect of process variables such as degree of solution acidification, liquor circulation rate, and production rate on equipment performance and crystallizer operating characteristics.

7. Heat transfer efficiency of the crystallizer heat exchanger, to determine heat exchanger size requirement for a given ACH production capacity.

8. Effect of factors such as excessive temperature differential between liquor and coolant streams, large temperature decrease in liquor through the heat exchanger, and presence of a noncondensable or nonabsorbable gas component, such as air, in the HCl gas feed, which could significantly decrease heat exchanger efficiency.

9. Suitability of different materials of construction under the required operating conditions, to provide data for estimating initial cost and projected lifetime of major crystallizer components.

10. Environmental impact of the crystallization process.

Laboratory tests were designed to determine the solubility and impurity concentration data, and an estimate of the crystallization reaction heat was made as part of an independent study. However, a large-scale experimental program was needed to make the remaining determinations and provide verification of the laboratory scale and independent study results. Thus, a crystallization test program was initiated by the Bureau of Mines to obtain as much of the required information as possible. Program objectives were to obtain the needed crystal size distribution and heat transfer efficiency data, determine the effect of process variables on crystallizer operation, observe the durability of the selected construction materials during an extensive test campaign, and provide sufficient chemical purity data to compare with the results of laboratory tests. Heat transfer data for comparison with experimental data were also to be used to determine the heat generated by the crystallization process in steady-state operating conditions. The miniplant work area was monitored for process emissions, such as HCl vapor, as part of the environmental evaluation.

ACKNOWLEDGMENT

The authors thank Stephen M. Glasgow, assistant manager, Crystallizer and Evaporator Dept., Struthers Scientific and International Corp., Warren, Pa., for substantial contributions to the description of crystallizer design and operation and the analysis of experimental results.

ALUMINUM CHLORIDE HEXAHYDRATE CRYSTALLIZATION CHEMISTRY

The technique of producing relatively pure compounds by precipitating chlorides from solution with an excess of HCl is well known (10-11). Purified salts, such as NaCl, $BaCl_2 \cdot 2H_2O$, and $AlCl_3 \cdot 6H_2O$, have been prepared by saturating their solutions with HCl, precipitating the desired salt, and leaving in solution the elements for which the chloride salt solubility products are not exceeded by the HCl addition. Precipitation can be almost quantitative if the solution HCl content is raised sufficiently high. Thus, precipitation with HCl gas has been used as a combination purification-recovery process.

Mass Balance Data

In the clay-HCl process, purification and recovery of an alumina product is made from concentrated liquor containing 28 to 31 wt-pct $AlCl_3$ and less than 0.5 wt-pct HCl. Addition of HCl gas decreases the solubility of $AlCl_3$ and precipitates $AlCl_3 \cdot 6H_2O$. The solubility of $AlCl_3$ in HCl solution must be known to determine the material balance for the crystallization step.

As support for the miniplant crystallization study, experimental work was performed at the Bureau of Mines Albany (Oreg.) Research Center to determine solubility curves for the system $AlCl_3$-HCl-H_2O at temperatures between 25° and 85° C (6). The curve for this system at 65° C is given in figure 2. Solubility data for 65° C were used for the miniplant studies because this temperature was the closest to the actual crystallization temperature of 140° F (60° C) for which data were available. Because the solubility change of $AlCl_3$ with temperature was less than 2 wt-pct over the entire range investigated, a negligible error in mass balance determination was expected using this approximation.

Heat Balance Data

The enthalpy change for the crystallization reaction must be known to determine the process heat balance. The heat released by the reaction is the sum of the heat of HCl dissolution and heat of ACH crystallization. This heat must be removed from the reaction products to keep the temperature of the resulting solution sufficiently below its boiling point to prevent significant loss of HCl.

Dissolution of HCl and crystallization of $AlCl_3 \cdot 6H_2O$ are represented by equations 1 and 2 respectively:

$$HCl(g) \dashrightarrow HCl(aq.), \tag{1}$$

$$AlCl_3(aq.) + 6\ H_2O \dashrightarrow AlCl_3 \cdot 6H_2O(s). \tag{2}$$

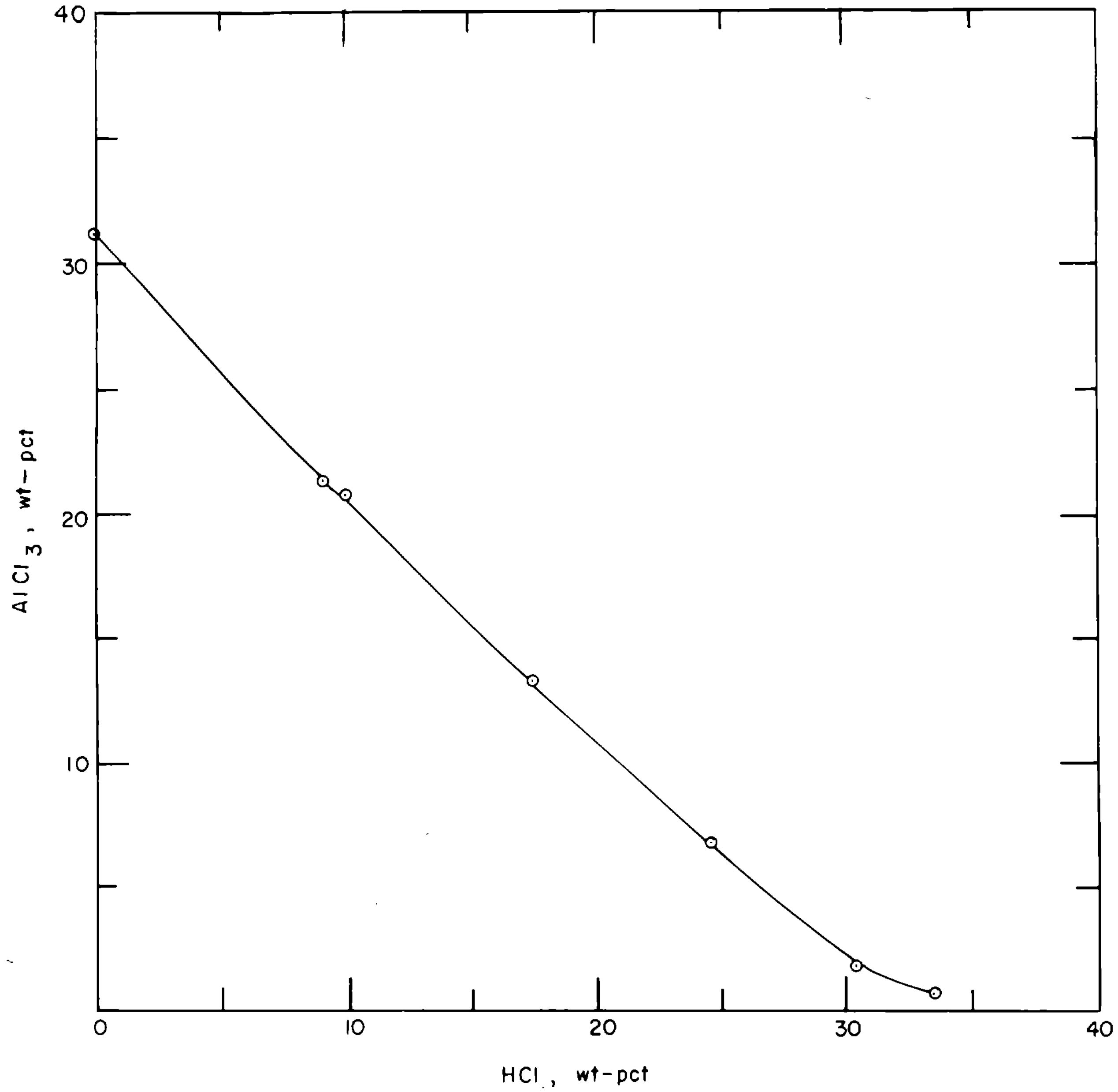

FIGURE 2. - Aluminum chloride solubility in hydrochloric acid solution at 65° C.

The best value available for the heat of dissolution of HCl in a solution saturated with HCl and $AlCl_3$ was 587 Btu per pound of HCl absorbed (3). The heat of crystallization was reported to be small. Although reaction conditions were not defined, the data indicated that approximately 270 Btu of heat per pound of ACH crystallized would be generated. This is the amount of heat that must be removed from the system by heat exchange, assuming that the HCl gas and $AlCl_3$ liquor are added at reaction temperature.

LABORATORY IMPURITY CONCENTRATION STUDIES

Chemical purity of the alumina product from the clay-HCl process is a primary measure of the overall effectiveness of the process. Concentrations of impurities must be low for the product to be acceptable electrolytic cell feed, as shown in table 1. In the decomposition of ACH,

$$2\ AlCl_3 \cdot 6H_2O \longrightarrow Al_2O_3 + 6\ HCl + 9\ H_2O, \qquad (3)$$

impurities in the ACH report to the Al_2O_3. Because the weight of Al_2O_3 product is less than ACH by a factor of 4.7, the impurity limits for ACH are less than those for Al_2O_3 by that factor. This fact illustrates the need to decrease impurity concentrations in the ACH to extremely low levels.

TABLE 1. - Target specifications for alumina product

Impurity[1]	Product specification, maximum wt-pct in Al_2O_3	Impurity[1]	Product specification, maximum wt-pct in Al_2O_3
P_2O_5.....	0.001	NiO......	0.005
B_2O_3.....	.001	CuO......	.01
MgO......	.002	Fe_2O_3....	.015
MnO......	.002	SiO_2.....	.015
Cr_2O_3....	.002	ZnO......	.02
V_2O_5.....	.002	Ga_2O_3....	.02
TiO_2.....	.005	CaO......	.04
K_2O......	.005	Na_2O.....	.40

[1] Results of impurity element analyses of Al_2O_3, ACH, and $AlCl_3$ liquor are normally reported as concentrations of the oxides, regardless of the forms in which the elements are actually present.

Chemical Purity of Aluminum Chloride Hexahydrate

A major purpose of ACH crystallization is to separate aluminum from acid-soluble impurities. However, even though ACH tends to crystallize as a pure compound, other elements in solution, such as phosphorus and magnesium, may precipitate or cocrystallize to some degree and hence report to the alumina decomposition product. Therefore the impurity element concentrations in the ACH and alumina would depend to some degree on the concentrations of those elements in the $AlCl_3$ feed liquor. Other factors that were expected to affect the purity of the ACH were degree of solution acidification, production rate, and crystallization temperature. Because of the large number of tests needed to determine the effect of all factors, a series of bench-scale experiments was initiated at the Boulder City (Nev.) Engineering Laboratory.

The effect of impurity separation on the process flowsheet is shown by figure 1. Most of the mother liquor containing the rejected impurities is recycled to the leaching step, with a bleed stream being treated to remove the impurities from the process. The greater the efficiency of the separation, the higher the concentrations of impurities that can be tolerated in the feed liquor and recycled acid, and hence the smaller the bleed stream that must be treated.

Impurity Concentrations in Recycled Leach Liquor

Feed solutions used in the miniplant tests were made with concentrations of impurity elements which would be expected in the clay-HCl process. Because impurity concentrations in the leach liquor increase as the liquor is recycled, the rate at which impurities accumulated in the liquor was determined. Therefore, before the miniplant crystallization tests were begun, a closed-loop recycle leaching test designed to duplicate the proposed process through the crystallization step without a bleed stream was made. The major difference was the fact that the laboratory test was made batchwise rather than continuously. Impurity concentrations in the leach liquor and in the crystallized ACH were determined for up to 20 process cycles.

Liquor impurity concentrations after 1, 4, 8, and 20 leaching cycles are given in table 2 (8). These concentrations were chosen as targets for feed liquor compositions used in the miniplant program. The relationship between ACH product and feed liquor impurity concentrations from the miniplant crystallizer tests could then be compared with the results of the laboratory test series to determine the validity of basing predictions for large-scale tests on results from bench-scale experiments.

