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Utilization of Waste Fluosilicic Acid

(In Two Sections)

1. Laboratory Investigations

2. Cost Evaluation

UNITED STATES DEPARTMENT OF THE INTERIOR

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By H. E. Blake, Jr., W. S. Thomas, K. W. Moser,
J. L. Reuss, and H. Dolezal

UNITED STATES DEPARTMENT OF THE INTERIOR
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UTILIZATION OF WASTE FLUOSILICIC ACID

(In Two Sections)

1. Laboratory Investigations

by

H. E. Blake, Jr.,[1] W. S. Thomas,[2] and K. W. Moser[3]

ABSTRACT

This report describes two processes for utilizing the waste fluosilicic acid (H_2SiF_6) generated by the manufacture of phosphatic fertilizers. The first process involves conversion of fluosilicic acid to an acid-grade fluorspar (CaF_2) by first precipitating the silica with ammonia and filtering, and then reacting the ammonium fluoride (NH_4F) filtrate with $Ca(OH)_2$. Over 95 percent of the fluoride is converted to CaF_2. The second process involves neutralizing the H_2SiF_6 with $Ca(OH)_2$ and silica and filtering and then volatilizing HF from the dry precipitate by pyrohydrolytic action at 1,050° C. The HF-H_2O vapors are condensed and the fluoride precipitated as NaF·HF by addition of NaF to saturation. Anhydrous HF is recovered from NaF·HF by pyrolysis at 400° C. By this method, over 80 percent of the fluoride in H_2SiF_6 is recovered as anhydrous HF. A cost evaluation of the two processes is included in Section 2 of this report.

Preliminary tests on the synthesis of cell-grade aluminum fluoride (AlF_3) from the rotary reactor offgases and activated alumina showed that an 82-percent AlF_3 product could be produced.

INTRODUCTION

This Bureau of Mines research was initiated to develop methods for the economic recovery of suitable fluorine compounds from waste fluosilicic acid.

Recent data show that of the nearly 700,000 tons of CaF_2 used annually in this country only about 200,000 tons are produced by U.S. mines. Other data estimate that the quantity of fluorine discarded or lost during the processing of phosphate rock approximates the annual fluorspar imports into the United States, and further, that the total fluorine contained in all the U.S. reserves of phosphate rock is equivalent to about 900 million tons of

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[1] Physical science technician.
[2] Chemist.
[3] Chemical engineering technician.
All authors are with the Albany Metallurgy Research Center, Bureau of Mines, Albany, Oreg.

fluorspar (1-8).[4] Improved methods of recovery and conversion of this fluorine resource into marketable fluorides could serve to lessen the country's dependence on foreign imports of fluorspar as well as reduce the cost of processing domestic phosphate rock.

Fluosilicic acid is formed when fluorine-bearing phosphate rock is treated by either a thermal or acid process, the fluorine being evolved as silicon tetrafluoride (SiF_4) (9). Nearly all phosphate rock contains 3 to 5 percent fluorine, which is present as the mineral fluorapatite ($Ca_3(PO_4)_3F$). Most phosphate rock processors collect the volatilized SiF_4 in scrubbing towers to prevent serious air pollution problems. The SiF_4 represents a potentially large fluorine resource as it hydrolyzes in the scrubbers according to the equation:

$$3\ SiF_4 + 2\ H_2O \longrightarrow SiO_2 + 2\ H_2SiF_6$$

These scrubber solutions have a concentration of from 18 to 24 percent H_2SiF_6 after separation of excess silica (SiO_2). Most of this H_2SiF_6 is neutralized with lime and discarded into storage ponds to prevent pollution of local water sources. A small amount is used in fluoridation of municipal water supplies but this is a limited market.

The difficulty in separating the fluorine from silicon has been the major obstacle to using H_2SiF_6 as a principal source of fluorine or other fluoride salts. A recent patent (3) describes a process for producing cryolite (Na_3AlF_6) from H_2SiF_6. In this process, the silicon is precipitated with sodium carbonate, and the resultant sodium fluoride (NaF) solution is reacted with sodium aluminate ($NaAlO_2$) to form cryolite. In another process, an Austrian firm has produced aluminum fluoride (AlF_3) using H_2SiF_6 as a source of fluoride (10). Previous investigations by the Bureau of Mines have included studies on defluorination of phosphate rock by pyrohydrolysis (5), recovery of cryolite from silicious fluoride offgases (4), preparation of aluminum fluoride from dilute fluoride solution and alumina hydrate (2), and the separation of HF from $HF\text{-}SiF_4\text{-}H_2O$ mixtures (7).

ACID-GRADE CaF_2 FROM WASTE H_2SiF_6

The process for making acid-grade CaF_2 (at least 97.5 percent CaF_2) from waste H_2SiF_6 is based principally on two simple operations, (1) removing the silica and other occluded impurities by precipitation with ammonia and, (2) reacting the NH_4F filtrate with lime to form CaF_2 accompanied by the evolution of ammonia, which is available for recycle to the silica precipitation stage. The overall process can be represented by the following sequence of reactions:

$$(1)\quad H_2SiF_6 + 6\ NH_3 + 2\ H_2O \xrightarrow{\text{pH } 9} 6\ NH_4F + SiO_2\downarrow$$

$$(2)\quad 6\ NH_4F + 3\ Ca(OH)_2 + 3\ H_2O \longrightarrow 3\ CaF_2\downarrow + 9\ H_2O + 6\ NH_3\uparrow$$

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

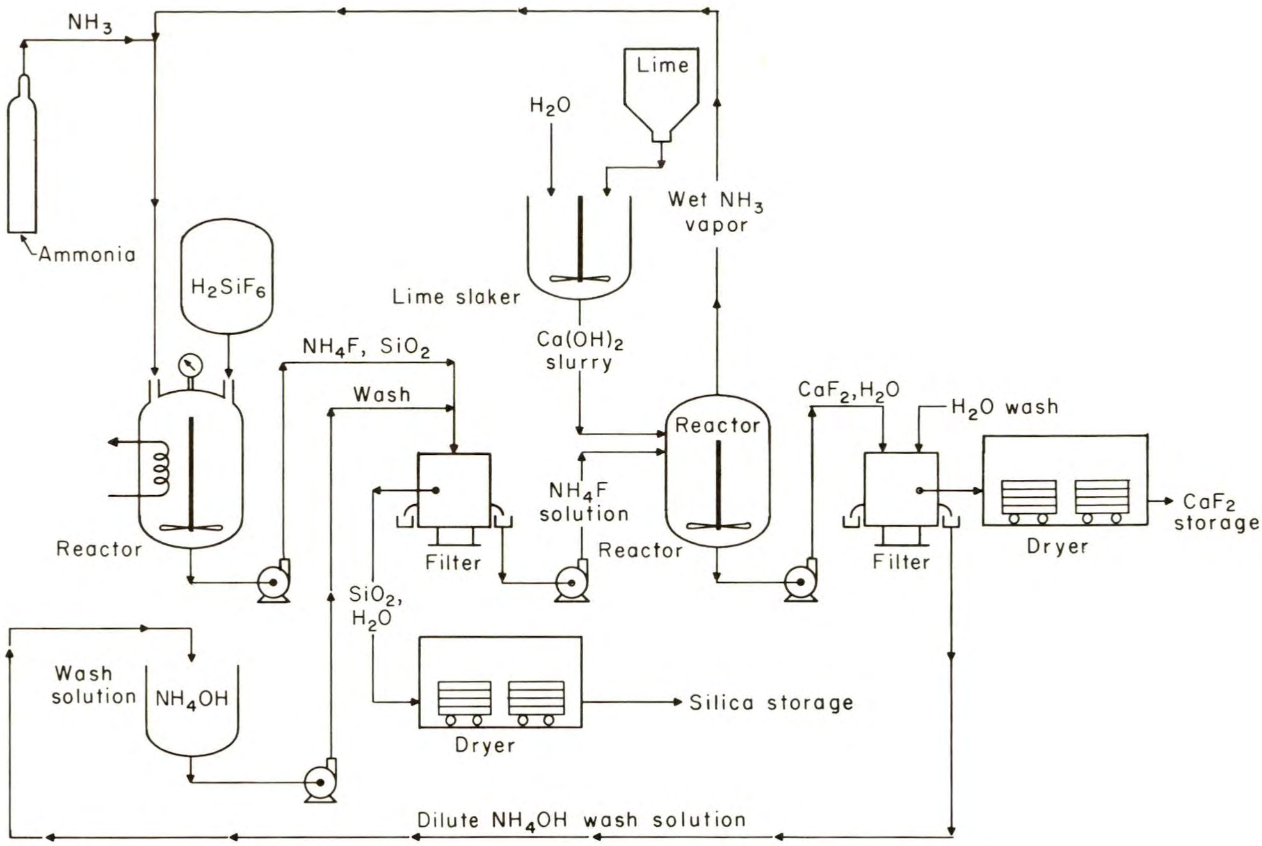

FIGURE 1. - Preparation of Acid-Grade Fluorspar.

The fluosilicic acid used in this study was a crude product that had the following composition in grams per liter: 261 F, 66.5 Si, 4.5 P, 5.9 Ca, 1.11 SO_4, 0.25 Fe, and 0.1 Al. The calcium hydroxide ($Ca(OH)_2$) used was of high purity containing less than 0.5 percent SiO_2 and MgO. Anhydrous ammonia gas was the neutralizing agent.

A schematic flowsheet is presented in figure 1.

Precipitation of Silica by Ammoniation

Ammoniation of the H_2SiF_6 to precipitate SiO_2 was done in a 6-liter-capacity stainless steel vessel. This vessel was water cooled and fitted with a pressure-tight cover and a sampling tap near the bottom. The stirring mechanism passed through the center of the cover and was fitted with a teflon bearing and seal. A pressure of about 2 inches of mercury and a temperature of about 40° to 50° C was maintained during ammoniation. The NH_3 was introduced near the bottom of the vessel while the H_2SiF_6 solution was continually being stirred. The NH_3 inlet was fitted with a valve so that air could be added as a dilutent at the beginning of the neutralization until a pH of about 6 was reached and the heat of reaction had subsided; the air was turned off and neutralization completed with anhydrous NH_3 to pH of about 9.0. The cover of the vessel was also fitted with a vent to a water scrubber that trapped any unreacted NH_3. Experimental data (table 1) showed that a pH of about 9 was necessary to precipitate all the silica and to form an easily filtered and washed precipitate. A suitable ammonia addition rate was about 45 liters per minute, and about 150 percent of stoichiometric NH_3 was required under these conditions. Washing the precipitated SiO_2 with dilute NH_4OH prevents peptization. Over 99 percent of the silica can be removed and also over 99 percent of the fluoride recovered in the filtrate as NH_4F.

