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EVAPORATIVE CRYSTALLIZATION OF ALUMINUM CHLORIDE HEXAHYDRATE

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

C	centigrade	kg/h	kilogram per hour
cm	centimeter	L	liter
g	gram	min	minute
h	hour	mL	milliliter
in	inch	mm	millimeter
kg	kilogram	pct	weight-percent
kg/cycle	kilogram per cycle	s	second

EVAPORATIVE CRYSTALLIZATION OF ALUMINUM CHLORIDE HEXAHYDRATE

By F. H. Nehl[1] and L. J. Nicks[1]

ABSTRACT

As part of a U.S. Bureau of Mines research program to study processes for extraction of alumina from domestic resources, a bench-scale evaporative crystallizer was operated with solutions of impure aluminum chloride hexahydrate (ACH). The purpose of the research was to determine the distribution of impurities in the bleedstream section of a proposed clay-Hcl process. Impurities including Mg, P, Na, K, Cr, and S were determined in ACH crystals produced from feed solutions with a threefold range of impurities and at varied crystallizer slurry percent solids. Phosphorus was the limiting contaminant; 0.83 pct of the process alumina would have to be discarded for control. Crystallizer slurry in the range of 10 to 25 pct solids had little effect on crystal purity.

INTRODUCTION

The United States produces about 30 pct of the world's annual output of primary aluminum, but imports more than 90 pct of its bauxite and alumina requirements used to make the aluminum. Bauxite is the principal aluminum ore and is treated by the Bayer process to produce the pure aluminum oxide needed for electrolytic aluminum smelting.

Domestic bauxite reserves are small, but the United States has very large deposits of aluminum-rich minerals that can be used as sources of alumina. Clays and anorthosite each contain about 28 pct Al_2O_3 and constitute an identified domestic resource of more than 155 billion tons of Al_2O_3 (1).[2] The problem with these and other potential non-bauxitic aluminum resources is that they cannot be treated by conventional Bayer processes because of high silica content.

The Bureau of Mines has examined a number of aluminous materials and extraction processes for technical and economic feasibility (2). A major research program compared six acid processes for recovery of alumina from kaolin clay (3). A HCl-based process including HCl gas-induced crystallization of aluminum chloride was judged best and a preliminary design was completed for a 25 ton per day pilot plant (4-5). A block diagram of the process is given in figure 1.

The preliminary design indicated several areas lacking experimental data for a final pilot plant design. One area is bleedstream treatment. The bleedstream has two major functions. The first is rejection of excess water which is introduced in the system, mostly as wash water for filtration. Secondly, the soluble impurities leached with aluminum from the clay must be controlled at an acceptable level by bleeding them from the system.

The bleedstream treatment section (fig. 4) must recover most of the contained chloride for recycle, minimize loss of extracted aluminum, and make the impurity-containing waste stable and innocuous.