TABLE 2. - Leach liquor impurity concentrations versus leaching cycle

Impurity	Concentration in solution, wt-pct			
	1st cycle	4th cycle	8th cycle	20th cycle
P_2O_5...	0.020	0.051	0.078	0.123
MgO....	.015	.059	.11	.22
MnO....	.004	.015	.015	.023
Cr_2O_3..	.003	.010	.015	.026
K_2O....	.013	.052	.078	.15
NiO....	.003	.008	.013	.021
CuO....	<.0001	.0004	.0007	.0032
[1]Fe_2O_3..	.002	.002	.001	.001
CaO....	.008	.036	.063	.117
Na_2O...	.006	.025	.041	.078

[1] Iron was removed by solvent extraction after each leaching cycle.

ALUMINA MINIPLANT CRYSTALLIZER

A large-scale HCl gas sparging crystallizer was constructed and operated to acquire the information necessary for the proposed pilot plant design. A major objective in the choice of crystallizer type was to select a relatively simple design from which operating parameters such as production rate could be used to determine the size and operating characteristics of a pilot or full-scale unit. The choice of design was made to minimize the use of exotic or relatively expensive construction materials and to provide an estimate of the projected lifetime of materials under the operating conditions used. The actual design of the crystallizer and major components was made by Struthers Scientific and International Corporation, Warren, Pa., and was based on Bureau of Mines experimental data and pilot plant tests by Struthers.[5]

Design

The principle of operation is that of a growth or Oslo-type crystallizer. The crystallizer unit and miniplant operation area are shown in figure 3, and configuration, major components, and flow scheme are illustrated in figure 4. The essential components of this type of unit are (1) a chamber or vessel for crystal suspension and growth, (2) a liquor circulation system to provide sufficient upward flow through the suspension chamber to fluidize the crystals, (3) a circulation pump to give the required flow, (4) equipment for monitoring and controlling the circulation flow rate, and (5) a heat exchanger with sufficient capacity to maintain constant system temperature.

Suspension Chamber and Circulation Loop

In steady state operation, concentrated aluminum chloride liquor and hydrogen chloride gas are introduced into the circulation loop to produce a hydrochloric acid solution supersaturated with $AlCl_3 \cdot 6H_2O$. This solution enters the suspension chamber, which contains ACH already crystallized. The circulating liquor enters the bottom of the crystallizer magma chamber from the downcomer tube and flows upward through the fluidized crystal bed. Supersaturation of the solution is relieved by both the growth of ACH on the surface of existing crystals and the formation of new nuclei. The latter can also occur to some degree in the circulation loop. Crystals are removed from the chamber by periodic withdrawal of slurry consisting of ACH product and acidic mother liquor.

Design of the suspension chamber and circulation system is based on several interrelated factors (9). Crystal growth rate is dependent on temperature and driving force, which is the supersaturation of the salt to be crystallized. At a given temperature, the rate of liquor circulation is dictated

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[5] Reference to specific manufacturers, brands of equipment, and trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

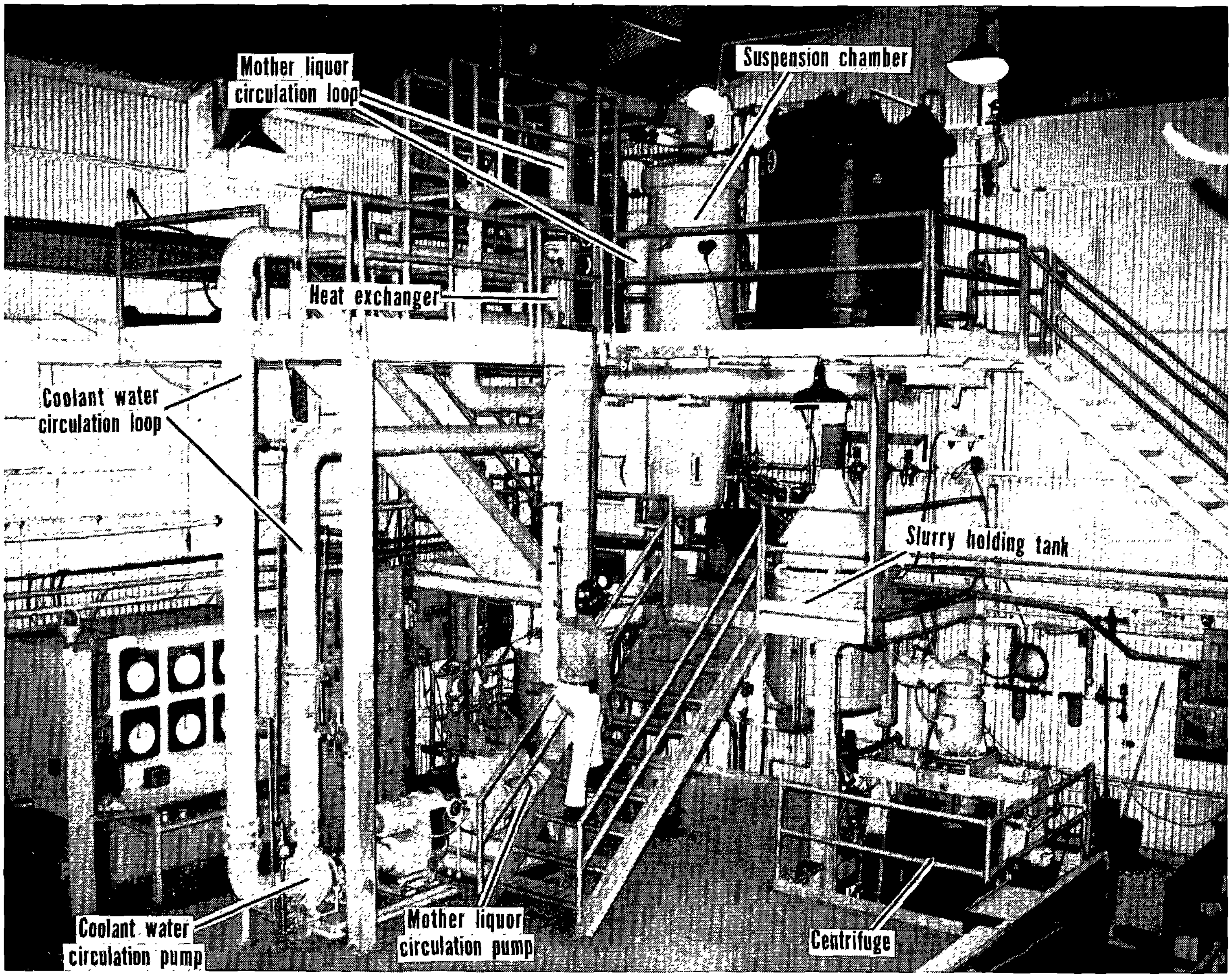

FIGURE 3. - Miniplant HCl gas sparging crystallizer.

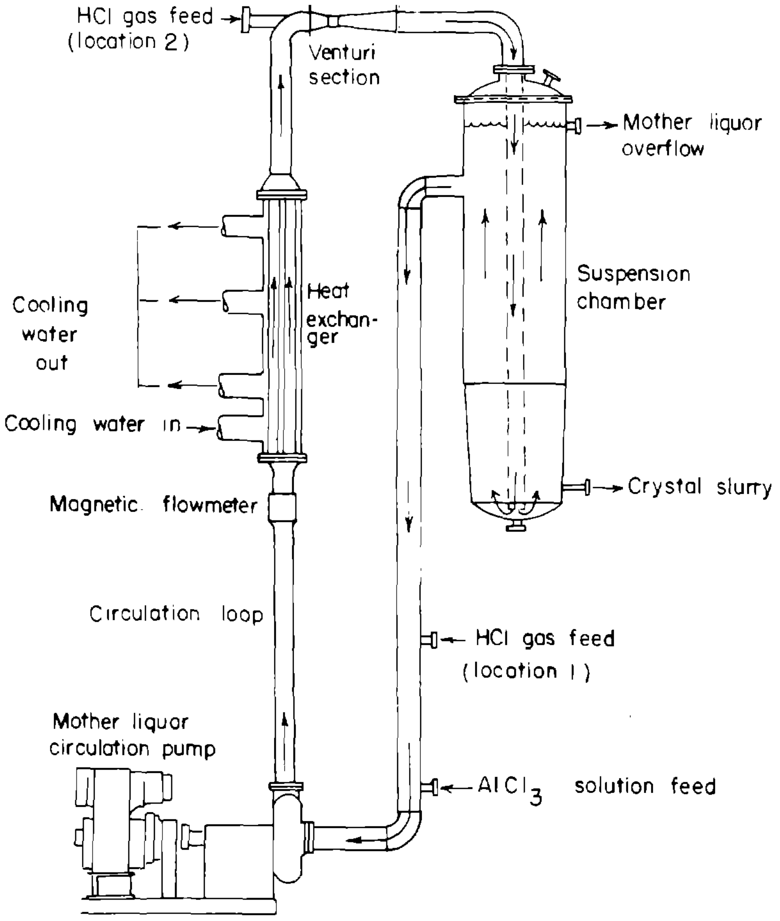

FIGURE 4. - Crystallizer flow scheme.

by the required crystal production rate and the crystallization driving force. Once the circulation rate is fixed, the cross-sectional area of the suspension chamber is chosen so that enough upward velocity for fluidization is provided, and the volume of the chamber is chosen to allow sufficient residence time for crystal growth. Total volume required for growth is dependent on the solids fraction in the suspension chamber. The higher the solids fraction, the longer will be the residence time for a given chamber volume.

Although degree of supersaturation in the mother liquor is a major basis for crystallizer design, this parameter cannot be chosen without consideration of other factors. In the case of ACH crystallization, for example, dissolution of HCl gas in the mother liquor/new feed mixture is exothermic. The degree to which the liquor can be cooled by the heat exchanger may be limited, as explained in the next section. Also, the relationship between supersaturation and crystal size must be determined experimentally.

The necessity for pilot-scale testing to predict crystal size is illustrated by the example of increasing production rate while maintaining constant circulation rate, operating temperature, mother liquor composition, and solids fraction. When supersaturation is higher, the crystallization growth rate increases, which tends to produce larger crystals. However, retention time decreases and nucleation rate increases, both of which tend to produce smaller crystals. The net effect of all factors cannot be predicted.

The alumina miniplant crystallizer was designed for a minimum production capacity of 150 pounds of ACH per hour and was not intended to operate specifically as a classifier. The suspension chamber was 29-1/2 inches ID by approximately 10 feet high, with a 6-inch ID downcomer pipe extending to 2 inches from the bottom of the chamber. Circulation loop piping was 4- to 6-inch ID. Total usable volume of the chamber and loop was approximately 336 gallons, or

45 ft^3. The circulation pump was a centrifugal type with a 14-inch-diameter impeller and a 7-1/2-hp drive. The anticipated range of circulation flow rates was 150 to 250 gal/min with an upward flow rate of 33 to 55 gal/(ft^2)(min) in the suspension chamber. Flow rate was monitored by a magnetic flowmeter and controlled by manual adjustment of the pump drive.

Heat Exchanger

Heat generated by crystallization was expected to be approximately 270 Btu per pound of ACH produced. For crystallizer operation at 150 pounds of ACH per hour, a heat exchange capacity of 40,500 Btu/hr was needed to maintain constant system temperature if no other method of cooling, such as adding feed liquor at a lower temperature, was available. Design of the heat exchange equipment was a critical element of the overall crystallizer design.

The heat exchanger tested was a baffled shell-and-tube type designed for cooling by water circulation in the shell, as shown in figure 5. The exchanger contained nine zirconium tubes, each 1-1/2 inches by 0.065 inches, in an 8-inch ID shell. Total heat exchange area between the bottom of the coolant water inlet and the top of the upper outlet was 18.56 ft^2, based on the outside area of the tubes. The exchanger was installed in the circulation loop. A liquor flow velocity of 3.6 to 6.0 ft/sec through the tubes was obtained.

A major objective of the crystallization test program was to evaluate heat exchanger performance, which involves determination of the overall heat transfer coefficient and capacity.