TABLE 1. - Precipitation of SiO_2 by ammoniation

(Feed solution: 100 ml H_2SiF_6; 14.3 grams SiO_2)

pH (±0.2)	SiO_2 precipitated, percent	pH (±0.2)	SiO_2 precipitated, percent
2.0	9.0	7.5	71.0
4.0	12.8	8.0	90.1
4.5	25.8	9.0	99.6
6.0	60.5	9.5	99.4

The dried silica precipitate contains nearly all the calcium and phosphorus that was in the crude H_2SiF_6. If this contaminant can be tolerated, then the dried SiO_2 might be useful as a byproduct for use in the paint, rubber, or ceramic industries. Table 2 gives the typical analyses of wet silica filter cakes from several NH_3 neutralizations of crude and purified H_2SiF_6. Table 3 shows ammonia recovery data.

TABLE 2. - Analyses of SiO_2 filter cakes

Wet filter cake		Analyses after ignition at 1,000° C for 1 hour, percent				
Weight, grams	H_2O, percent	SiO_2	CaO	P_2O_5	Fluorine	NH_3
506[1]	15.5	87.0	5.8	7.0	<0.5	<0.2
511[1]	16.0	87.3	5.5	7.2	<.5	<.2
503[1]	14.8	86.8	5.9	7.1	<.5	<.2
536[2]	20.0	99.1	.3	.4	<.5	<.2
529[2]	19.0	99.0	.2	.5	<.5	<.2
517[2]	17.2	98.8	.3	.3	<.5	<.2

[1] Crude H_2SiF_6 used.
[2] Purified H_2SiF_6 used.

TABLE 3. - Ammonia recovery from ammoniation

(Feed solution: 3,000 ml H_2SiF_6-783 grams fluorine, 199.5 grams silicon)

Maximum temperature, ° C	Final, pH	NH_3 used, grams	NH_3 recovery,[1] grams				Percent accounted for[2]
			Filtrate	Wash 1	Wash 2	Total, grams	
45	9.0	996	792	90.6	20.2	902.8	90.6
51	9.2	1,043	852	75.3	16.1	943.4	90.5
49	9.4	1,065	876	80.4	9.4	965.8	90.7
45	9.0	988	856	73.7	14.3	954.0	96.6
60	9.3	1,013	756	63.6	10.6	830.2	81.9

[1] Wash solution No. 1 contained 10 grams per liter of NH_3 and is included in "NH_3 used" column. Wash solution No. 2 was plain water.
[2] Unaccounted for excess NH_3 was lost during vacuum filtration.

Precipitation of Acid-Grade CaF_2 From NH_4F Solution

When the silica-free NH_4F filtrates from the neutralization step are reacted with $Ca(OH)_2$, NH_3 is evolved and CaF_2 is formed as indicated in the following equation:

$$2\ NH_4F + Ca(OH)_2 + H_2O \longrightarrow CaF_2\downarrow + [2\ NH_3 + 3\ H_2O]\uparrow$$

This reaction was carried out in the stainless steel neutralization vessel at about 70° to 75° C. The $Ca(OH)_2$ was added in the stoichiometric amount as a thick slurry with vigorous stirring to keep the solids in suspension until the reaction was completed in about 15 minutes. The wet ammonia vapors were drawn off by vacuum and vented to a water scrubber. These vapors were calculated to be about 80 percent NH_3 and contained over 65 percent of the NH_3 contained in the NH_4F filtrate from the silica precipitation step. Recycle of the ammonia-rich vapors was not attempted in this investigation, but it is possible and no doubt necessary to do so for economic reasons.

The CaF_2 precipitates were readily filtered and washed. The slurries from the CaF_2 reactor were usually in the range of 15 to 20 percent solids. The filter cakes contained about 20 percent moisture. Analyses of the filter cakes, dried at 150° C for about 2 hours, showed them to be acid-grade CaF_2 (6). Analyses of the CaF_2 product are shown in table 4, and fluorine and NH_3 data for the CaF_2 precipitation step are shown in table 5. An overall fluorine and NH_3 accountability for the whole process is presented in table 6.

TABLE 4. - Chemical analyses of CaF_2 products, analysis, percent

CaF_2	SiO_2	$CaCO_3$	P_2O_5	Silicon	H_2O
97.6	0.68	1.21	<0.1	<0.05	0.31
97.9	.73	1.36	<.1	<.05	.26
98.1	.56	1.06	<.1	<.05	.18
97.6	.66	1.43	<.1	<.05	.33
97.4	.94	1.65	<.1	<.05	.28

TABLE 5. - Fluorine and ammonia recovery from CaF_2 precipitation

NH_4F solution		Dry CaF_2	Fluorine		Ammonia	
NH_3, grams	Fluorine, grams	recovered, grams	Fluorine in CaF_2, grams	Fluorine recovered, percent	NH_3 in solutions, grams[1]	NH_3 evolved, percent[2]
792	701	1,438	684	97.5	271	65.8
852	688	1,410	674	98.0	238	72.1
876	761	1,550	743	97.7	254	71.0
856	723	1,471	701	97.0	257	69.9
756	709	1,439	684	96.5	249	67.0

[1] Total grams of NH_3 recovered in filtrate and three 100-ml washes.
[2] Calculated value from NH_3 in solutions and NH_3 in original NH_4F solution.

TABLE 6. - Fluorine and ammonia accountabilities for acid-grade CaF_2 process

(Feed solution: 3,000 ml H_2SiF_6-783 grams fluorine, 199.5 grams silicon)

Fluorine balance			Ammonia recovery			
Recovered		Total fluorine accounted for, percent[2]	Grams used	NH_3 recovery in scrubber, percent	NH_3 in washes and discard, percent	Total NH_3 recovered, percent[3]
Fluorine in CaF_2, grams	Fluorine in all solutions, grams[1]					
684	79.8	97.4	996	50.5	38.4	88.9
674	86.7	97.3	1,043	56.2	31.5	87.7
743	21.6	97.8	1,065	54.2	32.3	86.5
701	59.3	97.1	988	57.8	34.9	92.7
684	73.5	97.2	1,013	46.7	31.8	78.5

[1] Includes fluorine in combined filtrates and wash solutions from all steps of process.

[2] Difference between "percent fluorine accounted for" and 100 is amount fluorine lost in handling and minor losses in discard solutions.

[3] Difference from 100 percent is amount lost to atmosphere.

The preceding data show that waste fluosilicic acid can be processed to produce an "acid-grade" fluorspar with at least a 97-percent recovery of the contained fluoride and that most of the ammonia reagent required could be recovered for recycle.

ANHYDROUS HF FROM WASTE FLUOSILICIC ACID

The recovery of anhydrous HF from waste fluosilicic acid is more difficult than the conversion of this byproduct to CaF_2. However, a method has been developed that will produce HF meeting commercial specifications (6). The process is based on heating a proportioned charge of SiO_2, CaO, and fluorine to about 1,050° C in the presence of water vapor to liberate fluorine as HF and then condensing the $HF-H_2O$ vapors.

The addition of sodium fluoride (NaF) to the dilute HF solution to saturation results in the formation of the relatively insoluble salt sodium bifluoride (NaF·HF). This compound is easily dissociated at about 400° C to NaF and anhydrous HF. The anhydrous HF is collected and condensed at a temperature of about 10° C.

The following equations indicate the general reactions that govern the process:

Neutralization

$$H_2SiF_6 + 3\,Ca(OH)_2 \longrightarrow 3\,CaF_2 + SiO_2 + 4\,H_2O \qquad (1)$$

plus 2 moles SiO_2

$$3\,CaF_2 + 3\,SiO_2 + 3\,H_2O \xrightarrow[1{,}050^\circ\ C]{\Delta} 3\,CaSiO_3 + 6\,HF \qquad (2)$$

Overall Reaction

$$H_2SiF_6 + 3\ Ca(OH)_2 + 2\ SiO_2 + 2\ H_2O \xrightarrow[1,050^\circ\ C]{\Delta} 3\ CaSiO_{3\,(s)} + [6\ HF + 3\ H_2O]_{(g)}\uparrow \qquad (2a)$$

$$6\ HF_{(aq)} + 6\ NaF_{(aq)} \longrightarrow 6\ [NaF \cdot HF]_{(s)}\downarrow \qquad (3)$$

$$6\ [NaF \cdot HF]_{(s)} \xrightarrow[400^\circ\ C]{\Delta} 6\ NaF_{(s)} + HF_{(g)}\uparrow \qquad (4)$$

Some $NaHF_2$ from reaction 3 remains in solution because of its slight solubility, but this can be scavenged as shown in the following equation:

$$6\ NaHF_2 + [Al_2O_3 \cdot H_2O] \longrightarrow 2\ Na_3AlF_6\downarrow + 4\ H_2O \qquad (5)$$

A schematic flowsheet is presented in figure 2.

Equipment and Apparatus

Because of the corrosive nature of dilute fluoride solutions and vapors, extensive testing was done on a variety of materials under varying conditions of temperatures and concentrations. The materials chosen for this laboratory investigation are not necessarily those that would be available or satisfactory for a large-scale extended operation, but do indicate the type of materials of construction which may be considered.

Nickel and 316-type stainless steel were entirely suitable for the 6-liter mixing vessel and steam generating apparatus. Monel or nickel was used for piping to transfer wet HF vapors at temperatures ranging from just over the dewpoint to about 600° C at the exit end of the rotary kiln used as the defluorination apparatus. Black iron was found to be completely inert to the anhydrous HF; however, type 446 stainless steel (25 percent chromium and 75 percent iron) was relatively stable in contact with dilute HF vapors generated during pyrohydrolysis at an operating temperature of 1,000° to 1,100° C. Thin-walled polyethylene tubing and bottles were used as the integral parts of the vapor-condensing apparatus and were satisfactory for temperatures under 100° C. Compressed asbestos gasket material was used to insure gas-tight connections where needed, and also as a bearing material for moving parts, particularly at the ends of the rotary reactor.