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

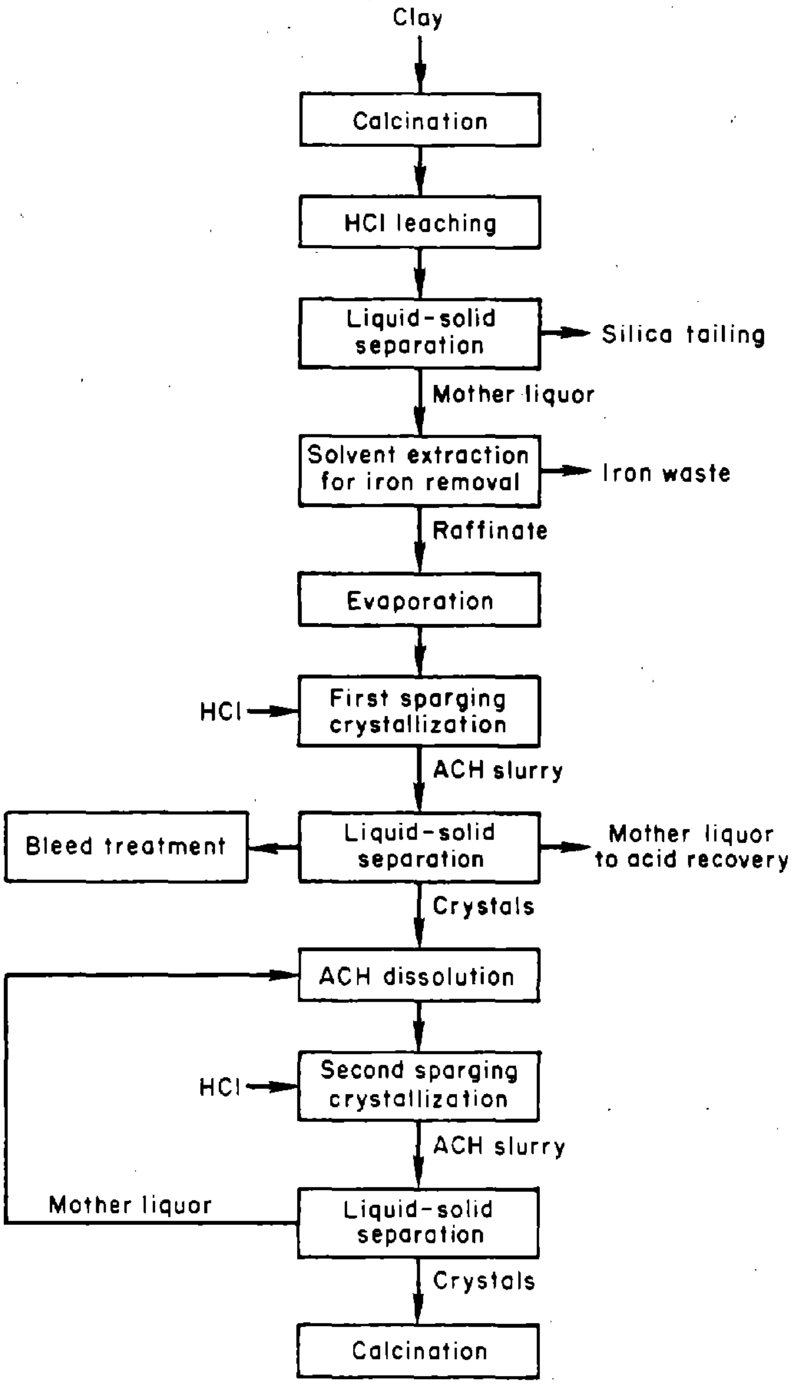

Figure 1.--Simplified proposed alumina-from-clay process.

The bleedstream contains approximately 29 pct HCl, 7.5 pct aluminum chloride hexahydrate (ACH) and less than 0.5 pct total dissolved impurities, primarily Mg, K, S, Na, Ca, and P. The HCl is removed in a stripper operation which is a distillation unit into which solid ACH is introduced to displace HCl from solution. The almost pure HCl overhead vapor is returned to the process. The bottom stream, which is almost HCl free and saturated with ACH, is evaporatively crystallized. Water rejection takes place here and the crystals produced are split into three fractions. The most pure ACH is returned to the process mainstream, a second fraction enters a closed loop with the HCl stripper, and the most impure fraction is calcined to recover HCl and generate a stable solid for disposal. This report describes a study of the evaporative segment of bleedstream treatment.

MATERIALS AND EQUIPMENT

A semicontinuous crystallizer was constructed of standard-taper 24/40 glassware (fig. 2). The crystallizer body, heated with an electric mantle, was a 0.5 L, three-necked round bottom flask. The center neck of the flask was fitted with a ground glass swivel joint lubricated with mineral oil. A glass stirring shaft, equipped with a Teflon[3] paddle, passed through this joint. The shaft was turned by a variable speed dc motor coupled to the glass shaft with a resilient coupling and permitted some misalignment.