A standard method exists for calculating the heat transfer coefficient for a given heat exchanger configuration and flow rates (15, p. 10-25). However, because this method gives only an approximate value, experimental data are needed to determine an accurate enough coefficient for design purposes. Determination of an experimental value of U_o was planned in the test program.

Another important factor in determining heat exchanger capacity is the maximum allowable temperature differential between the two fluid streams. If the stream temperature differential, ΔT, becomes too large for a given liquor, particularly a saturated or supersaturated salt solution, a layer of salt or scale becomes deposited on the inner heat exchanger tube wall, which increases the resistance of the wall to heat flow and can significantly decrease the heat transfer coefficient. This layer can form within hours or over a much longer period of time. A large decrease in liquor temperature from the heat exchanger inlet to the exit may also produce this effect.

Because the mother liquor from crystallization is saturated in aluminum chloride hexahydrate, salting would be initiated at some value of ΔT. Therefore, the maximum ΔT for which salting would not occur within the time limitation of the tests was determined.

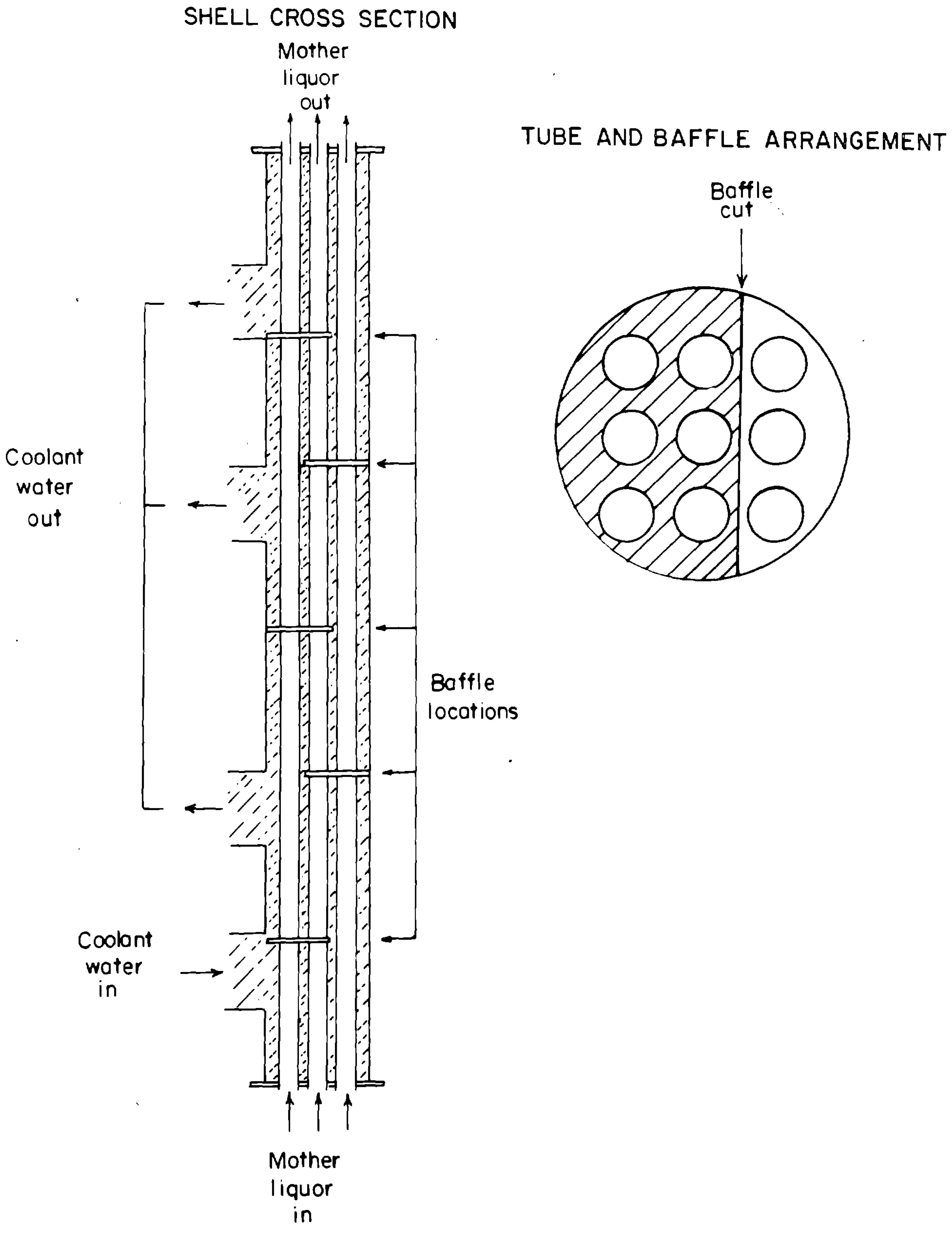

FIGURE 5. - Shell-and-tube heat exchanger design.

Coolant Water Circulation and Crystallizer Temperature Control

Coolant water was circulated through the heat exchanger shell by a centrifugal pump with an 8-1/4-inch impeller and 7-1/2-hp drive capable of circulating more than 400 gal/min. The temperature in the crystallizer was controlled by maintaining the coolant water at a sufficiently low temperature to provide the necessary temperature differential between coolant and liquor streams for the required heat transfer rate. Crystallizer temperature was monitored by a thermocouple probe. When the temperature increased above a setpoint, a valve was opened through which hot water was discharged from the coolant loop; the discharged water was automatically replaced by cold water from the plant water supply. When the temperature decreased to a second set point, the discharge valve was closed. Thus, the crystallizer temperature was maintained within a narrow range during the test runs. At design ACH production rate, the range was approximately 2° F.

Construction Materials

The highly corrosive nature of hot $HCl-AlCl_3$ solution was the major consideration in the selection of materials and equipment for crystallizer components. The suspension chamber and circulation loop were constructed of carbon steel and lined with 1/8- to 1/4-inch-thick hard natural rubber (Shore 90-95). The circulation pump casing and impeller were also rubber lined. Natural rubber is considered suitable for service in $HCl-AlCl_3$ solution and at temperatures up to 180 to 185° F.

The pump drive shaft sleeve and the heat exchanger tubes were constructed of zirconium 702 that was beta quenched and alpha annealed. This material is suitable for service under the required conditions, provided that ferric or cupric ions present in the solution are at low levels; concentrations as low as 50 ppm produce substantial surface pitting (7).

Pump packing used in most of the test runs was a soft Teflon material. A Teflon lantern ring was also used so that the packing gland could be flushed with water to prevent any leakage of mother liquor into the main drive shaft and mechanism, because this equipment could not tolerate contact with acid solution. Approximately 0.5 gallon of water per hour was added to the crystallizer through the pump packing gland. This rate of water addition had negligible effect on the material balance and operation.

The flowmeter used in the circulation loop to monitor the flow rate was a standard magnetic flow tube type with a Teflon liner and tantalum electrode and grounding rings.

Operation and Auxiliary Equipment

The crystallizer was operated as an individual miniplant unit independent of the leaching, solution treatment, decomposition, and acid recovery steps. The operation flowsheet for the crystallizer and auxiliary equipment is given in figure 6.

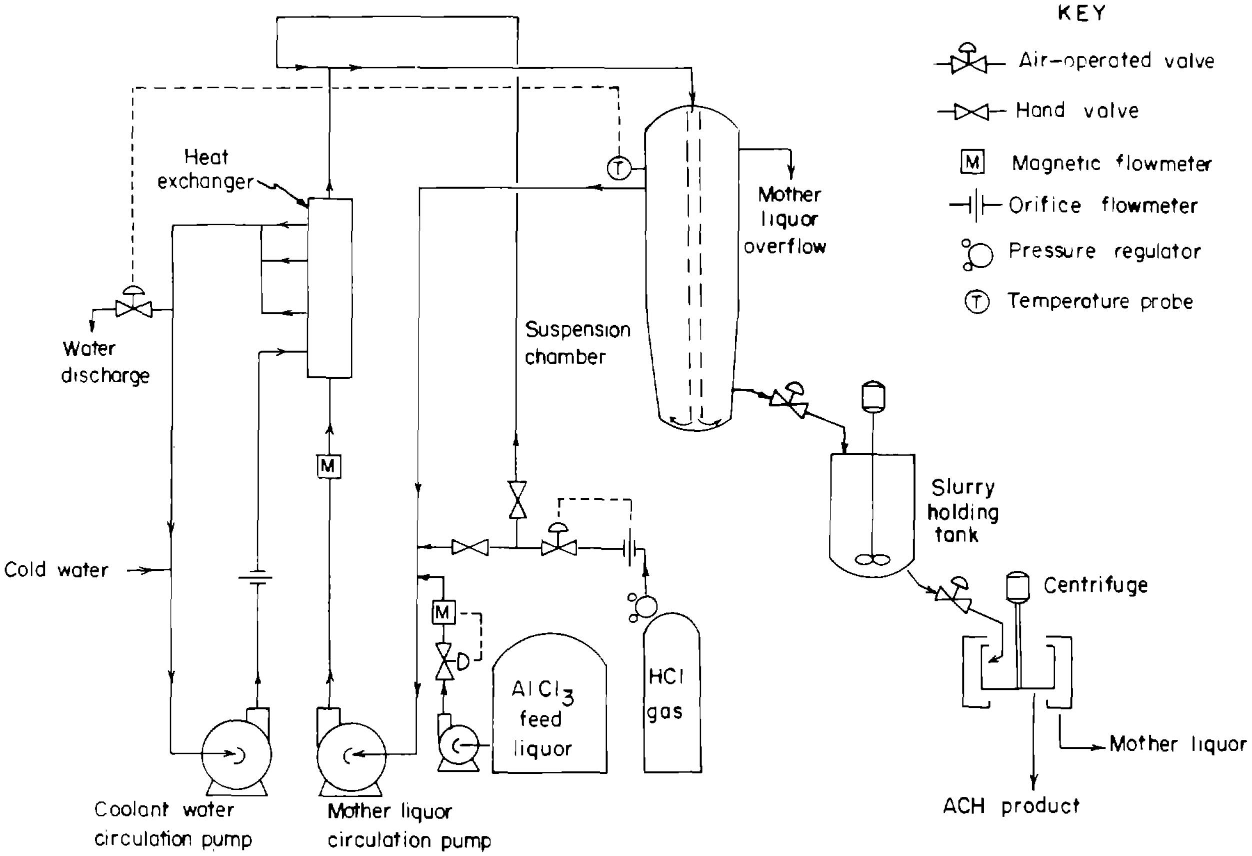

FIGURE 6. - Miniplant crystallizer operation flowsheet.

Aluminum chloride feed liquor was metered into the circulation loop through a control valve actuated by a magnetic flowmeter signal. Hydrogen chloride gas addition from high-pressure tanks was similarly controlled by a valve and orifice flowmeter. The gas pressure was regulated at 25 psig. Mother liquor HCl content was maintained at a given value by periodically sampling the crystallizer liquor, determining the acid content, and adjusting the HCl gas feed rate as required.

Crystal slurry was periodically discharged into a holding tank by a timer-actuated valve. Crystallizer solids fraction was controlled by measuring the ACH weight fraction in slurry samples and adjusting the discharge timing as necessary.

The efficiency of ACH/mother liquor separation was determined by a belt filtration study, which will be described in a separate report, and no data for this separation were acquired in the miniplant operation. Separation in the miniplant was made by centrifuge. The centrifuge cake was spray washed with either water or 26 wt-pct HCl to displace residual mother liquor and was discharged into plastic drums and stored wet. Except for samples that were dried and used for chemical analysis, screen size determination, or decomposition studies, ACH product from each test was saved only for the purpose of making $AlCl_3$ feed liquor for subsequent tests. Mother liquor from the centrifuge separation was stored and returned to the crystallizer as required.

All storage tanks and units in which solution or slurry contacted the atmosphere were vented to a scrubber, which is not shown in the flowsheet. This was necessary because of the high vapor pressure of HCl, especially in hot solutions. Scrubbing operation was performed by drawing the vapors through a spray of water that was kept slightly basic by addition of sodium hydroxide solution. Caustic solution was automatically added to the scrubber water whenever a pH probe sensed that the water acidity had increased to a set level.