The rotary kiln was an externally heated 446-stainless steel tube 6 feet long with a 4-inch I.D. and 3/8-inch wall. The kiln was fitted inside with four lifters parallel to each other and equidistant around the inside circumference. These lifters aided in tumbling the pelletized feed so that new surfaces were continually exposed to the water vapor flowing countercurrently. The kiln was rotated by an electric motor driving through a 100-to-1 transmission and a chain and sprocket. A sprocket was welded to the kiln and also served as a flat-bearing surface fitted to the hand-feeder. The opposite end also had a stainless steel flange that fitted tightly against the steam generator. These surfaces were covered with compressed gasket material and made a gas-tight seal when the kiln expanded because of heating. The kiln was sloped about 1/4 inch per linear foot away from the feed end. A 1-inch I.D. Monel pipe was inserted in the center and about half the length into the kiln to serve as an exit for the vapors, which were removed by vacuum through a water-cooled scrubbing system. The kiln itself was heated by mounting it in two electric tube furnaces 3 feet long placed end to end. Temperatures were monitored by thermocouples and pyrometers mounted at strategic points.

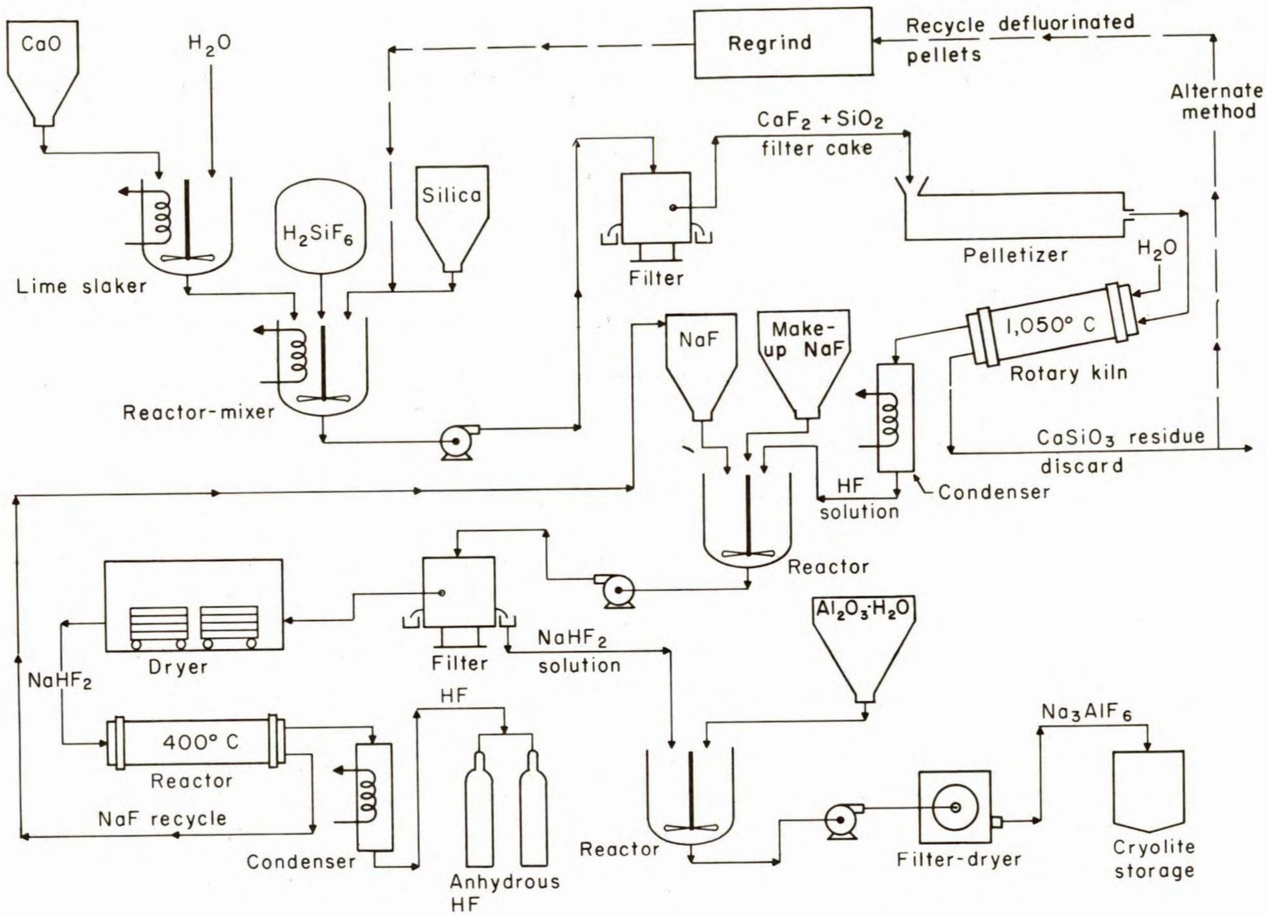

FIGURE 2. - Preparation of Anhydrous HF.

Steam was generated inside an externally heated copper or stainless steel tube into which was delivered the metered amount of water required for reaction. The amount of water needed was determined by experiment to be on the average about 1.2 grams per gram of feed material. The HF-H_2O vapors were drawn into the water-cooled condenser-scrubber by vacuum supplied by water aspiration. All sections of the entire apparatus were adjustable to accommodate sudden expansion or contraction due to changes in temperature.

The 400° C $NaHF_2$ dissociation reactor was a 2-inch-I.D. black iron pipe mounted in a tube furnace; the entrance end was capped after loading the charge of bifluoride. Exit vapors were passed through a chilled copper coil that led to a steel pressure cylinder that was also chilled in a dry ice-acetone bath. The pressure cylinder was designed so that it could be closed off and removed for weighing.

The complete apparatus was mounted on slotted-angle steel frames for strong support and easy access to parts that might need adjustment or repair.

Charge Preparation and Defluorination

Experiments had shown that a pH of at least 9.0 to 9.5 was necessary to completely precipitate all the SiO_2 and fluorine from H_2SiF_6 (table 7). Other experiments confirmed the fact expressed in equation 2 that a 1-to-1 mole ratio of CaO/SiO_2 was necessary to achieve a satisfactory degree of defluorination by pyrohydrolysis (table 8). Tables 9 and 10 show the effect of temperature and water, respectively, on fluorine removal from charge material.

TABLE 7. - Effect of pH on precipitation of fluorine and SiO_2, percent

(Feed solution: 125 grams aqueous H_2SiF_6 - 26.2 grams fluorine, 6.3 grams silicon)

pH	Precipitated	
	Fluorine, percent	Silicon, percent
6.0	88.9	88.4
7.0	92.8	91.9
8.0	98.3	97.1
9.0	99.9	99.7
9.5	99.8	99.7

TABLE 8. - Effect of CaO/SiO_2 mole-ratio on defluorination

(1,050° C, 1.2 ml H_2O per gram of charge, 25.2 grams fluorine in charge)

Stoichiometric SiO_2, percent[1]	Fluorine removed	
	Grams	Percent
50	9.6	38.1
75	14.3	56.6
85	16.9	67.0
95	22.6	89.5
105	24.9	98.5
120	24.6	97.6

[1] 100 percent of stoichiometry is equal to a 1-to-1 mole-ratio of SiO_2 and CaO.

TABLE 9. - Effect of temperature on defluorination[1]

(Charge contains 100 grams-27.4 grams fluorine; 1.2 ml/gram of charge)

Temperature, ° C	Fluorine removed, percent
700	13.1
800	25.9
900	59.1
1,000	79.5
1,100	93.0
1,200	97.7

[1] Static-bed tests.

TABLE 10. - Effect of water on defluorination[1]

(1,050° C; charge contains 100 grams-26.6 grams fluorine)

H_2O used, ml/g of charge	Fluorine removed, percent
0.60	53.7
.80	71.0
1.0	89.0
1.2	96.9
1.4	95.5

[1] Static-bed tests.

Based on the data from the preceding tables and reaction equations 2a, a series of tests was made in the rotary kiln to determine optimum feed rates and retention times for this apparatus. One liter (1,253 grams) portions of H_2SiF_6 were neutralized with lime to pH 9.0 to 9.5 and the calculated stoichiometric amount of SiO_2 added. The slurry was thoroughly blended and filtered to remove excess moisture, and then the filter cakes were dried at about 150° C. The wet filter cakes averaged about 35 percent moisture. After being dried, the cakes were ground and repulped to about 25 percent water and pelletized on a disk pelletizer to pellets of about 1/4 inch. The pellets were dried before use. Each of five batches was analyzed, and equal weights were charged to the kiln at varying rates while keeping other control variables constant. The results are tabulated in table 11. Normally the wet filter cake would be pelletized and fed to the defluorinator without drying.

TABLE 11. - Effect of feed rate on defluorination

Feed rate, grams/minute[1]	Charge,[2] fluorine, percent	Discharge		Defluorination, percent
		Weight, grams	Fluorine, percent	
5	22.4	713	2.86	90.9
10	22.6	722	3.81	87.9
12	21.9	740	7.26	75.6
15	22.7	789	13.9	51.5
20	23.2	826	14.8	47.5

[1] All tests run at 1,050° C and H_2O added at a ratio of 1.2 ml/gram of charge.
[2] 1,000 grams pellets used in each test.

Another set of tests was run to determine the composition of the condensed vapors from the kiln. The condensates were then used to prepare anhydrous HF. These data are listed in table 12 and show high recoveries of liberated fluorine and very little silicon contamination.

TABLE 12. - Analyses of condensates from rotary kiln defluorination tests

(1,000-gram charge)

Fluorine charged, grams	Defluorination, percent[1]	Condensate		
		Volume, ml	Fluorine, g/liter	Silicon, g/liter
226	80.6	1,190	149.5	0.03
231	86.3	1,089	170.5	.04
219	84.1	1,176	152.0	.07
217	79.6	1,143	145.9	.03

[1]All tests run at 1,050° C at a feed rate of 10 grams per minute and H_2O flow rate of 1.2 ml per minute.

Precipitation of Sodium Bifluoride and Cryolite Recovery

One thousand milliliters of each of the four condensates were next saturated with sodium fluoride at room temperature to precipitate the HF as NaF·HF. The filtered precipitates were vacuum dried at 120° C. The amount of NaF added was somewhat empirical in that it was calculated from the requirement of the HF in solution plus an amount equal to the approximate solubility value for NaF in water. The NaF·HF that remained in solution was then reacted with alumina to precipitate cryolite. Data are in tables 13 and 14.