One side neck of the crystallizer body was equipped with an adjustable-height dip tube, and fitted with an O-ring for vacuum retention. This was also fitted with a vacuum release valve and a 12-in length of capillary tubing. The capillary tubing permitted a continuous, small flow of air through the crystallizer and condenser, minimized condensate holdup in the condenser and served to control the system vacuum.

The third neck of the crystallizer was equipped with a glass "y." One arm of the "y" was connected to a mechanical pressure gauge. The remaining arm of the "y" surrounded the feed tube and was connected to a thermometer and condenser with a glass adapter.

The 30-cm Graham condenser was connected to tap water for cooling. The condenser was attached to the receiver with a 30-cm length of silicone tubing. The tubing was necessary so that the balance on which the receiver was placed could operate normally. The receiver, a 4-L, three-necked round bottom flask, received condensate through the center neck. One of the side necks was connected to a vacuum pump with rubber vacuum tubing. The other neck was sealed. All exposed glass was covered with polypropylene mesh to eliminate the danger of flying glass in the event of an implosion.

The feed reservoir was a 4-L Erlenmeyer flask equipped with a glass dip tube extending to the bottom. Attached to the dip tube was a plastic tube which was connected to the feed flowmeter.

Measurement of the feeding rate was accomplished by using a modified buret as the feed flowmeter. This was a 50-mL buret with the restricting tip removed and teed into the feed line. Both the feed reservoir and the feed flowmeter were at atmospheric pressure. The feed line was connected to a flowmeter and to a 50-mL vacuum flask which served as a settling vessel to remove crystalline particles in the feed. From the settling vessel, the feed was metered through a Teflon needle valve and into the crystallizer.