Because of the corrosive nature of the materials being handled and the relatively large size of the operation, materials and equipment selection were also important for the auxiliary equipment such as pumps, piping, valves and storage tanks, needed for the crystallizer operation.

Aluminum chloride liquor feed pumps were centrifugal type with Kynar heads and impellers and ceramic face seals. The liquor feed rate flowmeter was a magnetic flow tube type, the same type used in the circulation loop. The pneumatically operated control valve contained a PVC needle and seat.

Regulators used for high-pressure HCl gas were stainless steel with Teflon trim, designed for up to 1,500-psig pressure on the feed side. The gas flowmeter orifice was Hastelloy C, and the control valve was a globe type of stainless steel internal construction.

Transport of mother liquor from the centrifuge separation was made by two types of pumps. Metering pumps with Teflon diaphragms and alumina ball check valves were used when controlled flow rates were required; for example, in the return of liquor to the crystallizer. Centrifugal pumps with epoxy plastic heads and impellers and carbon-ceramic face seals were used for transport of liquor to storage, where larger flow rates were necessary.

Most piping and valves in the solution and gas feed systems were PVC or CPVC, depending on the temperature requirement. Acid and solution storage tanks were fiber reinforced plastic (FRP) constructed of DeraKane, a vinyl ester, reinforced with fiberglass mat. Vent lines to the scrubber were PVC and FRP. For the piping from the high-pressure (500-700 psig) HCl gas tanks, the high-pressure and some of the low-pressure lines were Schedule 80 mild steel. Since mild and stainless steels are suitable for use with dry but not wet HCl, provisions were made to dry the lines with an air or nitrogen flow before each test. The slurry holding tank and centrifuge curb were rubber-lined steel, and the tank impeller and centrifuge basket were coated with Plastisol, a heat-curable compound based on PVC. Metal parts for which periodic contact with acid solution was anticipated were made of Hastelloy B. These parts included the centrifuge plow gear rack and miscellaneous hardware. The coolant water circulation system was made from standard Schedule 40 mild steel pipe.

MINIPLANT CRYSTALLIZATION TEST PROGRAM

Fourteen tests were completed on the miniplant crystallizer. A summary of test objectives and operating conditions is given in table 3. Runs 1 to 3 were made to test equipment operation and provide operating experience for personnel. Runs 4 to 14 were production tests.

TABLE 3. - Summary of HCl gas sparging crystallizer test conditions

Run	Feed solution leaching cycle	Sparging stage[1]	ACH production rate, lb/hr	Duration of operation, hours	Major objectives
1-2	NAp	1	150-200	104	Equipment test.
3	NAp	2	150-200	48	Do.
4	8	1	90	132	Product impurities study. Crystal size distribution (CSD) determination.
			150	60	
5	8	2	100	55	Do.
			150	50	
6	20	1	100	55	Do.
			150	58	
			270	20	
7	20	2	100	57	Do.
			150	56	
8	4	1	100	39	Do.
			150	78	
9	4	2	100	35	Do.
			150	39	
10	NAp	1	100	33	Recrystallization of 4th leaching cycle product. CSD determination.
			150	21	
11	1	1	100	36	Product impurities study. Effect of noncondensable gas. CSD determination.
			150	99	
			250	72	
			350	4	
12	1	Full	100	16	Product impurities study. CSD determination.
			300	45	
13	NAp	Full	100	45	Recrystallization of 1st leaching cycle product. Heat exchanger data. Effect of noncondensable gas. CSD determination.
			150	39	
			225	7	
14	NAp	Full	100	10	Maximum production rate determination. Heat exchanger data. Effect of noncondensable gas. CSD determination.
			150	26	
			250	17	
			350	12	
			450	20	

NAp Not applicable.

[1] First stage: $AlCl_3$ liquor sparged from 0 to 15 wt-pct HCl; second stage: $AlCl_3$ liquor sparged from 15 to 26 wt-pct HCl; full stage: $AlCl_3$ liquor sparged from 0 to 26 wt-pct HCl.

All crystallization tests were made at 140° F. Circulation of mother liquor is more efficient at higher temperatures because of decreased viscosity, thus a temperature was chosen that was high, but within the service range of the rubber lining of the crystallizer system. The temperature of the liquor from the concentration step was also expected to be near this value. Finally, the exothermic nature of the crystallization reaction would result in an operating temperature higher than ambient.

All variables expected to affect product purity were examined except for crystallization temperature, which was the same for each test. The relationship between ACH product impurity concentrations and feed liquor composition, degree of solution acidification, and ACH production rate were determined in tests 4 to 9, 11 and 12 for comparison with the laboratory results. Impurity contents of products were compared with the target specifications.

Feed liquors used were made by two methods. Before the crystallization test program was started, the alumina miniplant leaching circuit was operated for two runs, which produced enough liquor from calcined kaolin for the two crystallization tests (runs 11 and 12) which used first leaching cycle solution. For the other tests, the use of synthetic liquor was necessary because the HCl leaching section of the clay-HCl miniplant could not produce the large volume of liquor required. Synthetic liquor was made by purchasing $AlCl_3$ solution in bulk quantities or by dissolving ACH in water and adding impurity element compounds to produce concentrations equal to those in the 4th, 8th, and 20th cycle liquors obtained in the laboratory studies. The use of different feed liquors provided the opportunity to observe any changes in crystallizer operation caused by differences in physical properties of actual kaolin pregnant liquor and synthetic solution.

The use of kaolin-derived feed liquor for two crystallization runs resulted in a large quantity of ACH being produced from kaolin clay. The product could then be used in future decomposition tests, making possible the preparation of a final alumina product from the original kaolin raw material entirely by the clay-HCl process.

The effect of acidifying feed liquor to different HCl concentrations was examined by using one of three different modes of sparging for each test in the series. Liquor was sparged from 0 to 15 (first stage), 15 to 26 (second stage), or 0 to 26 (full stage) wt-pct HCl. Each of the four different solutions was used for two runs, with a different sparging stage used for each of the two runs.

Product purity for the design production rate of 150 pounds of ACH per hour was determined in each test. Data were obtained for higher rates in runs 6, 11, and 12. Additional purity data were obtained in runs 10 and 13, in which ACH product from previous tests was dissolved and recrystallized. Thus, data were obtained using a two-step purification technique for comparison with the one-step results.

Crystal size distribution (CSD) was monitored throughout each test to obtain scale-up data. Steady state crystal size distributions will be the same for crystallizers of different volumes provided that the following operating parameters are the same for both units: (1) production rate in pounds per hour per unit crystallizer volume, (2) temperature, (3) mother liquor HCl concentration, (4) solids fraction in suspension chamber, (5) upward velocity in suspension chamber, and (6) degree of supersaturation in circulation loop. These parameters, which determine crystallization driving force, growth time, and growth rate, were continuously monitored and controlled during each test.

Run 14 was made to determine the maximum production rate at which the crystallizer could be operated and to compare the resulting CSD with that obtained at design production rate. Additional data for rates higher than design were obtained in runs 6, 11, 12, and 13. Because tests were made using different sparging stages, the resulting CSDs were compared to determine any differences resulting from this variable.

Heat exchanger efficiency and heat balance determinations were made during test runs 13 and 14. A monitoring system based on thermistor probes was used in these tests to measure temperatures of heat exchanger liquor and coolant water streams and $AlCl_3$ liquor and HCl gas feeds. The system was designed for an accuracy of ±0.5° F. The remaining data needed were the flow rates and specific heats of liquor, coolant, and feed streams. Flow rates were measured with sufficient accuracy by flowmeters.

The effect of a noncondensable component, such as air, in the HCl gas feed was determined during runs 11, 13, and 14. In the clay-HCl process, HCl gas to the crystallizer comes primarily from the decomposition of $AlCl_3 \cdot 6H_2O$ to Al_2O_3, HCl, and H_2O. Air entrained in the ACH decomposition feed would be present in the gas stream to the crystallizer. Therefore, tests were made in which some air was introduced into the HCl gas feed to observe the effect on the crystallizer operation. The primary effect was expected to be a decrease in heat exchanger efficiency due to an increase in resistance to heat flow at the heat exchange surface.

Effect of process variables on crystallizer operation was observed throughout the test series. In addition to using different sparging stages and production rates, the liquor circulation rate was set at values that covered the design range.

As part of the total environmental impact evaluation for the process, the atmosphere in the miniplant area was monitored continuously during all tests to determine HCl vapor and nonvolatile particulate exposure to operating personnel. Scrubber off gas was also monitored to determine the effectiveness of HCl removal from process emissions.

Evaluation of construction materials was made upon completion of the test program, at which time the major components were examined for corrosion and wear.

EXPERIMENTAL RESULTS

ACH impurity concentrations were determined for several feed liquor compositions, sparging stages, and production rates. Crystal size distributions were evaluated for the different sparging stages and for production rates up to the capacity of the crystallizer. The overall heat transfer coefficient was determined, a range of liquor and coolant stream temperature differentials was investigated, and the effect of air in the HCl gas feed on heat transfer efficiency and crystallizer circulation rate was observed. Heat transfer data were used to calculate the heat of reaction for steady state crystallization at the operating temperature of 140° F. Effect of process variables on operating characteristics was determined. The monitoring study of HCl vapor in the work area and scrubber off gas was completed. The crystallizer was operated for nearly 1,400 hours, which provided a long-term exposure of equipment and materials for evaluation of corrosion and wear.

Aluminum Chloride Hexahydrate Impurity Concentrations

The results of the product purity studies using feed solutions representing 1st, 4th, 8th, and 20th leaching cycle liquors are summarized in table 4, which gives concentrations in feed liquors and corresponding ACH products. For cases in which feed liquor was sparged to first stage in one test and the resulting mother liquor was sparged to second stage in the following test, analyses for the original feed liquor were used.

The product analyses given in table 4 are the highest concentrations obtained for products from different sparging stages and production rates. Although concentrations varied slightly with production rate and sparging stage, the differences were not greater than normal variations in analytical results. For the limited data from this test series, no variations were observed in product purity with production rate and sparging stage. However, enough information was acquired to indicate two important conclusions. First, the impurity relationship was essentially the same as that observed in the most recent laboratory scale tests, indicating that the results of small scale tests can be used to predict results of large scale operations (22). Second, impurity specifications cannot be met for phosphorus and magnesium even for product from single cycle pregnant liquor. Additional purification is essential.

Because specification product could not be made by a single crystallization, purification by recrystallization was investigated. ACH product from the 4th cycle liquor crystallization tests (8-9) was dissolved in deionized water and crystallized a second time in run 10. The first product had been washed with hydrochloric acid solution in the centrifuge and contained little mother liquor with its dissolved impurities from the first crystallization. Feed liquor for test 13 was made by the same method using ACH product from the 1st cycle liquor tests (11-12). All chemical purity specifications were met for both recrystallization products, as shown in table 5. However, the concentrations of some elements, including phosphorus and magnesium, were close to the specification limit.