TABLE 13. - Precipitation of sodium bifluoride

(1,000-ml solution)

Fluorine, g/liter	NaF added, grams[1]	Total fluorine used, grams	Fluorine in filtrate, grams[2]	Fluorine recovery, percent
149.5	360	312.5	26.1	91.6
170.5	405	353.5	28.6	91.9
152.0	365	317.0	25.8	91.9
145.9	355	306.9	24.6	92.0

[1]Added as a slurry to aid in mixing.
[2]Assumed to be solubility of NaF·HF in this system.

TABLE 14. - Recovery of soluble $NaHF_2$ as cryolite

Fluorine in solution, grams	$Al_2O_3 \cdot H_2O$ added, grams[1]	Fluorine recovery as Na_3AlF_6	
		Grams	Percent
26.1	13.8	24.8	95.0
28.6	15.0	26.0	90.7
25.8	13.6	23.6	91.4
24.6	13.0	23.1	93.8

[1]Calculated according to stoichiometry.

Dissociation of Sodium Bifluoride

Nearly complete recovery of the available HF in the bifluoride was readily achieved by dissociation of $NaHF_2$ at 400° C. However, the economics of the process would depend to a large extent on the necessity to recycle the residual NaF dissociation product. Small-scale tests with pure reagents indicated that the NaF could be recycled many times, but this was not the case with NaF that had been reacted with the HF condensate from the rotary kiln. The maximum number of recycles was three and sometimes two. After the second or third recycle, the residual NaF would melt or fuse and become unreactive. It was indicated that this was due to impurity buildup. Chemical analyses of the melted, dark-colored NaF showed the presence of iron, nickel, chromium, and some SiO_2. This buildup of harmful impurities might be alleviated by use of other materials of construction. Dissociation data are shown in table 15, and analyses of the condensed HF are listed in table 16.

TABLE 15. - Dissociation of $NaHF_2$ at 400° C

$NaHF_2$ taken, grams	Calculated HF in $NaHF_2$, grams	Anhydrous HF recovered, grams	HF recovered, percent
480	149	148.0	99.1
550	171	170.5	99.5
485	150	148.6	98.9
470	146	144.3	98.9

TABLE 16. - Analyses of HF product (percent)

HF	H_2O	Iron	Silicon	Copper	Nickel[1]	Chromium[1]
99.4	0.25	<0.02	<0.05	<0.01	N.D.	N.D.
99.8	.18	<.02	<.05	<.01	N.D.	N.D.
99.6	.36	<.02	<.05	<.01	N.D.	N.D.
99.7	.20	<.02	<.05	<.01	N.D.	N.D.

[1]N.D.--Not detected.

Recycle of Fluorine-Depleted Pellets

In consideration of the economic feasibility of the process, tests were made to determine if the kiln discharge material could be recycled as a source of silica and also as part of the $Ca(OH)_2$ for neutralization and precipitation. Test results showed that this discharge material could be used. Only about one-half as much lime and no additional silica were required for complete neutralization and precipitation for 1 liter of 33 percent H_2SiF_6. In addition, much less waste material was generated, about 230 grams instead of nearly 800 grams per test cycle when starting with 1 liter of 33 percent H_2SiF_6. To confirm the data, an extended defluorination campaign was conducted that included four recycle stages using the discharge from each previous run. The data are shown in table 17.

TABLE 17. - Recycle defluorination tests[1]

Test	H_2SiF_6 taken, ml	Fluorine, grams	$Ca(OH)_2$ needed to pH 9.5, grams	SiO_2 to stoichiometry, grams	Charge[2] Weight, grams	Charge[2] Fluorine, percent	Discharge Weight, grams	Discharge Fluorine, percent	Fluorine recovery, percent
Initial......	3,000	783	1,743	720	2,750	24.5	1,925	7.04	79.8
1st recycle..	1,960	512	495	None	2,665	22.2	2,470	4.00	83.3
2d recycle...	1,500	392	165	None	2,400	18.2	2,226	2.80	85.7
3d recycle...	1,500	392	525	None	2,000	19.2	1,693	3.70	83.7
4th recycle..	1,500	392	330	None	2,454	22.1	2,220	3.65	84.5

[1] Each test was run at 1,050° C using 1.2 ml H_2O per gram of charge.
[2] Difference between grams fluorine in H_2SiF_6 taken and grams fluorine charged is that not all of the material was recovered in the initial test due to losses during pelletizing.

This data shows that 1,000 ml of H_2SiF_6 required 581 grams of $Ca(OH)_2$ and 240 grams of silica and that defluorination was 79.8 percent; but when the discharge material was recycled, no silica and only 234 grams $Ca(OH)_2$ was required, and that defluorination averaged 84.3 percent.

Summary of Anhydrous HF Process

The HF-H_2O vapors from the tests listed in table 17 were all condensed and analyzed for HF content and impurities. The average HF content of all the condensates was 152 grams per liter, which represented a recovery of over 99 percent of the evolved fluorine. The silicon content was below 0.1 gram per liter. Some nickel and iron were present because of slight corrosion of the equipment, but they were considered relatively unimportant to this investigation.

One liter of a composite mixture of the condensates from the recycle tests was next taken through the remainder of the process and confirmed loss data on the earlier single tests. Average losses for each step are tabulated in table 18. On the basis of this investigation it is indicated that over 80 percent of the fluorine in a waste fluosilicic acid solution can be recovered as anhydrous HF.

TABLE 18. - Average fluorine losses for anhydrous HF process

Step	Average fluorine loss, percent of total
Precipitation and neutralization....	0.29
Average handling loss..............	1.50
Defluorination.....................	15.7
Condensation step..................	.25
$NaHF_2$ and cryolite precipitation....	.49
$NaHF_2$ dissociation................	.90
Total........................	19.13

ALUMINUM FLUORIDE FROM WASTE FLUOSILICIC ACID

A brief investigation was made of the feasibility of converting the kiln offgases into cell-grade aluminum fluoride (AlF_3). The HF-H_2O offgases were passed through a bed of 1/4-inch activated alumina at a temperature of about 250° to 275° C. The gas-solid reaction would be as follows:

$$Al_2O_{3\,(s)} + [6\ HF + H_2O]_{(g)} \xrightarrow[250°\ \text{to}\ 275°\ C]{\Delta} 2\ AlF_3 + 4\ H_2O \uparrow$$

The HF-H_2O vapors were generated in the same way as in the anhydrous HF process. Because of the brevity of this work, only one variable was studied and that was the effect on the reaction due to varying mole percentages of HF in the vapors passing through the charge. This was done by varying the water flow to the defluorination reactor. The data in table 19 show that AlF_3 can be produced by this reaction but that optimum conditions were not necessarily attained. Further work on this system may be warranted.

TABLE 19. - Aluminum fluoride from HF-H_2O offgas and activated alumina

HF in offgas, mole-percent[1]	Grade AlF_3, percent[2]	Stoichiometric HF used, percent[3]	Evolved fluorine in AlF_3, percent
5.5	46.1	125	74.6
8.6	53.6	200	53.1
11.5	66.3	200	50.6
12.9	69.4	250	51.4
23.1	82.2	350	48.6

[1] Calculated value.
[2] Chemical and spectrographic analyses indicated no impurities other than unreacted alumina.
[3] Approximate values.

CONCLUSIONS

The data in this report show that waste fluosilicic acid can be readily converted into more salable products.

When H_2SiF_6 is neutralized with ammonia, the silica is completely precipitated. The filtrate contains the fluorine as ammonium fluoride. If the filtrate is then reacted with a stoichiometric amount of lime, the ammonia is volatilized, and CaF_2 meeting acid-grade specification is precipitated. An average of about 85 percent of the ammonia can be recovered for recycle, and over 95 percent of the fluorine is recovered as CaF_2.

A second product of importance that can be recovered from waste H_2SiF_6 is anhydrous HF and byproduct cryolite. The recovery of HF is more difficult, and recovery of fluorine values tends to be lower than when CaF_2 is the end product. The process involves liberation of HF from a pelletized precipitate formed by neutralizing H_2SiF_6 with lime and silica to a pH of 9.0 to 9.5, by the pyrohydrolytic action of H_2O at about 1,050° C. It is this step that tends to make the process more troublesome than the CaF_2 process. Fluorine liberation is about 85 percent, and a relatively high temperature is required. However, after saturation of the condensed vapors with sodium fluoride, the resulting precipitate of $NaHF_2$ can be dissociated into high-purity HF. The soluble $NaHF_2$ can be treated for recovery of byproduct cryolite.

Since HF can be generated from CaF_2, it would seem that the first process would be preferred since it is much simpler and more easily managed. However, it should be noted that the F equivalent in anhydrous HF commands a much higher price per ton than the F equivalent in acid-grade fluorspar.

Preliminary tests indicated the technical feasibility of synthesizing cell-grade AlF_3 by passing the dilute HF offgases from the anhydrous HF process through a moderately heated bed of activated alumina. Only about half of the evolved HF reacted with the alimina under these conditions; but an 80 percent AlF_3 product was made in which the only impurity was unreacted alumina. However, the fluoride vapors passing through the reactor can be collected in water-scrubbers and recovered as cryolite by the addition of sodium aluminate. This AlF_3 product should be of use in aluminum reduction cells since they require the periodic additions of both alumina and aluminum fluoride.

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UTILIZATION OF WASTE FLUOSILICIC ACID

(In Two Sections)

2. Cost Evaluation

by

J. L. Reuss[1] and H. Dolezal[2]

ABSTRACT

An evaluation was made to determine the economics of utilizing waste fluosilicic acid for production of (1) calcium fluoride, and (2) anhydrous hydrogen fluoride. Two versions of each process were considered and compared. The evaluation showed that both products could be produced and marketed competitively. Lowest estimated product sales prices required to yield a 25-percent return on investment before taxes (discounted cash flow basis) was $339.34 per ton of hydrogen fluoride and $48.64 per ton of calcium fluoride.

INTRODUCTION

The objective of this Bureau of Mines evaluation was to determine the economic feasibility of recovering marketable fluoride products from waste fluosilicic acid (H_2SiF_6) solutions. On the basis of data obtained from research described in Section 1, hypothetical processes were designed to produce either calcium fluoride or anhydrous hydrogen fluoride. Two versions of each process are considered. The calcium fluoride process is evaluated with and without production of byproduct silica. The hydrogen fluoride process is evaluated with and without recycle of calcine to increase recovery and reduce raw material costs. Development of designs for the hypothetical processes required minor alterations of the laboratory flowsheets to conform to the operating characteristics of production size equipment. Also, because the proposed processes were not subjected to continuous pilot plant test programs, this estimate must be considered to be of a study nature only.