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

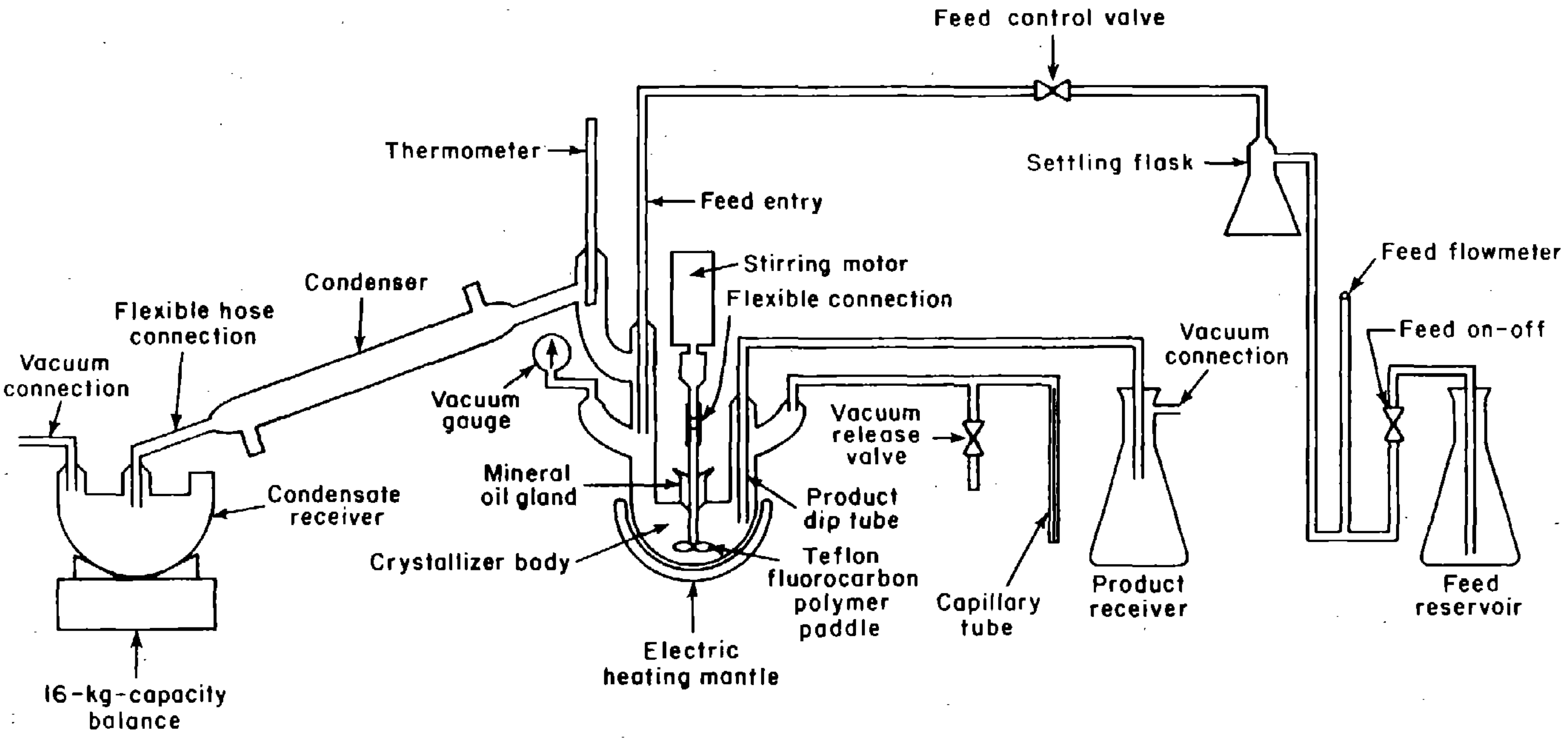

Figure 2.--Diagram of the experimental apparatus.

Product withdrawal was done with the crystallizer dip tube. The tube was connected to a vacuum flask with flexible plastic tubing. The vacuum flask was connected to a vacuum with a three-way valve. The valve would permit either vacuum or atmospheric pressure to be introduced into the product receiver.

Temperatures were measured at the vapor entrance to the condenser with a standard mercury-in-glass thermometer. Stirring rate was unchanged in all experiments.

FEED SYNTHESIS

Since a continuous aluminum-from-clay pilot plant has not been run, one simulation was performed to obtain typical stream analyses (6). Eisele repeatedly leached batches of clay with recycled leaching liquor. Each time the liquor was recycled, a complete analysis was made. These analyses were used to determine the composition of liquor which had been used to leach clay 5 times (5 cycle), 10 times (10 cycle), and 20 times (20 cycle). The feed solutions were made up with technical grade ACH, distilled water and, usually, the chloride salts of the impurities. Elements added as chloride salts were Al, Na, K, Ca, Mg, Mn, Cu, Ni, and Pb. Fluoride was added as NaF, Cr as $K_2Cr_2O_3$, P as H_3PO_4, and S as H_2SO_4.

OPERATION

For each experiment, 10,000 g of feed solution was prepared. One-half the prepared feed was placed in the feed reservoir, stirring was started, vacuum was adjusted to 100 mm Hg, and heating was begun. When vapor, which occurred at a temperature of about 50° C, began entering the condenser, feeding was begun. Product withdrawal was a batch operation. When the slurry level had risen 1 cm from its initial level of 4 cm, product was removed until the slurry level was decreased to 4 cm. This required 20 to 30 s every 15 to 20 min. Feed rate was determined by closing the line from the feed reservoir to the feed flowmeter and measuring the rate of decrease of the liquid in the feed flowmeter.

Condensate flow rate was measured by monitoring the weight of the condensate receiver when condensate flow was steady and between product withdrawals. Product was withdrawn by applying a vacuum to the product receiver and permitting air into the crystallizer body. The product was blown from the crystallizer body into the product receiver.

After 3 L of feed passed through the crystallizer to achieve steady state, the crystallizer was run until at least six samples of product slurry were obtained, this taking 1.5 to 2 h.

Experiments were performed with three different feed solutions, 5, 10, and 20 cycle. Each feed was used in two experiments at different slurry solids which were typically 13 and 25 pct. Slurry solids were varied by changing the feeding rate or the heating rate. Conditions for each experiment are summarized in table 1.