TABLE 4. - Impurity concentrations in aluminum chloride hexahydrate products from kaolin leach liquor and synthetic solutions

Impurity	Concentration, wt-pct[1]								Product specification, wt-pct in Al_2O_3
	1st leach cycle[2]		4th leach cycle		8th leach cycle		20th leach cycle		
	Feed liquor	ACH product	Feed liquor	ACH product	Feed liquor	ACH product	Feed liquor	ACH product	
P_2O_5	0.018	0.008	0.046	0.010	0.083	0.009	0.113	0.024	0.001
B_2O_3	.00002	.0014	ND	ND	ND	ND	ND	ND	.001
MgO	.025	.005	.056	.006	.10	.005	.22	.013	.002
MnO	.0012	.0004	.0058	.001	.029	.001	.023	.0014	.002
Cr_2O_3	.0029	<.0002	.0066	.003	.0054	<.004	.011	.004	.002
V_2O_5	.0038	<.0004	<.002	<.0005	.043	.0014	.003	<.0005	.002
TiO_2	<.005	<.0004	<.005	<.0005	.006	<.0005	.007	<.0005	.005
K_2O	.016	.0024	.040	.002	.064	.0014	.15	.0038	.005
NiO	.0021	.007	.0048	.007	.011	.005	.017	.0052	.005
CuO	.0013	<.0014	.0004	<.0014	.0011	<.0014	.0019	<.0014	.01
Fe_2O_3	.0020	.013	ND	ND	ND	ND	ND	ND	.015
SiO_2	<.02	.004	ND	ND	ND	ND	ND	ND	.015
ZnO	.0007	.0009	ND	ND	ND	ND	ND	ND	.02
Ga_2O_3	<.005	<.014	ND	ND	ND	ND	ND	ND	.02
CaO	.037	<.004	.030	<.004	.042	<.004	.065	<.004	.04
Na_2O	.019	.002	.050	.003	.043	.004	.11	.0028	.40

ND Not determined.

[1] Concentrations in ACH product are reported on the basis of weight percent in Al_2O_3. To obtain these values, concentrations in ACH are multiplied by 4.7.

[2] First cycle tests were made using kaolin leach liquor; 4th, 8th, and 20th cycle tests were made using synthetic solutions.

TABLE 5. - Impurity concentrations in recrystallized aluminum chloride hexahydrate

Impurity	Concentration, wt-pct[1]				Product specification, wt-pct in Al_2O_3
	1st leaching cycle		4th leaching cycle		
	Feed liquor	ACH product	Feed liquor	ACH product	
P_2O_5....	0.0022	0.0008	0.0015	0.0009	0.001
B_2O_3....	ND	.0005	ND	.0009	.001
MgO.....	.0035	.0003	.0011	.0009	.002
MnO.....	.0002	.0015	.0002	.0009	.002
Cr_2O_3...	.0005	.00005	.0004	.00024	.002
V_2O_5....	.009	.00005	.002	.0005	.002
TiO_2....	.024	.00005	.005	.0005	.005
K_2O.....	.0012	.0009	.0005	.0009	.005
NiO.....	.0006	.004	.0003	.005	.005
CuO.....	.0001	.0014	.0001	.0014	.01
Fe_2O_3...	.0012	.011	.0008	.018	.015
SiO_2....	.02	.014	.02	.002	.015
ZnO.....	.0001	.0005	.0001	.0015	.02
Ga_2O_3...	.001	.015	ND	ND	.02
CaO.....	.0024	.004	.0005	.004	.04
Na_2O....	.0024	.0009	.0008	.0014	.40

ND Not determined.

[1] Concentrations in ACH product are reported on the basis of weight percent in Al_2O_3.

The possibility was considered that some elements were present in isomorphous substitution in the $AlCl_3 \cdot 6H_2O$ crystal structure, which would explain the difficulty in separating these elements from the product. A sample of ACH was sent to the Salt Lake City (Utah) Research Center for analysis to determine the nature of the phosphorus in the product. Indirect evidence from petrographic examination and scanning electron microscope analysis showed that the phosphorus could be present either in solid solution, as a discrete phase, or in a fluid inclusion in the crystals. No conclusions could be reached.

The degree to which phosphorus and magnesium must be decreased in the crystallization feed liquor is illustrated by the concentration curves for P_2O_5 and MgO in product versus feed liquor shown in figure 7. Although there is some spread in the data, the curves indicate that feed liquor should contain 0.01 wt-pct or less MgO and 0.003 wt-pct or less P_2O_5 to produce specification ACH.

More than 700 pounds of product fron run 13, which was recrystallized ACH made from miniplant kaolin leach liquor, were washed and dried for decomposition tests.

Crystal Size Distribution

The crystal size distribution (CSD) of the ACH product determines the effectiveness of the separation of ACH and mother liquor and the rate of fines or dust production in the decomposition of ACH to alumina. If the fraction of small ACH crystals is high, the ACH/mother liquor separation will be difficult

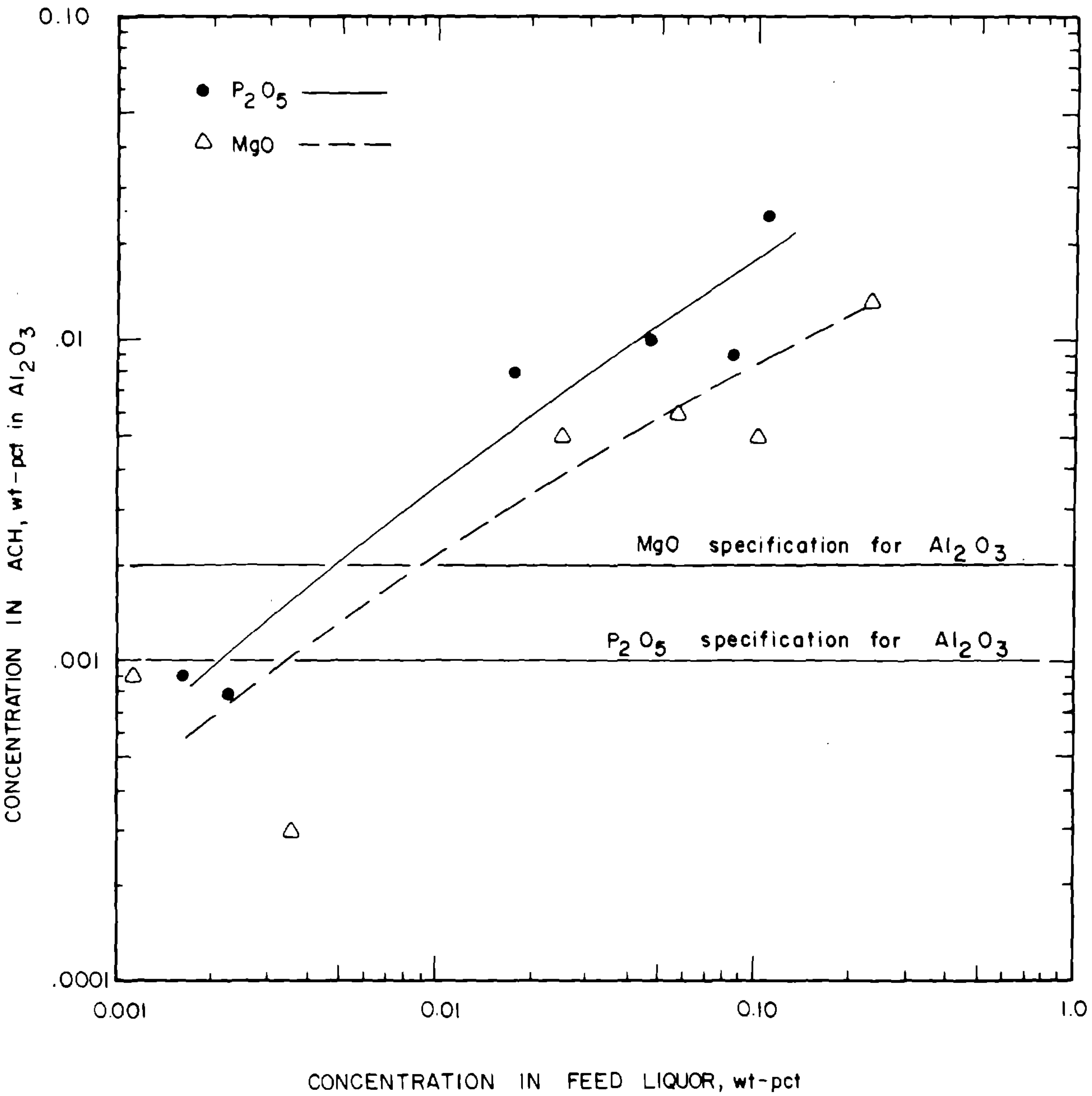

FIGURE 7. - Effect of phosphorus and magnesium feed liquor on aluminum chloride hexahydrate product purity.

and the fraction of fines produced in decomposition will be undesirably high. Although no specific size requirement has been set, the fraction of plus 100 mesh crystals should be maximized to enhance the removal of mother liquor in the solids-liquid separation step. Screen sizes monitored were plus 35, 48, 65, and 100 mesh, with particular attention focused on the latter two sizes.

Crystal size distributions for five test runs are shown in figures 8-12. The CSDs for runs 5 and 8 (fig. 8-9) are representative of the tests made at the design production rate of 150 pounds of ACH per hour. In these runs, as in all tests, the crystal sizes oscillated throughout the duration of the run. The data indicate that steady state operation was approached but never achieved. This size variation for a long period of time is not usually observed in commercial operations; however, when size oscillations occur, the steady state sizes are within the range of the oscillations (9). In both tests, the final sizes at 150 pounds of ACH per hour were 90 pct or more plus 100 mesh and 75 pct or more plus 65 mesh.

In test run 12 (fig. 10), operation was at an ACH production rate of 300 lb/hr for 45 hours. Final CSD at this rate was 80 pct or more plus 100 mesh and more than 50 pct plus 65 mesh.

The highest ACH production rate for which CSD data were obtained was 450 lb/hr for 14 hours during run 14 (fig. 12). Sizes of more than 80 pct plus 100 mesh and 65 pct plus 65 mesh were maintained. Operating parameters for the time period were

Production rate	10 lb of ACH/(hr)(ft^3)
Temperature	140° F
Mother liquor HCl concentration	26 wt-pct
Solids fraction in suspension chamber	35 wt-pct
Upward velocity in suspension chamber	55 gal/(min)(ft^2)
Supersaturation in circulation loop	30 lb of ACH per 1,000 gal (0.42 pct)

If these conditions are duplicated in the operation of a larger crystallizer, the same CSD is predicted. In the ACH crystallization process, the exact upward velocity is not important if it is sufficient to fluidize the crystals. Supersaturation of ACH in mother liquor is equal to the ACH production rate in pounds per minute divided by the flow rate in the circulation loop in thousands of gallons per minute. Supersaturation in percent is the ACH production rate in pounds per minute times 100 percent divided by the mother liquor circulation rate in pounds per minute, the weight fraction of solids in the circulating slurry being subtracted from the total weight to obtain the latter figure. The production rate possible with a large scale crystallizer will be 10 lb of ACH/(hr)(ft^3) with a steady state CSD the same as obtained in the miniplant unit.