Each of the four hypothetical plants considered in this evaluation would be located adjacent to existing phosphate fertilizer operations and are designed to process 200 tons of waste acid containing 53.15 tons of H_2SiF_6 per day.

[1]Metallurgist.
[2]Research chemist.
Both authors are with the Salt Lake City Metallurgy Research Center, Bureau of Mines, Salt Lake City, Utah.

To facilitate this evaluation the processes were divided into unit operations and both capital and operating costs are presented for each such unit. The method used for estimating costs, which is briefly described, should provide an accuracy of ±25 percent. After describing the methods of estimation, assumptions as to the nature of raw materials needed for the processes are outlined. The chemistry of each process is recounted briefly and the hypothetical plant designed for the implementation of each process is described by following the flow of materials through the various processing steps. Estimated costs are presented in turn for each of the processes.

CAPITAL COSTS

Established fixed capital costs are based on the delivered cost of equipment, and they are estimated separately for each item of equipment. These costs are for second quarter 1970 and correspond to a Marshall and Stevens average equipment cost index of 301.

The total direct construction cost for each unit operation consists of the delivered cost of all equipment to be installed plus the cost of labor to erect it and the cost of additional construction required to support, house, protect, and make it operable. These various construction costs were estimated by factors applied to the total delivered equipment cost. A miscellaneous cost item was added to cover minor equipment or construction that might be overlooked.

Forty percent was added to the direct cost. This approximates the addition of 10 percent for field indirect expense plus the following percentages of successive resulting subtotals: 5 for engineering plus 5 for administration and overhead; 10 for contingencies; and 5 for contractor's fees. The field indirect cost covers field supervision, inspection, temporary construction, equipment rental, and payroll overhead.

Interest during construction was obtained by multiplying the sum of all direct and indirect costs, including contingencies and fees, by the average interest rate for the period of construction.

Where significant items of mobile, or not-installed equipment were required, the cost of this equipment becomes part of the total direct construction cost for the unit operation (without construction factors).

The fixed capital cost of general plant facilities was estimated as 10 percent of the total fixed capital cost of the production units of the plant. These facilities include buildings and equipment for offices, laboratory, shops, and warehouses, plus fencing, roads, railroad spur, fire protection facilities, and safety equipment.

The fixed capital cost of the plant utilities was estimated as 12 percent of the total fixed capital cost of the production units. Plant utilities include the cost of construction and equipment necessary to conduct them to the plant from an outside source, and to distribute them to the various buildings or operating units of the plant.

The working capital requirements were estimated as the sum of 1 month's supply of raw materials, 1 month's out-of-pocket expense, and 2 month's product inventory.

OPERATING COSTS

Operating costs are estimated in two ways, (1) on the basis of charges against individual unit operations, and (2) on the basis of charges against the integrated plant. Costs obtained by the first method indicate how costs might be affected by possible modifications in the unit of operations.

In estimating operating costs for unit operations, each unit was treated as though it were an independent operation charged with the operating costs of the plant utilities and general plant facilities on a basis prorated on their consumption and use. The estimated fixed costs for unit operations include only the taxes, insurance, and depreciation on the fixed capital cost for the operating unit. The utilities are charged at gross rates, which include the operating labor, maintenance, and fixed costs for the portions of the utilities that are consumed in the operating units. The indirect costs include the operating labor, maintenance, and fixed costs for the general plant facilities and for that portion of the utilities that is consumed in the general plant facilities.

The cost of raw materials are the same for both estimating methods. Shipping costs were included in the cost of all raw materials with the exception of fluosilicic acid. Utility requirements were calculated for the unit operations and totaled for the integrated plant. Rates for the integrated plant are those charged by the utility companies. With added charges, these rates are higher for the unit operations.

The direct labor and plant maintenance, payroll overhead, and operating supplies costs were estimated for the unit operations and these costs were totaled for the integrated plant estimate. Direct labor cost was based on a rate of $3.60 per hour and the cost of supervision was taken as 15 percent of this labor cost. Plant maintenance labor varies between 2 and 3 percent of the fixed capital cost without interest for the various unit operations. Maintenance labor supervision is 20 percent of the labor cost. The material cost was assumed to be equal to the labor cost. Payroll overhead was estimated as 25 percent of the cost of labor and supervision for operation and maintenance. Operating supplies were assumed equal to 20 percent of the cost of maintenance.

Indirect operating costs include the cost of maintaining the plant facilities and utilities, the expense of accounting, control and research laboratories, engineering, plant protection and safety, warehousing, shipping, and the executive and administrative offices. The indirect cost for the integrated plant was estimated as 40 percent of the cost of labor, maintenance, and operating supplies. With other prorated charges, the percentage is a little higher for the unit operations.

Fixed costs include the annual cost of taxes, insurance, and depreciation of the plant. Taxes and insurance combined were estimated as 2 percent of the fixed capital cost without interest. Depreciation cost was estimated on the basis of straight-line depreciation over a life of 12.5 years (8 percent per year). Such costs are higher for the integrated plant estimate where they include costs for plant utilities and facilities.

SUMMARY OF COSTS

The number of men employed for direct labor, capital costs for plants, and the annual operating costs with a percentage breakdown of operation sections of the plants are summarized in their respective sections. These summaries also show the unit production costs and the selling price needed for assumed rates of return on investments of 20, 25, 30, and 35 percent before taxes.

Such rates of return are calculated on a discounted cash flow basis in which all cash flows over the life of the operation are discounted to the present date and equated to the initial investment. This relationship, assuming no salvage value of plant or equipment at the end of the operation, is shown by the following equation:

$$P + W = R\left[\frac{(1 - i)^n - 1}{i\,(1 + i)^n}\right] + \frac{W}{(1 + i)^n} \qquad (1)$$

in which i is the annual rate of return on investment, n is the project life in years, P is the fixed capital cost of the plant, R is the annual cash flow (annual return from sales plus annual cost of plant depreciation less manual operating cost), and W is the working capital.

RAW MATERIALS

With the exception of fluosilicic acid, all of the raw materials used in these processes are purchased. The composition and availability of crude fluosilicic acid has been described in Section 1. Ammonia is used in gaseous form but is stored as a liquid. For all operations, pebble lime is used for the preparation of slaked lime slurry. Silica must be sized to below 200-mesh but does not have to meet glass manufacturers' standards of purity. The alumina is a trihydrate ($Al_2O_3 \cdot 3\ H_2O$) such as that produced as an intermediate by bauxite processors. Sodium fluoride requirements are satisfied by using a 97-percent salt.

CALCIUM FLUORIDE PROCESS WITH SILICA RECOVERY

In this process (fig. 3) the crude fluosilicic acid is neutralized with ammonia to form ammonium fluoride and precipitate silica. The silica is dried and bagged, and the ammonium fluoride solution is reacted with calcium hydroxide to form calcium fluoride and generate ammonia for recycle. The calcium fluoride is filtered, dried, bagged, and sold as acid-grade fluorspar. This estimate is based on a fluorine recovery of 92.6 percent and an ammonia recovery of 85.0 percent. The value of the silica byproduct is estimated to be $20 per ton.

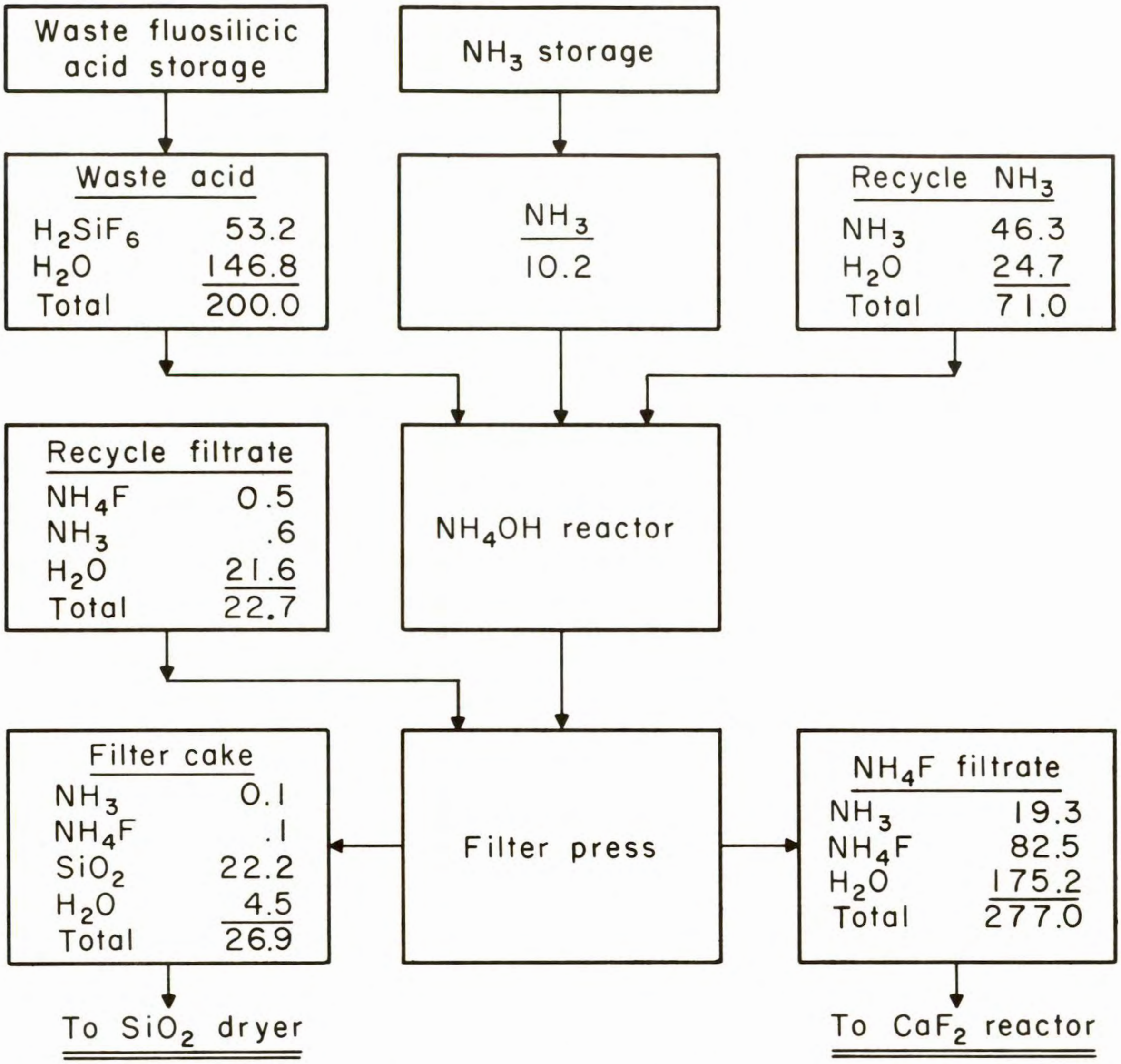

FIGURE 3. - Material Balance, Ammoniation Operation, Calcium Fluoride Recovery Process (Tons Per Day).