Table 1.--Typical experimental conditions, 21-in Hg vacuum, 49° to 52° C

Experiment	Feed rate, mL/h	Condensate rate, g/h	Slurry solids, pct	Feed cycle
1	404	85.9	25.0	5
2	363	42.9	13.3	5
3	439	93.5	25.5	10
4	378	50.0	13.8	10
5	430	34.2	9.7	20
6	428	93.3	25.4	20

EXPERIMENTAL RESULTS

Table 2 shows that evaporative crystallization did not approach sparging crystallization in purity of crystals produced. Evaporative crystals were more impure than those produced by sparging.

Data from the solutions used (table 3) show that feed composition for both sparging and evaporative crystallizers are comparable, but not identical. The difference in the mother liquor compositions (table 4) occurs because a sparging crystallizer does not decrease the volume of the feed liquor as an evaporative crystallizer does. Liquor impurities are concentrated in evaporative crystallization.

Although the crystallizer was operated at two different slurry solids for each feed, the slurry solids could not be varied independently of the evaporation rate. An upper limit on slurry solids was set at 26 pct because greater slurry solid caused problems with stirring and product withdrawal. Mother liquor composition determined crystal purity and phosphorus and magnesium were the most troublesome contaminants.

DISCUSSION

Evaporative crystals are not as pure as those produced by sparging, but a better comparison can be made with a separation factor, which is the ratio $C_M:C_C$, where C_M is the concentration of the impurity in the mother liquor and C_c is the concentration of the same impurity in the crystal. Table 5 lists these ratios for five elements and compares them with those obtained in a sparging crystallization (7). Examination of table 5 indicates that sparging and evaporative crystallization have about the same crystal purification performance.

The crystals produced by the first bleedstream crystallizer will be returned to the evaporator (fig. 1) and need not be of product-level purity. The bleedstream crystallizer must control the impurity level in the main stream by removing as much impurity as is introduced with each leaching cycle.

After the first crystallization, the mother liquor is separated from the crystals. About 35 pct of the mother liquor, which carries 35 pct of the dissolved impurities, is routed to the bleedstream (fig. 3). The remainder of the mother liquor, which is diluted with wash from the second sparging crystallizer, is pumped to the acid recovery section. Of the 4,582 kg water entering liquid-solid separation from the crystallizer and 2,135 kg water entering liquid-solid separation in the wash stream, 1,581 kg water is sent to the bleedstream, or 25 pct of the free water. This would correspond to a cycle 4 leach. Since the mother liquor has a high acid content (20 pct), very little ACH is left in solution. Thus, although 35 pct of the mother liquor is sent to bleedstream, only 2.3 pct of the available ACH reports to bleedstream (4).

Table 2.--Comparison of sparged and evaporative crystals, percent

Experiment	Crystallizing process, solid content, pct	Feed cycle	MgO	P_2O_5	Na_2O	K_2O	Cr_2O_3	SO_4
1	Evap., 25.0	5	0.0028	0.0025	0.0008	<0.0023	0.0007	-
2	Evap., 13.3	5	.0025	.0023	.0012	<.0024	.0010	-
3	Sparge	5	.0019	.0031	.0008	.0005	.0006	<0.01
4	Evap., 25.5	10	.0066	.0037	<.0007	.0053	.0020	-
5	Evap., 13.8	10	.0048	.0046	<.0013	.0053	.0020	-
6	Sparge	10	.0010	.0012	.0006	.0018	<.0003	.010
7	Evap., 9.7	20	.0073	.0056	<.0007	.0067	.0017	-
8	Evap., 25.4	20	.0094	.0058	<.0007	.0090	.0020	-
9	Sparge	20	.0031	.0030	.0006	.0005	.0006	.004

Table 3.--Typical feed composition, percent

Experiment	Cycle	System	MgO	P_2O_5	Na_2O	K_2O	Cr_2O_3
1	5	Evap.	0.078	0.062	0.046	0.059	0.012
2	5	Sparge[1]	.082	.074	.039	.072	.010
3	10	Evap.	.138	.090	.080	.116	.028
4	10	Sparge	.130	.098	.053	.100	.016
5	20	Evap.	.227	.130	.097	.188	.027
6	20	Sparge	.210	.120	.096	.170	.025

[1] Sparging data from ref. 7.