The HCl gas was fed into the system at a different location in tests 13 and 14 than in previous tests. Referring to figure 4, location 2 was used for those two tests instead of location 1. The major reason for the change was related to the noncondensable gas effect, which will be discussed in a later section. However, the effect on CSD was also noted. As shown in figure 11,

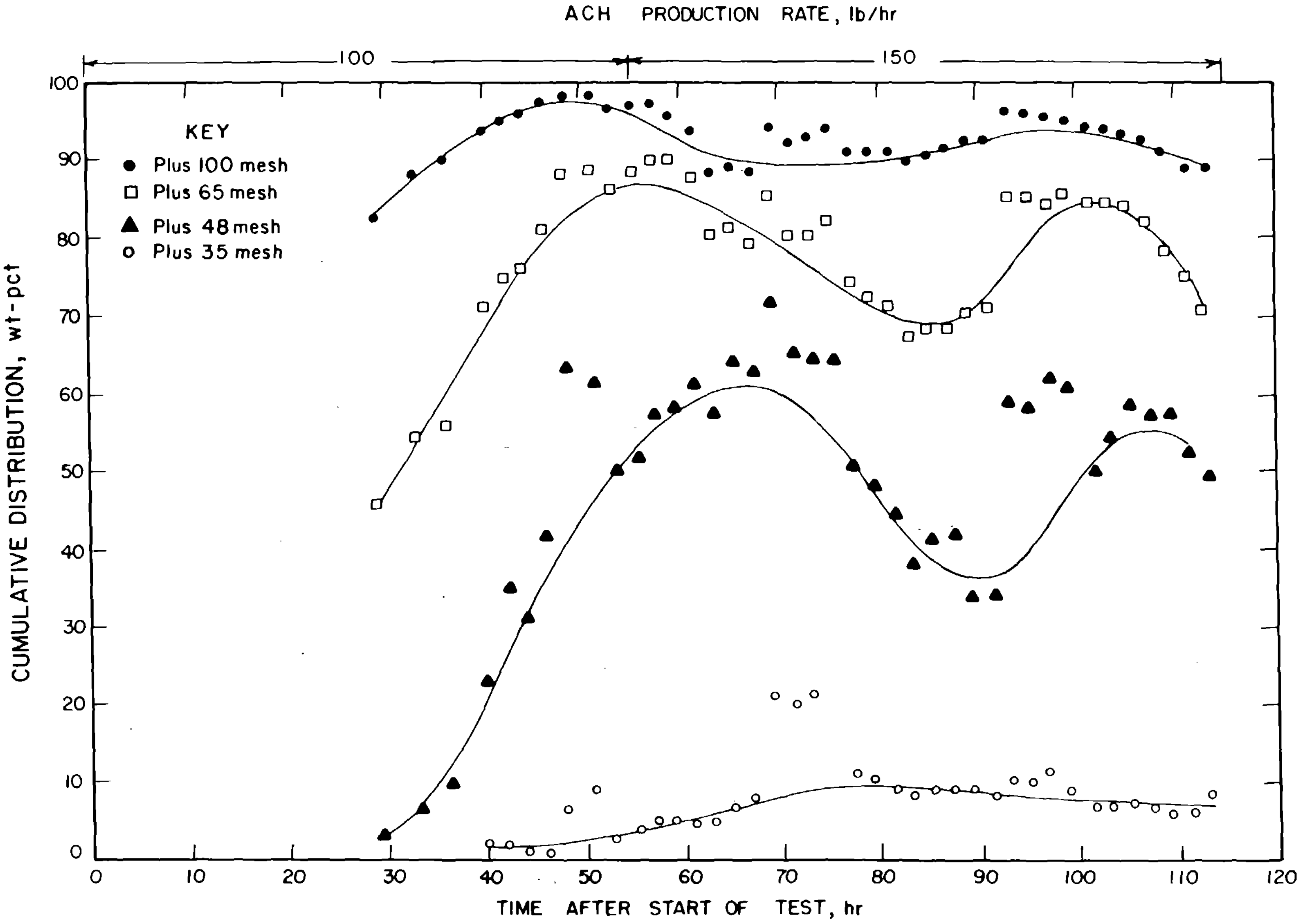

FIGURE 8. - Crystal size distribution, HCl gas sparging crystallizer test run 5.

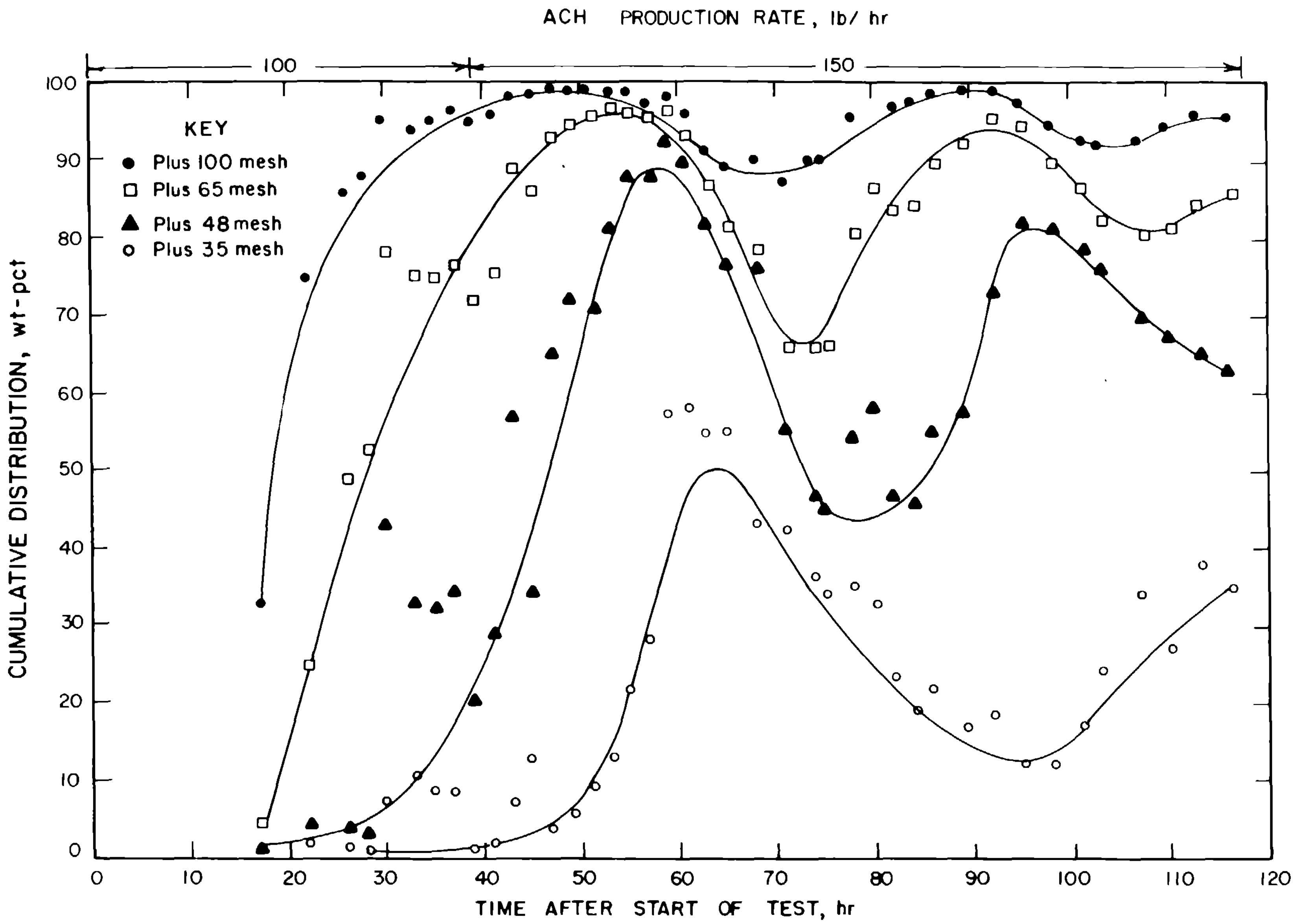

FIGURE 9. - Crystal size distribution, HCl gas sparging crystallizer test run 8.

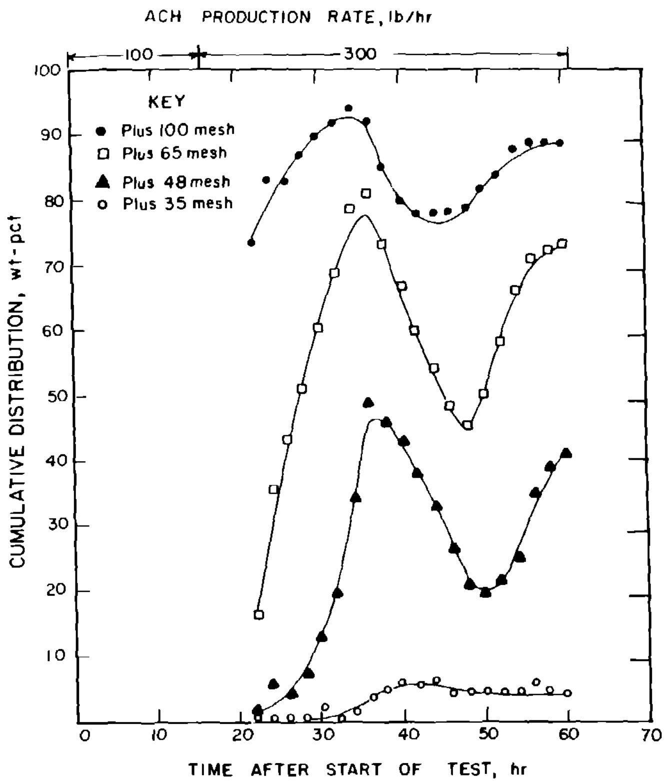

FIGURE 10. - Crystal size distribution, HCl gas sparging crystallizer test run 12.

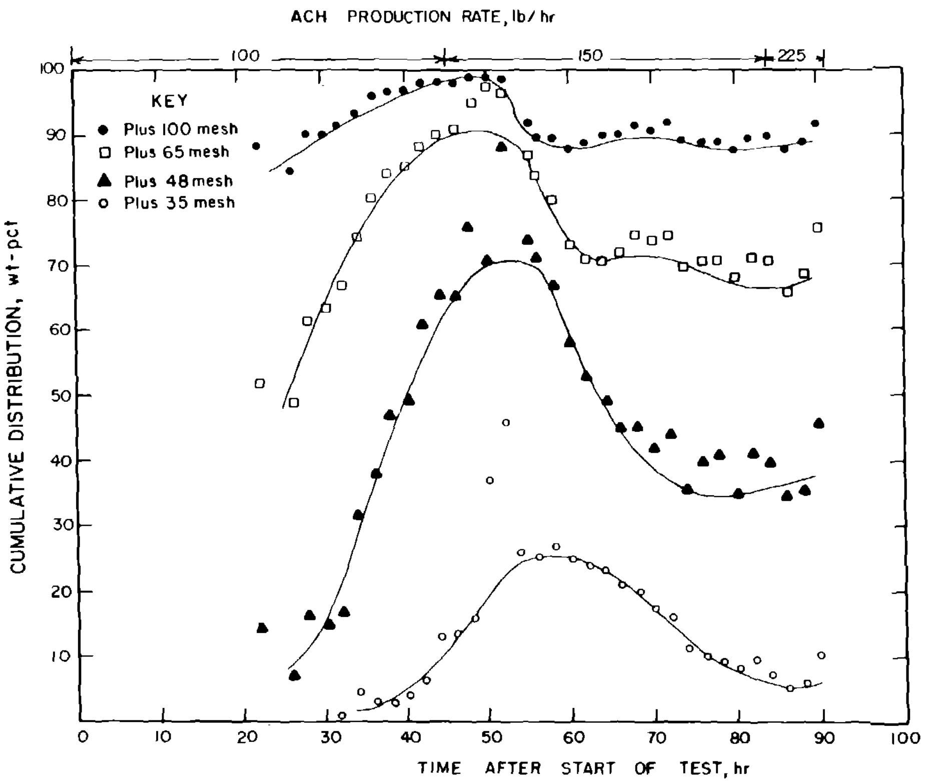

FIGURE 11. - Crystal size distribution, HCl gas sparging crystallizer test run 13.