The process is divided into four major unit operations: (1) ammoniation, (2) silica drying and bagging, (3) calcium fluoride and ammonia recovery, and (4) calcium fluoride drying and bagging. Major equipment items for this process are shown in table 20. Detailed material balance and fixed capital costs are shown in figures 3-6 and tables 21-24, respectively. The operating costs for each of the units are shown in table 25. The annual operating costs for the integrated plant are shown in table 26, and the summary of costs and operating personnel are shown in table 27.

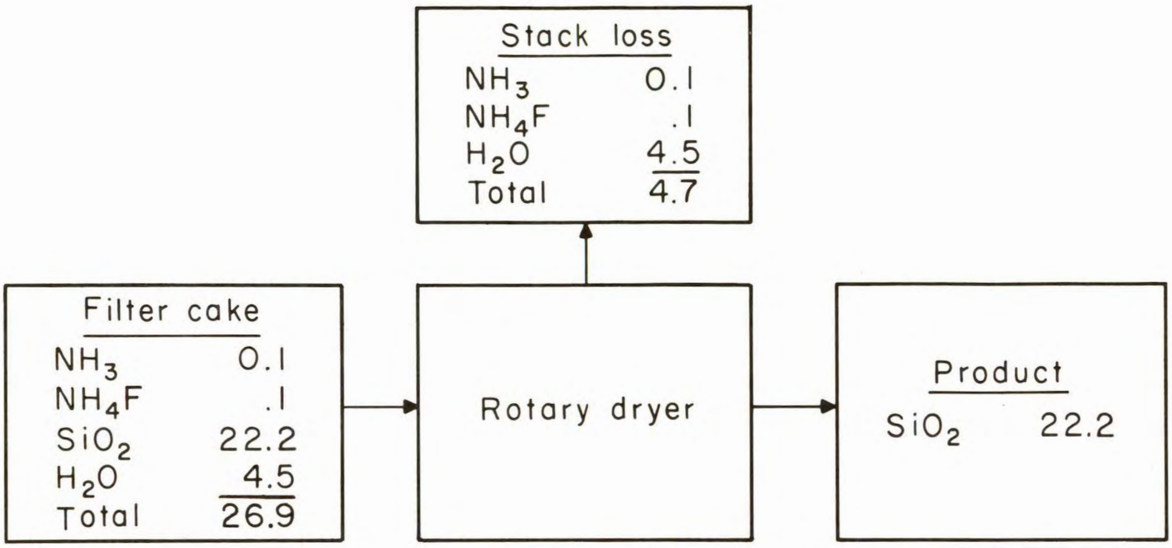

FIGURE 4. - Material Balance, Silica Drying and Bagging Operation, Calcium Fluoride Recovery Process (Tons Per Day).

TABLE 20. - Major equipment for the CaF_2 processes

Item	Number	Horsepower	Size	Capacity, each	Purpose
Rubber-lined tank.......	1	-	21 by 16 ft	40,000 gal	H_2SiF_6 storage.
Tank....................	2	-	12 by 12 ft	1,335 cu ft	NH_3 storage.
2-stage compressor......	1	15	-	45 cfm	NH_3 compressor.
Agitated tank, stainless	3	4.5	5 ft dia, 4½ ft deep	660 gal	H_2SiF_6-NH_3 reactor.
Cooling tower...........	1	6.0	-	130 gpm	Reactor cooling.
Filter press............	2	-	200 sq ft	1.0 tph	SiO_2 separation.
Rotary dryer[1]...........	1	10	3 by 20 ft	1.5 tph	SiO_2 dryer.
Storage silo............	1	-	30 by 60 ft	15,000 cu ft	CaO storage.
Lime slaker.............	1	11.5	-	150 tpd	-
Agitated tank, stainless	4	12	6 ft dia, 6½ ft deep	174 cu ft	NH_4F-$Ca(OH)_2$ reactor.
Boiler..................	1	8	-	255 MBtu/hr	Steam generation.
Thickener...............	1	.75	10 ft dia	550 cu ft	CaF_2 separation.
Disk filter.............	1	3.5	44 sq ft	6.0 tph	CaF_2 dewatering.
Rotary dryer............	1	100	10 by 24 ft	6.0 tph	CaF_2 dryer.

[1]Required only for process in which SiO_2 is recovered.

TABLE 21. - Fixed capital cost summary for ammoniation operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
STORE TANK H2SIF6		1	27900.	1700.	29600.
SS ACID FEED PUMP		1	600.	0.	600.
STORAGE TANK (NH3)		2	36100.	4300.	40400.
COMPRESSOR-2 STAGE		1	2500.	100.	2600.
NH3 REACTOR 5X4.5		3	6300.	900.	7200.
PUMP 1.5X1.5		1	600.	0.	600.
COOLING TOWER		1	6200.	900.	7100.
FILT STORAGE TANK		1	1900.	100.	2000.
FILTER PRESS		2	15800.	2400.	18200.
DIAPHRAGM PUMP		1	2400.	100.	2500.
STORAGE TANK		1	2500.	200.	2700.
BIN, FILTER CAKE		1	600.	100.	700.
TOTAL			103400.	10800.	114200.
FOUNDATIONS	.060				6200.
STRUCTURES	.060				6200.
BUILDINGS	.300				31000.
INSULATION	.000				0.
INSTRUMENTATION	.040				4100.
ELECTRICAL WORK	.150				15500.
PIPING	.250				25900.
PAINTING	.020				2100.
MISCELLANEOUS	.100				10300.
TOTAL	.980				101300.
TOTAL DIRECT CONSTRUCTION COST					215500.
INDIRECT COST, CONTINGENCY, AND FEE	.400				86200.
INTEREST DURING CONSTRUCTION	.018				5400.
TOTAL FIXED CAPITAL COST					307100.

TABLE 22. - Fixed capital cost summary for SiO_2 drying and bagging operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
FEEDER, ROTARY		1	2600.	200.	2800.
BELT CONVEYOR		1	5300.	1100.	6400.
DRYER, 3X20FT		1	14900.	3000.	17900.
DUST COLLECTOR		1	1000.	200.	1200.
THICKENER 8X7		1	3400.	500.	3900.
DIAPHRAGM PUMP		1	1300.	100.	1400.
O.F.PUMP 1X1		1	300.	0.	300.
KILN DISCH CONV		1	7300.	1500.	8800.
PRO STORAGE BIN		1	1500.	200.	1700.
BAGGING MACHINE		1	5100.	500.	5600.
TOTAL			42700.	7300.	50000.
FOUNDATIONS	.080				3400.
STRUCTURES	.060				2600.
BUILDINGS	.400				17100.
INSULATION	.000				0.
INSTRUMENTATION	.050				2100.
ELECTRICAL WORK	.050				2100.
PIPING	.050				2100.
PAINTING	.015				600.
MISCELLANEOUS	.100				4300.
TOTAL	.805				34300.
TOTAL DIRECT CONSTRUCTION COST					84300.
INDIRECT COST, CONTINGENCY, AND FEE			.400		33700.
INTEREST DURING CONSTRUCTION			.018		2100.
TOTAL FIXED CAPITAL COST					120100.

TABLE 23. - Fixed capital cost summary for calcium fluoride and ammonia recovery operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
LIME STORAGE BIN		1	9000.	1100.	10100.
LIME HOPPER		1	3200.	400.	3600.
BUCKET ELEVATOR		1	4100.	900.	5000.
VIBRATING FEEDER		1	1100.	100.	1200.
CONST WT FEEDER		1	2200.	400.	2600.
LIME SLAKER		1	24400.	2900.	27300.
LIME SURGE TANK		1	13700.	1600.	15300.
SLURRY PUMP		2	2100.	100.	2200.
LIME FEEDSYSTEM		1	300.	0.	300.
CAF2 REACTOR		3	9700.	1500.	11200.
BOILER,125 LB		1	6800.	700.	7500.
FEED WATER TANK		1	1400.	100.	1500.
FEED PUMP		1	600.	100.	700.
THICKENER,10 FT D.		1	4400.	700.	5100.
DIAPHRAGM PUMP		1	1300.	100.	1400.
PUMP		1	200.	0.	200.
DISK FILTER		1	3800.	400.	4200.
VAC PUMP		1	700.	100.	800.
VAC RECEIVER 30X7		1	300.	0.	300.
FILTRATE PUMP,1X1		1	300.	0.	300.
CONV.BELT,14-IN		1	5900.	1200.	7100.
STORAGE BIN 12X16		1	1600.	200.	1800.
S.S. TANK		1	4500.	500.	5000.
GEAR PUMP		1	400.	0.	400.
BLOWER		1	1300.	100.	1400.
TOTAL			103300.	13200.	116500.
FOUNDATIONS	.070				7200.
STRUCTURES	.060				6200.
BUILDINGS	.400				41300.
INSULATION	.050				5200.
INSTRUMENTATION	.040				4100.
ELECTRICAL WORK	.150				15500.
PIPING	.250				25800.
PAINTING	.020				2100.
MISCELLANEOUS	.100				10300.
TOTAL	1.140				117700.
TOTAL DIRECT CONSTRUCTION COST					234200.
INDIRECT COST, CONTINGENCY, AND FEE			.400		93700.
INTEREST DURING CONSTRUCTION			.018		5900.
TOTAL FIXED CAPITAL COST					333800.