Table 4.--Mother liquor composition, percent

Experiment	Cycle	System, pct	MgO	P_2O_5	Na_2O	K_2O	CrO_3
1	5	Evap., 25	0.102	0.094	0.061	0.071	0.016
2	5	Evap., 13.3	.092	.076	.056	.067	.014
3	5	Sparge[1]	.082	.074	.039	.027	.010
4	10	Evap., 25.5	.213	.130	.126	.190	.041
5	10	Evap., 13.8	.177	.110	.102	.152	.033
6	10	Sparge	.160	.121	.063	.130	.020
7	20	Evap., 25.4	.342	.200	.148	.283	.040
8	20	Evap., 9.7	.270	.150	.112	.224	.031
9	20	Sparge	.270	.160	.120	.230	.033

[1] Sparging data from ref. 7.

Table 5.--Composition of separative factors, C_M/C_C

Experiment	Cycle	System, pct	MgO	P_2O_5	Na_2O	K_2O	CrO_3
1	5	Evap., 25	36	38	77	>31	22
2	5	Evap., 13.3	37	33	46	>28	14
3	5	Sparge[1]	43	24	49	144	17
4	10	Evap., 25.5	32	35	180	36	21
5	10	Evap., 13.8	37	24	>78	29	17
6	10	Sparge	160	101	105	72	>67
7	20	Evap., 25.4	36	34	>211	31	20
8	20	Evap., 9.7	37	27	>160	33	18
9	20	Sparge	87	53	200	204	55

[1] Sparging data from ref. 7.