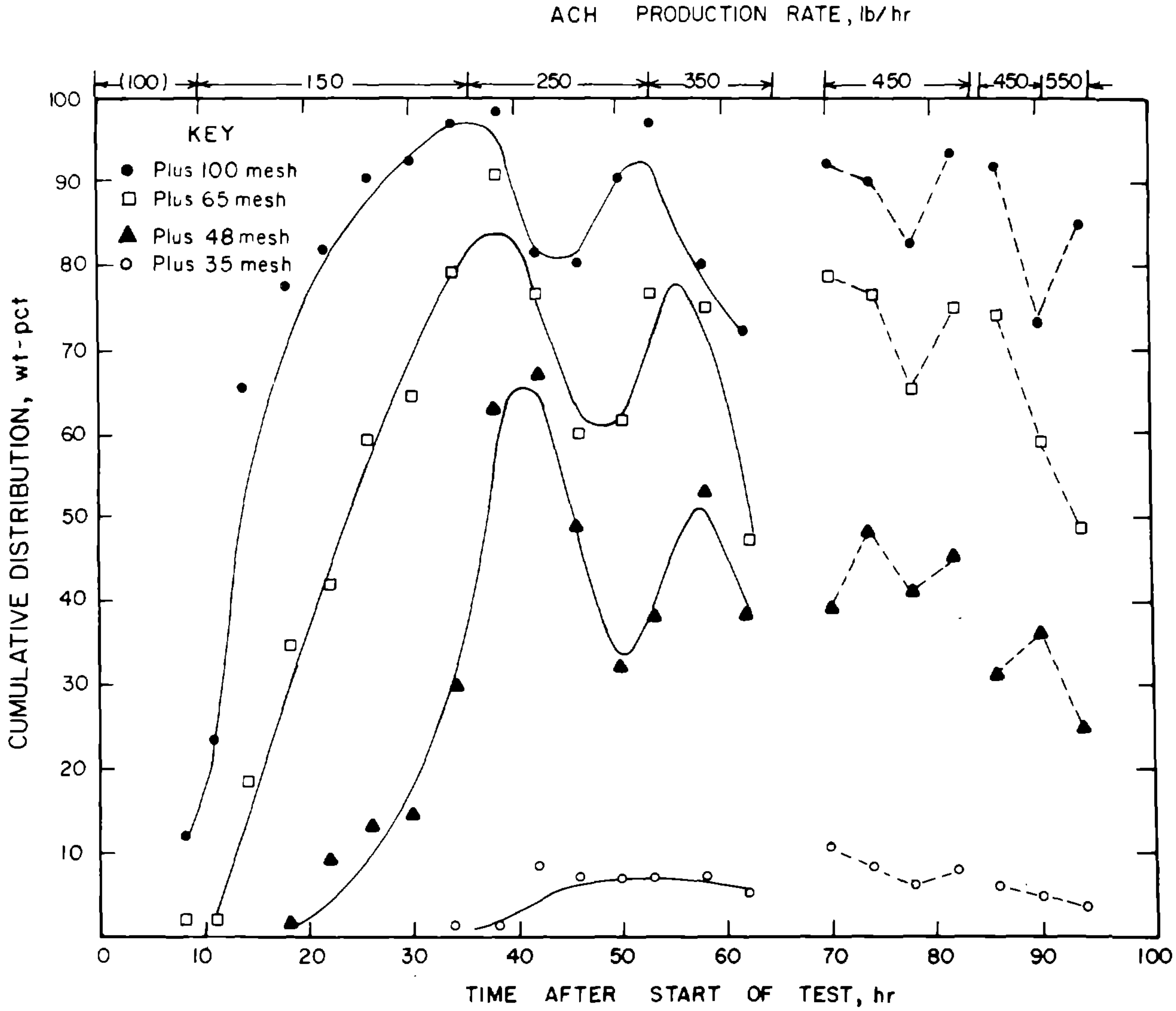

FIGURE 12. - Crystal size distribution, HCl gas sparging crystallizer test run 14.

the final fractions of plus 100 and 65 mesh crystals were the same as those in test 5, which was made at the same ACH production rate of 150 lb/hr but using gas feed location 1. No significant effect on CSD was observed in changing the gas feed location.

In comparing the results of runs 4 to 14 for different sparging stages, no significant differences were observed in the CSD between first, second, and full stage sparging tests.

Maximum Production Rate

The miniplant crystallizer was designed for an ACH production rate of 150 lb/hr, or approximately 3.3 lb/(hr)(ft^3). In order to minimize initial capital costs for a pilot or production plant, determination of the maximum production rate possible per unit crystallizer volume was required. Test run

14 was made to determine the maximum rate. Additional objectives were to determine the CSD at the maximum rate and the factors that prevented operation at higher rates.

An ACH production rate of 450 lb/hr was maintained for a continuous period of 14 hours. Mother liquor HCl content and slurry percent solids were controlled within 2 wt-pct during most of that period and within 1 wt-pct after operation was stabilized at 26 pct HCl and 35 pct solids.

When an attempt was made to operate at an ACH production rate of 550 lb/hr, stable conditions could not be maintained. Small variations in HCl gas feed and slurry discharge rates produced large changes in the control parameters, and these changes occurred faster than corrections could be made. Mother liquor HCl content and solids fraction could not be maintained within sufficiently narrow ranges to control the mass balance of the operation. Based on the results from run 14, the ACH production capacity of the crystallizer was 450 to 500 lb/hr, or 10 to 11 lb/(hr)(ft^3).

Effect of Process Variables on Crystallizer Operation

Many variables can affect the physical operation of the crystallization process. These include production rate, operating temperature, impurities in feed solution, air or other noncondensable gas in circulation loop, sparging stage, mother liquor circulation rate, and the use of synthetic feed solution versus actual leach liquor. Production rate effect and choice of operating temperature have been discussed. The chemical effect of impurity elements, including traces of iron and copper, in the feed liquor was cumulative and will be reflected in the final equipment and materials evaluation. The study of air in the circulation system was important enough to warrant a separate section for discussion.

Sparging stage is a most important variable because it determines the mass balance for the crystallization process. Each test run was made using one of three different sparging modes, as indicated in table 3. Sparging $AlCl_3$ feed liquor in two stages has three potential advantages. First, equipment corrosion and wear for the first stage with mother liquor containing 15 pct HCl may be less severe than for 26 pct HCl liquor. Higher operating temperatures may be used because of decreased HCl vapor pressure. Finally, more effective impurity rejection may be possible for first stage operation because of either increased temperature or the nature of the crystallization mechanism.

One disadvantage of sparging in two stages as opposed to one stage is that equipment for first and second stage sparging may be of different design because of the different mother liquor acid concentrations. This equipment would not be interchangeable, and plant operations would be less flexible. This disadvantage could be overcome if total equipment cost was decreased or if impurity rejection was sufficiently more effective to eliminate an additional purification step that would otherwise be necessary.

No differences in crystallizer operation were observed among first, second, and full stage sparging tests. In full stage sparging, one consideration that must be made is that mother liquor is discharged from the system in the crystal slurry faster than it is produced when the slurry contains 35 wt-pct solids. As shown by the mass balance given in figure 13, 1.789 pounds of mother liquor are produced per pound of ACH. If the crystallizer slurry contained 36 wt-pct ACH, the two products would be discharged from the system in the same weight ratio as they were produced. For operation with less than 36 wt-pct solids, provision must be made to return some mother liquor to the system after separation from the ACH product to maintain the liquor inventory in the crystallizer. This provision involves only a minor change in operation and is not an important cost factor.

One characteristic of crystallizer operation that was the same for all three sparging modes and all production rates was that crystallization continued in the mother liquor after separation from the ACH product. Crystallization occurred in all tanks and piping. The cause was probably a combination of evaporation effect, residual supersaturation of the mother liquor from the crystallizer, and the slight solubility decrease as the liquor cooled. For any process design, provision must be made to periodically clear crystal buildup from the entire mother liquor transport and storage system.

No difference in product impurity concentrations was noted for the different sparging stages, although a more complete series of laboratory tests is needed to verify this observation. Based on the results of the miniplant tests, sparging in two stages has no advantage over sparging in a single stage.

Mother liquor circulation rate determines the degree of fluidization of the crystals in the suspension chamber. Circulation rates used in the test

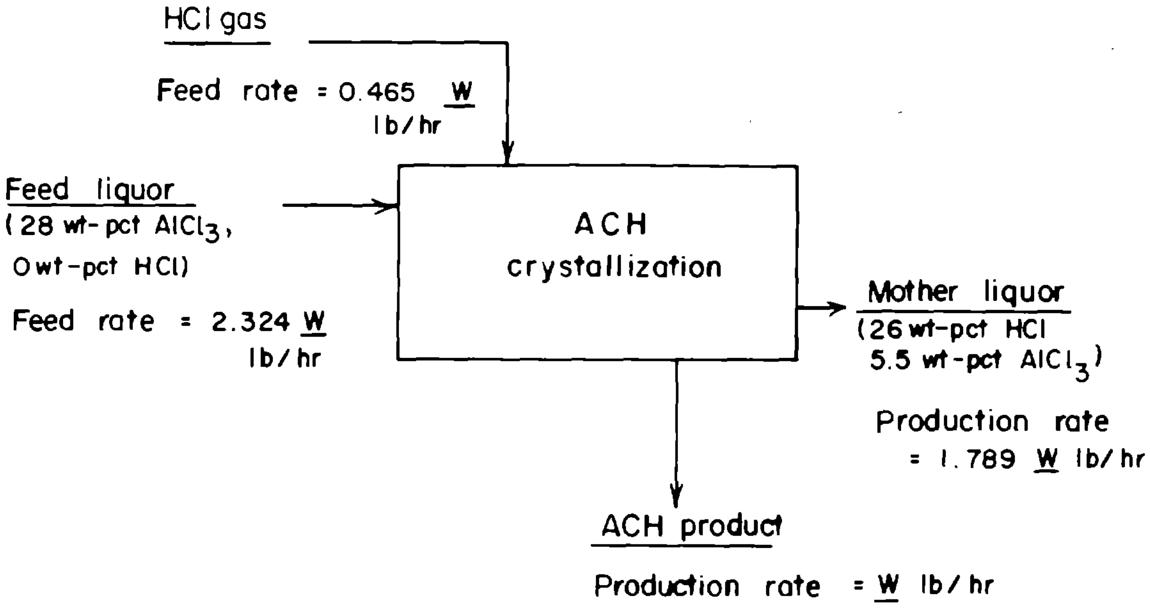

FIGURE 13. - Mass balance for aluminum chloride hexahydrate crystallization in full-stage HCl sparging.

series ranged from 33 to 55 gal/(min)(ft^2) upward velocity. Throughout this range, the ACH solids fraction in the circulation loop was the same as in the suspension chamber. The crystal bed was completely fluidized with no classification. Because classification is not necessary for this process, operation with any flow rate within the preceding range is acceptable and will result in fluidization equivalent to that used in the test series.

No differences in crystallizer operation or ACH product quality were observed that could be attributed to differences between synthetic solution and leach liquor made from calcined kaolin clay.

Reaction Heat and Heat Exchanger Efficiency

Accurate temperatures of liquor and coolant water streams were required to determine reaction heat and heat transfer coefficient. For tests 13 and 14, a temperature monitoring system using thermistor probes was installed to acquire the data. The system enabled measurement of liquor and coolant temperature differentials to within 0.1° F. The high accuracy was necessary because the actual differentials were as low as 2.7° F.

A method was required for maintaining more constant temperatures than those resulting from operation by automatic control because the control system allowed periodic variations of 2° F or more in mother liquor temperature. A procedure was used in which cold water addition to the coolant loop was manually controlled. The procedure maintained the temperature of the coolant water exiting the heat exchanger to within 0.2° F of a set point, minimizing variations in all system temperatures.

The rate at which heat was generated by the crystallization reaction was determined by measuring the rate at which heat was removed from the crystallizer system by the heat exchanger. This rate was calculated by multiplying the cold water addition rate, the heat capacity of the water, and the temperature difference between the cold water addition and hot water discharge streams. The method assumed that the rate of heat added to the coolant by the water circulation pump and the rate at which heat was dissipated by the crystallizer itself were negligible. These assumptions were made because the rate of heat generation by the pump had been previously determined to be negligible compared with reaction heat. Heat loss through the crystallizer suspension chamber and loop walls was minimized by insulation. When reaction heat was measured at ACH production rates of 150 to 450 lb/hr, consistent values were obtained.

Reaction heat was 240 to 280 Btu per pound of ACH produced when $AlCl_3$ solution was sparged from 0 to 26 wt-pct HCl at 140° F. This result agrees well with the value of 270 Btu/lb predicted from the available data. Therefore, 240 to 280 Btu per pound of ACH produced will be the heat load on the crystallizer heat exchanger if HCl gas and $AlCl_3$ feed liquor are added at the reaction temperature. The load can be decreased by adding the reactants at a lower temperature. This could occur if the liquor from evaporative concentration were cooled in storage before being used in crystallization. For example, based on estimated specific heats of HCl gas and $AlCl_3$ liquor, 150 to

190 Btu/lb must be removed from the system if the gas and liquor are added at 80° F instead of 140° F.

Overall heat transfer coefficients were calculated for several periods during run 14 for ACH production rates of 150 to 450 lb/hr. The values obtained for U_o were in the range 420 to 500 Btu/(hr)(ft^2)(° F). The highest coefficients expected in systems with water or aqueous solution on each side of the tubes are 250 to 300, including a fouling factor (15, p. 10-39). Therefore, good efficiency was achieved by the heat exchanger.