TABLE 24. - Fixed capital cost summary for CaF_2 drying and bagging operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
TABLE FEEDER		1	2600.	200.	2800.
DRYER FEED BELT		1	5700.	1100.	6800.
DRYER 10 FT DIAM		1	77800.	15600.	93400.
KILN DISCH CONV		1	8000.	1600.	9600.
STORAGE BIN		1	1600.	200.	1800.
BAGGING MACHINE		1	5100.	500.	5600.
BAG CONVEYOR		1	4700.	1000.	5700.
TOTAL			105500.	20200.	125700.
FOUNDATIONS	.080				8400.
STRUCTURES	.060				6300.
BUILDINGS	.400				42200.
INSULATION	.000				0.
INSTRUMENTATION	.050				5300.
ELECTRICAL WORK	.050				5300.
PIPING	.050				5300.
PAINTING	.015				1600.
MISCELLANEOUS	.100				10500.
TOTAL	.805				84900.
TOTAL DIRECT CONSTRUCTION COST					210600.
INDIRECT COST, CONTINGENCY, AND FEE			.400		84200.
INTEREST DURING CONSTRUCTION			.018		5300.
TOTAL FIXED CAPITAL COST					300100.

TABLE 25. - Annual operating cost of unit operations for CaF_2 process with SiO_2 recovery

	AMMONIATION	SIO2 DRYING AND BAGGING	CAF2 AND NH3 RECOVERY	CAF2 DRYING AND BAGGING
DIRECT COST				
MATERIALS				
AMMONIA	324900.	0.	0.	0.
CAO	0.	0.	372300.	0.
(TOTAL MATERIALS)	(324900.)	(0.)	(372300.)	(0.)
UTILITIES				
ELECTRICITY, 440 V.(LOW)	2700.	1500.	4900.	6500.
NATURAL GAS, CONSUMED	0.	2900.	10500.	9400.
WATER	7200.	0.	2400.	0.
(TOTAL UTILITIES)	(9900.)	(4400.)	(17800.)	(15900.)
TOTAL	334800.	4400.	390100.	15900.
DIRECT LABOR				
LABOR 3.600/MAN HOUR	35900.	20200.	35900.	20200.
SUPERVISION .150	5400.	3000.	5400.	3000.
TOTAL	41300.	23200.	41300.	23200.
PLANT MAINTENANCE				
LABOR	9100.	2900.	9800.	7400.
SUPERVISION .200	1800.	600.	2000.	1500.
MATERIALS	9100.	2900.	9800.	7400.
TOTAL	20000.	6400.	21600.	16300.
PAYROLL OVERHEAD .250	13100.	6700.	13300.	8000.
OPERATING SUPPLIES .200	4000.	1300.	4300.	3300.
TOTAL DIRECT COST	413200.	42000.	470600.	66700.
INDIRECT COST				
ADMINISTRATION AND OVERHEAD				
UNITS .44368	29000.	13700.	30000.	19000.
FIXED COST				
TAXES AND INSURANCE .020	6000.	2400.	6600.	5900.
DEPRECIATION 12.500 YR	24600.	9600.	26700.	24000.
TOTAL	30600.	12000.	33300.	29900.
TOTAL ANNUAL COST	472800.	67700.	533900.	115600.

TABLE 26. - Annual operating cost for CaF_2 process with SiO_2 recovery

	ANNUAL CONSUMPTION	UNIT COST	TOTAL OPERATION DOLLARS	PERCENT
DIRECT COST				
MATERIALS				
AMMONIA	3570.0TON	91.00	324900.	27.30
CAO	20685.0TON	18.00	372300.	31.29
(TOTAL MATERIALS)		(	697200.	58.59)
UTILITIES				
ELECTRICITY	1202.1231 MKWHR	10.00	12000.	1.01
NATURAL GAS, CONSUMED	54600.0 MCF	.40	21800.	1.83
(TOTAL UTILITIES		(	33800.	2.84)
TOTAL			731000.	61.43
DIRECT LABOR				
LABOR 3.600/MAN HOUR			112200.	9.43
SUPERVISION .150			16800.	1.41
TOTAL			129000.	10.84
PLANT MAINTENANCE				
LABOR			29200.	2.45
SUPERVISION .200			5900.	.50
MATERIALS			29200.	2.45
TOTAL			64300.	5.40
PAYROLL OVERHEAD .250			41100.	3.45
OPERATING SUPPLIES .200			12900.	1.08
TOTAL DIRECT COST			978300.	82.21
INDIRECT COST				
ADMINISTRATION AND OVERHEAD				
OVERALL .400			82500.	6.93
FIXED COST				
TAXES AND INSURANCE .020			25600.	2.15
DEPRECIATION 12.500 YR			103600.	8.72
TOTAL			129200.	10.86
TOTAL ANNUAL OPERATING COST			1190000.	100.00

TABLE 27. - Summary of costs and operating personnel for CaF_2 process with SiO_2 recovery

	NUMBER OF OPERATORS	CAPITAL COST	ANNUAL OPERATING COST	PERCENT ANNUAL OPERATING COST	UNIT PRODUCTION COST,$/LB CA F2
AMMONIATION	4.8	307100.	472800.	39.73	.00844
SIO2 DRYING AND BAGGING	2.7	120100.	67700.	5.69	.00121
CAF2 AND NH3 RECOVERY	4.8	333800.	533900.	44.87	.00953
CAF2 DRYING AND BAGGING	2.7	300100.	115600.	9.71	.00206
FACILITIES, 10.PCT		106100.			
UTILITIES, 12.PCT		127800.			
TOTAL FIXED CAPITAL		1295000.			
WORKING CAPITAL		347000.			
TOTAL	15.0	1642000.	1190000.	100.00	.02125

BYPRODUCTS		156100.	
OPERATING COST LESS BYPRODUCT CREDIT, OB		1033900.	.01846
OB LESS DEPRECIATION, OD		930300.	
RATE OF RETURN = .200000			
CASH FLOW =	357900., OD + CASH FLOW =	1288200.	.02300
RATE OF RETURN = .250000			
CASH FLOW =	431700., OD + CASH FLOW =	1362000.	.02432
RATE OF RETURN = .300000			
CASH FLOW =	507800., OD + CASH FLOW =	1438100.	.02568
RATE OF RETURN = .350000			
CASH FLOW =	585600., OD + CASH FLOW =	1515900.	.02707
SELLING PRICE, $ 63.250/TON			
RATE OF RETURN = .509650			
CASH FLOW =	840700., OD + CASH FLOW =	1771000.	.03162

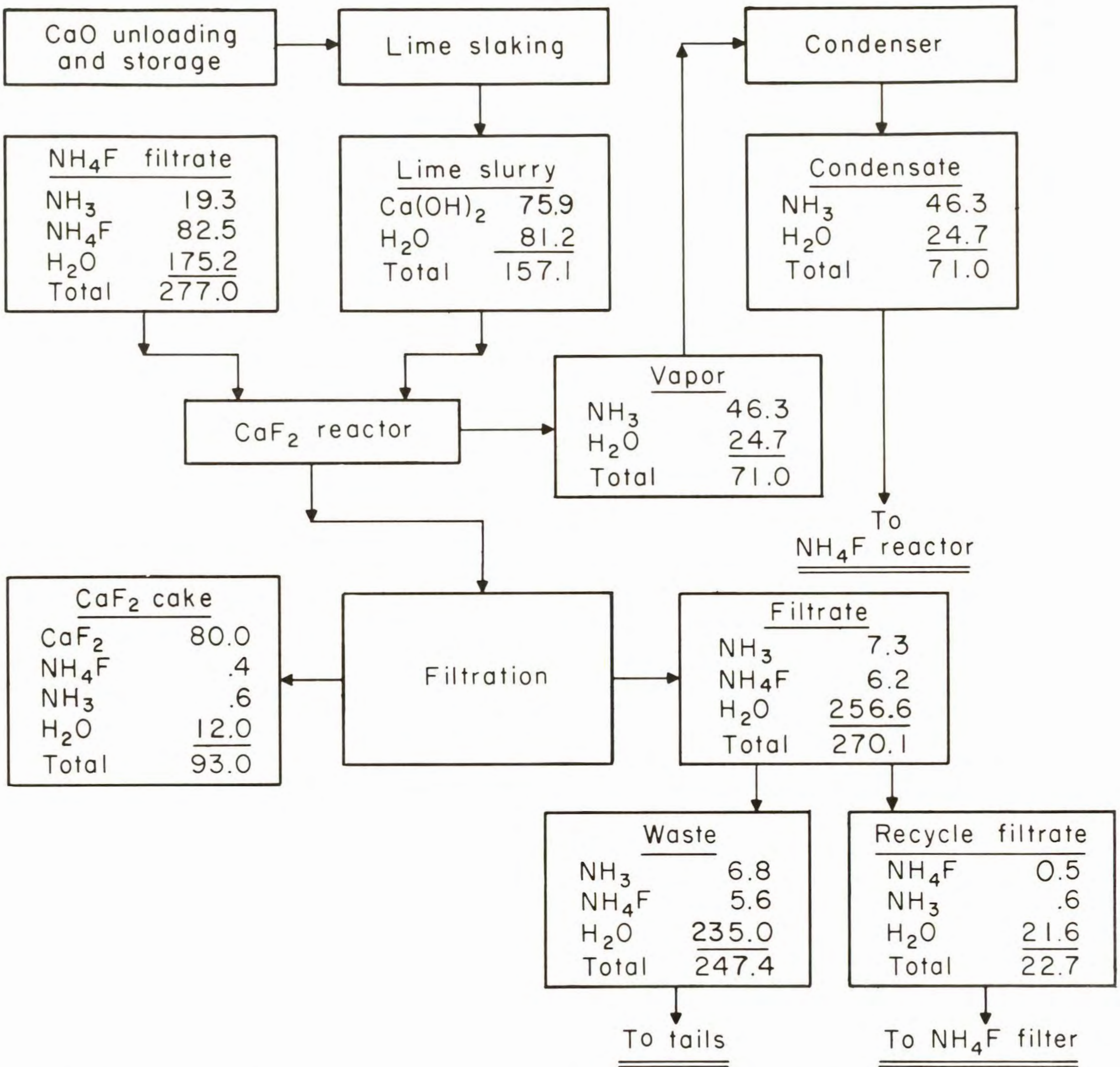

FIGURE 5. - Material Balance, Calcium Fluoride and Ammonia Recovery Operation, Calcium Fluoride Recovery Process (Tons Per Day).