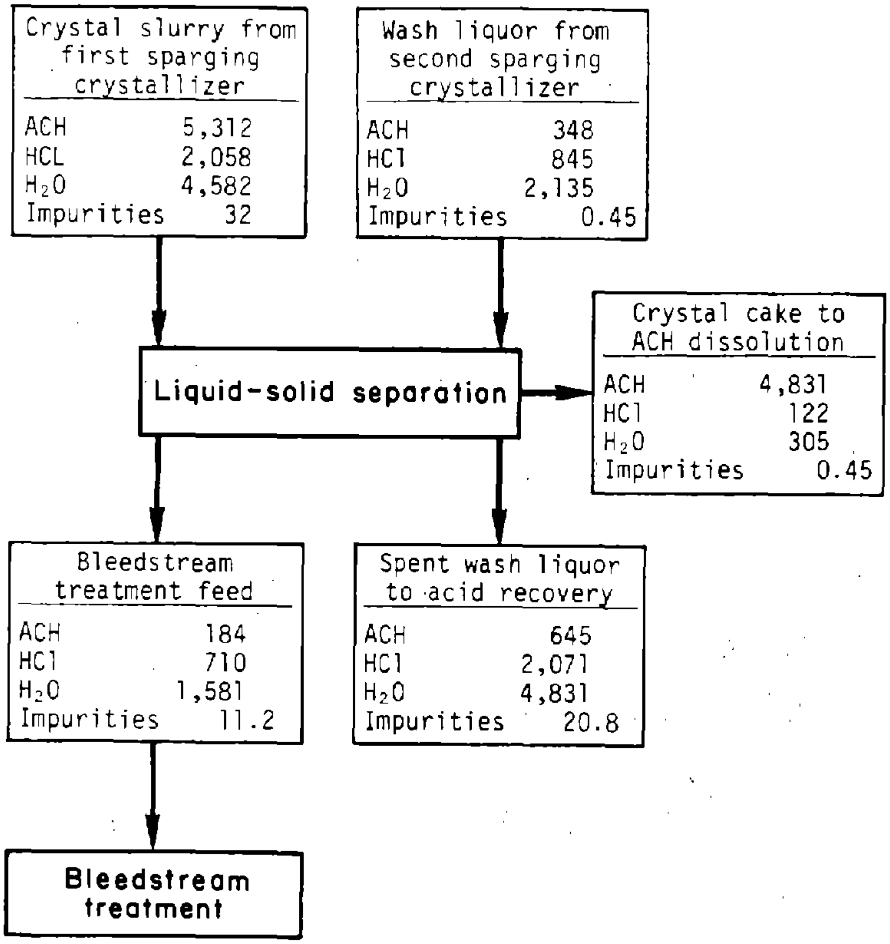

Figure 3.--Detailed balance around first liquid-solid separation.

Since 35 pct of the available impurities report to the bleedstream, and the mainstream is a cycle 4 leach with the expected impurity levels in a cycle 4 leach (table 6) bleedstream crystallizer performance can be calculated when separation factors (table 5) are determined for each impurity.

When the bleed stream enters the bleed section, it contains 29 pct HCl. This HCl will be recovered before crystallization by using an HCl stripper (fig. 4). Operation of the stripper will be countercurrent, with the bleedstream entering the top and contacting ACH introduced in the bottom, as in the ACH dissolver. HCl is displaced by ACH and a solution saturated in ACH and containing less than 0.5 pct HCl is obtained. Since a solution saturated in ACH with little HCl present contains approximately 45 pct free water, the final solution sent to the first bleedstream crystallizer has a total mass of 3,513 kg.

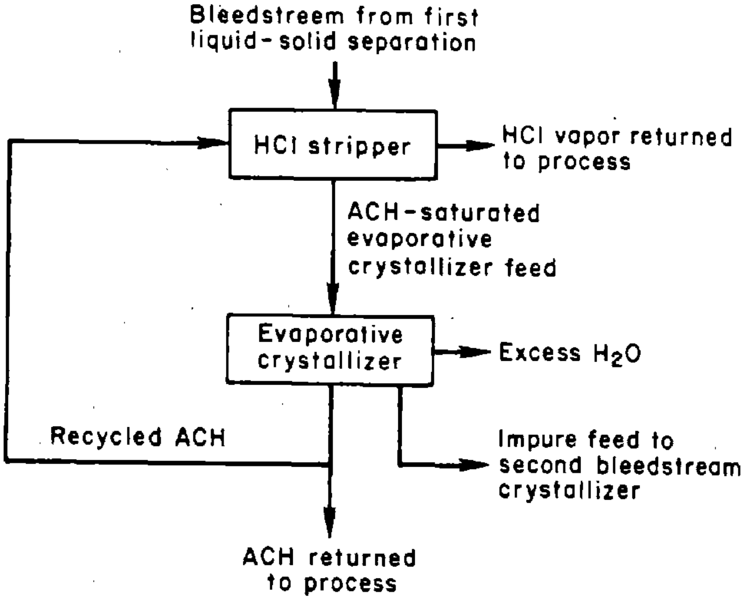

Figure 4.--Outline of bleedstream treatment.

Table 6.--Impurities in feeds sparged to 26 pct[1]

Impurity[2]	HCl, pct	Cycle									
		1	2	3	4	5	6	7	8	9	10
Na_2O	26	0.006	0.009	0.012	0.016	0.020	0.025	0.030	0.034	0.037	0.042
K_2O	26	.014	.021	.033	.037	.043	.053	.054	.063	.073	.074
CaO	26	.011	.016	.019	.026	.032	.040	.042	.048	.058	.057
MgO	26	.021	.026	.036	.044	.055	.068	.077	.085	.10	.10
P_2O_5	26	.018	.026	.034	.040	.048	.059	.061	.067	.076	.077
NiO	26	.002	.003	.004	.005	.002	.008	.008	.010	.011	.007
PbO	26	.001	.002	.003	.003	.001	.005	.006	.006	.004	.005
Cr_2O_3	26	.003	.005	.006	.007	.010	.012	.012	.016	.018	.017
CuO	26	.0004	.0003	.0004	.0005	.0008	.0006	.0008	.0010	.0013	.0006
MnO	26	.001	.002	.003	.003	.001	.005	.005	.006	.007	.004
F	26	.001	N	N	N	.002	N	N	N	N	.03
SO_4	26	.03	N	N	N	.11	N	N	N	N	.18

N Not analyzed.