During the period of highest ACH production rate in test run 14, a liquor and coolant stream temperature differential (ΔT) of 14 to 16° F was maintained for 2 hours. After the test, crystal deposits were found on sections of the inside walls (mother liquor side) of the heat exchanger tubes, indicating that a ΔT of greater than 14° F cannot be maintained even for a short period of time. Previously in the run, ΔT values of greater than 10° F had been maintained for a total of 10 hours, and greater than 8° F for 19 hours, with no observed effect on heat transfer properties. Based on these results, heat exchanger operation is possible for at least several hours with stream temperature differences as high as 10° F, and the maximum ΔT for which tube fouling will not occur within hours is in the range 10 to 14° F.

During the period of highest ACH production rate, the circulating mother liquor was cooled 1.6° F between the heat exchanger entrance and exit. Although the effect of liquor cooling on heat exchanger performance could not be observed independently of other variables, it is felt that this effect was negligible in view of the much larger coolant/mother liquor stream temperature differential and the fact that ACH solubility changes very little with temperature.

Effect of Noncondensable Component in Hydrogen Chloride Gas Feed

The HCl gas feed was injected into the crystallizer at location 1 (fig. 4) for the first 12 runs. Using this location, any air or other gas present in the HCl that could not be condensed or absorbed in the circulating liquor had to pass through the circulation pump, magnetic flowmeter, and heat exchanger before it could be vented through the suspension chamber.

During run 11, air was added to the HCl gas feed for several periods of time to determine its effect on these components. At a gas flow rate corresponding to ACH production of 150 lb/hr, a volume fraction of 3 pct air was added to the HCl gas feed for 5 hours. The indicated mother liquor circulation rate gradually decreased from 250 to 200 gal/min with a constant setting on the pump drive, and the stream temperature differential ΔT increased 2° F during this time. When the air fraction was increased to 5 pct, the indicated circulation rate decreased to less than 100 gal/min and ΔT increased from approximately 10° F to more than 40° F in 1 hour. An abnormally high ΔT existed for the remainder of the run even after the air addition was stopped. At the end of the test, all inner heat exchanger tube surfaces had a coating of ACH 1/8 to 1/2 inch thick. The indicated decrease in circulation rate was apparently caused by a combination of centrifugal pump efficiency loss due to cavitation and false reading by the magnetic flowmeter due to the presence of air bubbles in the circulating liquor. The increase in ΔT was caused by a decrease in heat transfer capability between the solution and the heat exchanger tubes due to air bubbles and a decrease in circulation rate. The net effect of an air fraction greater than 3 pct in the HCl feed was an unacceptable loss in heat exchanger efficiency.

For test runs 13 and 14, the HCl gas was fed into the system at location 2 (fig. 4) to avoid these problems. In run 14, at ACH production of 150 lb/hr and 250 gal/min circulation rate, a volume fraction of 10 pct air was added for 2 hours. The indicated circulation flow rate decreased 25 to 50 gal/min, showing that some air was being carried back into the loop from the suspension chamber, but sufficient circulation was maintained. No difference in stream temperature differential was detected. When the air fraction was increased to 13 pct, circulation rate decreased to 160 gal/min in 20 minutes, but again no increase in ΔT was observed. Thus, when the HCl gas was injected into the circulation loop downstream from the circulation pump and heat exchanger, the crystallizer could be operated with a greater noncondensable or nonabsorbable gas fraction in the feed than was possible when the gas was injected upstream from those components.

Changing the gas injection location resulted in more effective operation for two additional reasons. Using location 1, the gas was injected into the circulation loop perpendicular to the liquor flow. At high production rates, the circulation piping was subjected to severe vibration caused by cavitation that occurred as the gas was rapidly absorbed by the liquor. Also, large crystal deposits were formed on the pipe wall opposite the injection ports. The deposits blocked a significant fraction of the pipe cross-sectional area and increased the resistance to flow. In location 2, the gas was fed parallel to the liquor flow through a tube that extended to just beyond the venturi throat. The venturi section was added to provide better mixing. Also, the gas was added at a point of lower pressure in the circulation loop, which would decrease vibrations caused by the water hammer effect of HCl bubble collapse. No vibrations in the system occurred even at the highest gas feed rates. Although rapid variations in pressure were observed in the gas feed line at pressures of 1 psig or less, these variations were smoothed out by operating with a slightly increased gas pressure of 3 to 5 psig.

Operating at an ACH production rate of 150 lb/hr and using gas feed location 2 resulted in the formation of a crystal deposit 1/2 inch thick and less around the pipe wall at the point where the venturi section expanded to the full pipe diameter. The deposit did not significantly block the flow of liquor. Operating at higher production rates resulted in a smaller deposit being formed. Injecting the HCl gas feed parallel with, instead of perpendicular to, the liquor flow resulted in more effective crystallizer performance by eliminating vibrations at high gas feed rates and greatly decreasing the size of the crystal deposit formed on the circulation pipe walls near the injection point.

Equipment and Materials Performance

All of the equipment described in the section "Aluminum Miniplant Crystallizer" was used for the entire test campaign, with the following exceptions. Some sections of the circulation loop piping were replaced after 1,212 hours. The zirconium pump drive shaft sleeve was used for the last 1,240 hours of testing. Circulation pump packing was replaced frequently. The HCl gas regulators were also replaced frequently because of unexpectedly high corrosion rates. The centrifuge basket coating was repaired or completely replaced several times when imperfections, undetectable by visual inspection, were detected by spark testing.

The crystallizer and circulation loop rubber lining and zirconium pump shaft sleeve and heat exchanger tubes were intact at the end of the campaign, with the exception of one lining failure that occurred after 1,212 hours of operation. After run 12, a 1-inch long crack was found in the rubber lining of the loop near the entrance to the circulation pump. The crack was directly over a joint in the piping in which the two pipe sections were poorly alined, with an offset of 1/16 to 1/8 inch between the two sections and a corresponding sharp irregularity in the lining material over the joint.

During the test program, the rubber lining became noticeably harder due to continued exposure to heat and mother liquor, although no failures occurred other than the one discussed. To promote extended lifetime for the lining material under the conditions used, it would therefore be desirable to avoid vibration or other movement of the crystallizer and to minimize uneven expansion of steel pipe and rubber liner by maintaining constant system temperature to prevent cracking or separation of the lining.

The zirconium shaft sleeve in the mother liquor circulation pump showed no wear or corrosion at the end of the test series.

All auxiliary equipment performed as expected. However, components such as pump drives and automatic valve activation assemblies that were not expected to contact acid solution did receive exposure to solution spills and acid vapor. It was therefore necessary to provide additional protection for these components.

Environmental Impact of Crystallization Process

An extensive study was made to monitor the environmental consequences of operating the clay-HCl process (14).[6] Analyses were made during the sparging crystallizer test campaign for HCl gas and mist in the plant atmosphere, HCl in the scrubber off gas, and nonvolatile particles in the plant atmosphere.

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[6] Table 10 in this reference, which gives environmental limits for HCl, particulates, and other species, contains at least two errors related to the present study. The Clark County, Nev., limit given for HCl applies to particulates instead, and the units are $\mu g/m^3$, not mg/m^3. Thus, the Clark County limit for exposure to particulates is 150 $\mu g/m^3$ on a 24-hour average and 60 $\mu g/m^3$ on an annual average.

Hydrogen chloride content of plant atmosphere and scrubber off gas compared favorably with the environmental contamination limit given by the Occupational Safety and Health Administration (OSHA) of 10)l/l, or approximately 15 mg/m3, over an 8-hour period. Levels of HCl in plant atmosphere samples taken over periods of several hours were all within the limit. However, samples taken near the mother liquor transport pumps and centrifuge over shorter periods of time when spills occurred in those areas contained up to 30 mg of HCl/m3. Working conditions during these periods also caused irritation to operating personnel. Therefore, the causes of spills and leaks were corrected as quickly as they became evident. Scrubber off gas samples contained less than the OSHA limit for HCl when the scrubber was operating properly.

Physical activities during the miniplant crystallizer operation did not generate enough atmospheric dust to create a health hazard. A sample station for measuring the concentration of particulates in the plant atmosphere was operated during the crystallizer test runs. The average concentration of particulates in the samples was 45)g/m3, which is less than the standard of 60)g/m3 that has been established by the Clark County (Nev.) Board of Health.

CONCLUSIONS

The extensive and successful results of the miniplant HCl gas sparging crystallization test program are summarized and concluded as follws. The conclusions also form the basis for recommending engineering design parameters for an industrial crystallization system utilizing the HCl gas sparging of $AlCl_3$ feed liquor in the clay-HCl process flowsheet:

1. The relationship between impurity concentrations in the $AlCl_3 \cdot 6H_2O$ product and the aluminum chloride feed liquor was identical for laboratory and miniplant tests. Therefore, the results of laboratory-scale crystallization studies can be used to predict the behavior of impurity species in large-scale operations.

2. Impurity concentrations in the $AlCl_3 \cdot 6H_2O$ crystal product were independent of both production rate and stage of sparging in the miniplant crystallizer. Similarly, no difference in crystallizer operation or product quality was observed between synthetic feed solution and actual miniplant leach liquor feed derived from calcine kaolin.

3. It was not possible to meet phosphorus and magnesium impurity specifications by a single crystallization, even when using a first leaching cycle feed liquor. An additional purification step (recrystallization) was necessary to decrease these elements to acceptable levels.

4. A product crystal size distribution of more than 80 pct plus 100 mesh and 65 pct plus 65 mesh was maintained at a sustained maximum crystallizer production rate of 10 lb/(hr)(ft^3) under the following conditions:

Temperature	140° F
HCl concentration in mother liquor	26 wt-pct
Solids fraction in suspension chamber slurry	35 wt-pct
Upward liquor velocity in suspension chamber	55 gal/(min)(ft^2)
Supersaturation in circulation loop	30 lb of $AlCl_3 \cdot 6H_2O$ per 1,000 gal (0.42 pct)

Crystal size distribution was relatively independent of the location of the HCl sparging gas inlet and first-, second-, or full-stage sparging.

5. No differences in crystallizer operation were observed between first, second, and full stage sparging. In full-stage sparging at 35 pct solids, some mother liquor must be returned to the crystallizer after separation from the product to maintain the liquor level in the crystallizer.

6. Mother liquor circulation rates used in the test series gave complete fluidization of the crystals in the suspension chamber with no classification. The solids fraction in the circulation loop was essentially the same as that in the chamber.

7. Heat liberated per pound of $AlCl_3 \cdot 6H_2O$ produced ranged from 240 to 280 Btu when the feed liquor was sparged from 0 to 26 wt-pct HCl at 140° F. This agrees with a calculated value of 270 Btu/lb. The heat may be decreased to approximately 170 Btu/lb by adding both the crystallizer feed liquor and HCl sparging gas at 80° F.

8. The overall heat transfer coefficient for the zirconium tube heat exchanger in an unfouled condition was 420 to 500 Btu/(hr)(ft^2)(° F). However, tube fouling with an $AlCl_3 \cdot 6H_2O$ film or crust occurred in a short period of time when the temperature differential between the heat exchanger liquor and coolant stream exceeded a range of 10° to 14° F. A design of 10° F maximum should provide satisfactory service.

9. The addition of HCl gas (especially at high rates) parallel with, instead of perpendicular to, the liquor flow and at a point of lower pressure downstream from the circulation pump in the crystallizer circulation loop, eliminated severe hammering and decreased the rate of crystalline scale deposits on pipe wall surfaces. The addition of an HCl-air mixture containing up to 10 vol-pct air could be tolerated under these conditions.

10. The natural rubber lining in the suspension chamber and circulation loop was hardened by 1,392 hours of exposure to HCl/$AlCl_3$ solution at 140° F, but remained intact. The zirconium heat exchanger tubes and circulation pump shaft sleeve were intact at the end of the test program. The heat exchanger tubes were removed for closer inspection and showed microscopic pits.

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