[1] Corrected to 30.0 pct $AlCl_3$ basis, adapted from ref. 6.

[2] Fe_2O_3 was <0.002 pct for all cycles.

The weight faction of any impurity in solution and in the crystals in the crystallizer can be computed. If

Wi = total weight of impurity in solution
T = total weight of solution entering system
H = weight of water evaporated
A = weight ACH crystallized
W_c = weight-fraction impurity in the crystal
S = average separation factor (table 5).The weight fraction W_f of any impurity in solution can be calculated.

$$W_f = \frac{Wi}{T - H - A} \tag{1}$$

Since, for saturated feed to a crystallizer, any unit weight of water evaporated will crystallize 1.2 units of ACH, equation 1 can be simplified to:

$$W_f = \frac{Wi}{T - 2.2H} \tag{2}$$

To calculate the weight-fraction in the crystal, W_c, the weight fraction in the solution is divided by the separation factor, S.

$$\frac{W_f}{S} = \frac{Wi}{(T - 2.2H)S} = W_c \tag{3}$$

To obtain the total weight of an impurity (W_t) contained in the crystal, the weight-fraction must be multiplied by the weight of the crystals formed and since 1.2H = A, equation 3 becomes:

$$W_f = \frac{Wi\ 1.2H}{(T - 2.2H)S} \tag{4}$$

Solving for H:

$$W_f = \frac{W_tST}{1.2W_i + 2.2(W_t)S} \tag{5}$$

Equation 5 can be used to calculate how far crystallization producing crystals pure enough to be returned to the mainstream ACH treatment can proceed in the first-stage bleedstream crystallizer.

Since phosphorus and magnesium are the most troublesome contaminants, a sample calculation for phosphorus is presented.

With a 25-pct (4 cycle) water bleed, phosphorus in the mainstream would be 0.04 pct (table 6). At the projected first sparging crystallizer feed rate, 9,850 kg/h, the circulating load of P_2O_5 would be 3.94 kg. With the impurity bleed rate at 35 pct, 1.38 kg P_2O_5 would go into the bleedstream treatment. Using data from Eisele (5), the expected increase in P_2O_5 with each cycle is 0.007 pct of 0.69 kg/cycle.

Using equation 5 and setting W_t = 0.69, S = 32 (average separation factor for phosphorus, table 5), T = 3,513, Wi = 1.38, H is calculated to be 1,544 kg. If 1,544 kg of H_2O is evaporated, 1,887 kg of ACH will be crystallized. Since the solution is 55 pct ACH, 45 kg of ACH is routed to disposal. The 45 kg represents 0.83 pct of the ACH entering the first sparging crystallizer.

Calculations with other impurities can be performed, but phosphorus is the limiting impurity and requires the largest bleedstream. Magnesium, sodium, chromium, and potassium would require smaller bleedstreams than is required for phosphorus.

The above analysis indicates that the first bleedstream crystallizer could remove 1,544 kg of the entering 1,581 kg of water, or 98 pct of the available water and produce crystals pure enough to return to the mainstream. The remaining 2 pct could be sent to a second crystallizer for further water removal and subsequent calcination for disposal.

SUMMARY AND CONCLUSIONS

The first bleedstream crystallizer in the proposed alumina-from-clay process can remove 98 pct of the water from the entering bleedstream and produce ACH crystals pure enough for return to the ACH mainstream. This can be done while still controlling impurity buildup in the main stream. Phosphorus is the limiting contaminant which controls operation of the crystallizer. Slurry solids greater than 26 pct were difficult to process in the experimental crystallizer.

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