Ammoniation

Waste fluosilicic acid is neutralized to a pH of 9.0 in three enclosed agitated reactors operating in series. This reaction is exothermic, and temperature is maintained at 200° F by circulating cooling water through internal lead coils. The circulating water is cooled in a 54,500 Btu minute cooling tower. The reactor operates on a positive pressure of 2.0 psig, and the retention time is 30 minutes. The discharge from the neutralization reactors is pumped through two plate and frame filters, operated alternately. The filter cake, a hydrated silica, is discharged into a bin, from which it is fed to the

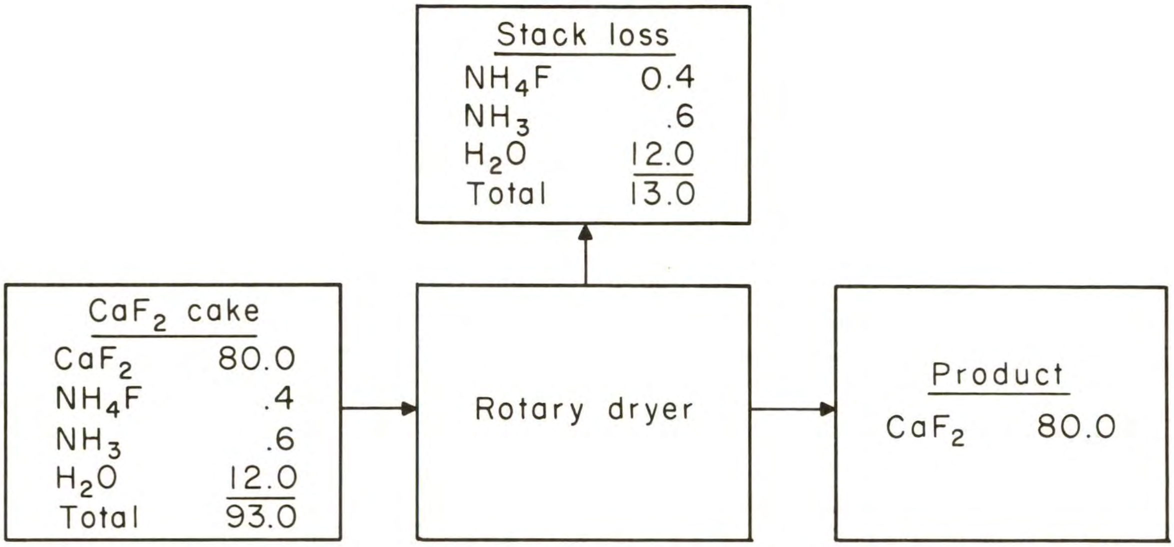

FIGURE 6. - Material Balance, Calcium Fluoride Drying and Bagging Operation, Calcium Fluoride Recovery Process (Tons Per Day).

drying operation. The filtrate, an ammonium fluoride solution, is pumped to a rubber-lined storage tank.

Silica Drying and Bagging

The wet filter cake is fed onto a belt conveyor that delivers it to a 3- by 20-foot direct-fired rotary dryer operated at 150° C. The dried silica is conveyed to a storage bin, from which it is discharged into a weighing and bagging machine. Dryer exhaust gases are scrubbed in a wet dust collector. The solids are collected in a thickener and can be recycled to the silica filter.

Calcium Fluoride and Ammonia Recovery

Pebble lime is received by rail and elevated into a storage silo from which it is fed to a standard lime slaker. The lime slurry and ammonium fluoride solution are both pumped to three enclosed agitated reactors arranged in series to provide a retention time of 45 minutes. Steam-heated lead coils are used to maintain the temperature of the reactors at 70° to 75° C, which is required for removal of the ammonia. The wet ammonia vapor is fortified with makeup ammonia and recycled to the ammonia operation. The reactor discharge slurry is stored in a 10-foot thickener, to provide reserve surge capacity, and pumped to a 4-foot-diameter disk filter (44 square feet) for separation of the calcium fluoride. Part of the filtrate is used in the ammoniation operation for washing the silica filter cake and the balance is discharged to waste. The calcium fluoride filter cake is conveyed to the feed hopper for the calcium fluoride drying and bagging operation.

Calcium Fluoride Drying and Bagging

The filter cake is fed to a 10- by 24-foot indirect-fired rotolouver dryer. This type of drying system was selected to prevent decomposition of the calcium fluoride by overheating. After drying, the calcium fluoride is conveyed to a storage bin from which it discharges into a weighing and bagging machine.

CALCIUM FLUORIDE PROCESS WITHOUT SILICA RECOVERY

This process is identical to the first calcium fluoride process except for omission of the silica drying and bagging operation. The list of major equipment (table 20) is applicable to both calcium fluoride processes. Removal of the silica drying and bagging operation does not affect the capital or operating costs of the other unit operations, but does influence the overall operating costs. The effect of these changes are shown in the annual operating cost of the integrated plant (table 28), and the summary of costs and operating personnel (table 29).

TABLE 28. - Annual operating cost for CaF_2 process without SiO_2 recovery

	ANNUAL CONSUMPTION	UNIT COST	TOTAL OPERATION DOLLARS	PERCENT
DIRECT COST				
MATERIALS				
AMMONIA	3570.0TON	91.00	324900.	28.98
CAO	20685.0TON	18.00	372300.	33.21
(TOTAL MATERIALS)		(	697200.	62.19)
UTILITIES				
ELECTRICITY	1087.8140 MKWHR	10.00	10900.	.97
NATURAL GAS, CONSUMED	47600.0 MCF	.40	19000.	1.70
(TOTAL UTILITIES		(	29900.	2.67)
TOTAL			727100.	64.86
DIRECT LABOR				
LABOR 3.600/MAN HOUR			92000.	8.21
SUPERVISION .150			13800.	1.23
TOTAL			105800.	9.44
PLANT MAINTENANCE				
LABOR			26300.	2.35
SUPERVISION .200			5300.	.47
MATERIALS			26300.	2.35
TOTAL			57900.	5.17
PAYROLL OVERHEAD .250			34400.	3.07
OPERATING SUPPLIES .200			11600.	1.03
TOTAL DIRECT COST			936800.	83.57
INDIRECT COST				
ADMINISTRATION AND OVERHEAD				
OVERALL .400			70100.	6.25
FIXED COST				
TAXES AND INSURANCE .020			22200.	1.98
DEPRECIATION 12.500 YR			91900.	8.20
TOTAL			114100.	10.18
TOTAL ANNUAL OPERATING COST			1121000.	100.00

TABLE 29. - Summary of costs and operating personnel for CaF_2 process without SiO_2 recovery

	NUMBER OF OPERATORS	CAPITAL COST	ANNUAL OPERATING COST	PERCENT ANNUAL OPERATING COST	UNIT PRODUCTION COST,$/LB CA F2
AMMONIATION	4.8	307100.	472100.	42.11	.00843
	.0	0.	0.	.00	.00000
CAF2 AND NH3 RECOVERY	4.8	333800.	533300.	47.57	.00952
CAF2 DRYING AND BAGGING	2.7	300100.	115600.	10.31	.00206
FACILITIES, 10.PCT		94100.			
UTILITIES, 12.PCT		112900.			
TOTAL FIXED CAPITAL		1148000.			
WORKING CAPITAL		331000.			
TOTAL	12.3	1479000.	1121000.	100.00	.02002

BYPRODUCTS		0.	
OPERATING COST LESS BYPRODUCT CREDIT, OB		1121000.	.02002
OB LESS DEPRECIATION, OD		1029200.	
RATE OF RETURN =	.200000		
CASH FLOW =	322000., OD + CASH FLOW =	1351200.	.02413
RATE OF RETURN =	.250000		
CASH FLOW =	388500., OD + CASH FLOW =	1417700.	.02532
RATE OF RETURN =	.300000		
CASH FLOW =	457200., OD + CASH FLOW =	1486400.	.02654
RATE OF RETURN =	.350000		
CASH FLOW =	527300., OD + CASH FLOW =	1556500.	.02779
SELLING PRICE, $	63.250/TON		
RATE OF RETURN =	.499080		
CASH FLOW =	741800., OD + CASH FLOW =	1771000.	.03162

HYDROGEN FLUORIDE AND CRYOLITE PROCESS WITHOUT RECYCLE OF CALCINE

In this process shown in figure 2, the fluorine is precipitated from the crude fluosilicic acid solution by treatment with calcium hydroxide and silica. This precipitate is then filtered, balled, and subjected to steam hydrolysis in an indirect-fired multiple hearth furnace at a temperature of 1,050° C. The steam and volatilized fluorine are condensed as a silica-free aqueous hydrofluoric acid containing approximately 12 to 15 percent hydrogen fluoride. The nonvolatile materials from the defluorination operation combine to form a fluorine-depleted $CaSiO_3$ residue, which is discarded.

The aqueous hydrofluoric acid from the defluorination operation is combined with sodium fluoride in an enclosed agitated reactor to produce sodium bifluoride ($NaHF_2$). The discharge from the sodium bifluoride reactor is filtered and the cake is dried in a rotary dryer. After drying, the filter cake is heated to 400° C in an indirect-fired rotary kiln to decompose the sodium bifluoride into anhydrous hydrogen fluoride and sodium fluoride. The sodium fluoride is recycled to the sodium bifluoride reactor and the hydrogen fluoride is liquified for marketing.

In the reaction between sodium fluoride and aqueous hydrofluoric acid, all of the resulting sodium bifluoride does not precipitate, approximately 11 percent of the sodium bifluoride remains in solution. To recover these fluoride values, the filtrate from the sodium bifluoride filter is mixed with hydrated aluminum oxide to produce cryolite (Na_3AlF_6). The cryolite precipitate is subsequently filtered, dried, and bagged for sale to the aluminum industry. (A credit of $300 per ton byproduct cryolite is taken in this evaluation on the basis of prices published in Oil, Paint and Drug Reporter, July 27, 1970.)

On the basis of data selected for this evaluation, the fluorine recovered from the crude fluosilicic acid solution is 79.0 percent; however, total fluorine recovery including fluorine contained in the makeup sodium fluoride is 80.6 percent. Distribution of total fluorine by products is as follows: 66.2 percent as HF, 14.3 percent as Na_3AlF_6, 18.4 percent as waste calcine, and 1.0 percent as waste solutions.

This process is divided into five major unit operations: (1) raw materials preparation and storage, (2) acid neutralization and balling, (3) defluorination, (4) anhydrous hydrogen fluoride by production and decomposition of sodium bifluoride, and (5) cryolite recovery. Major equipment items for this

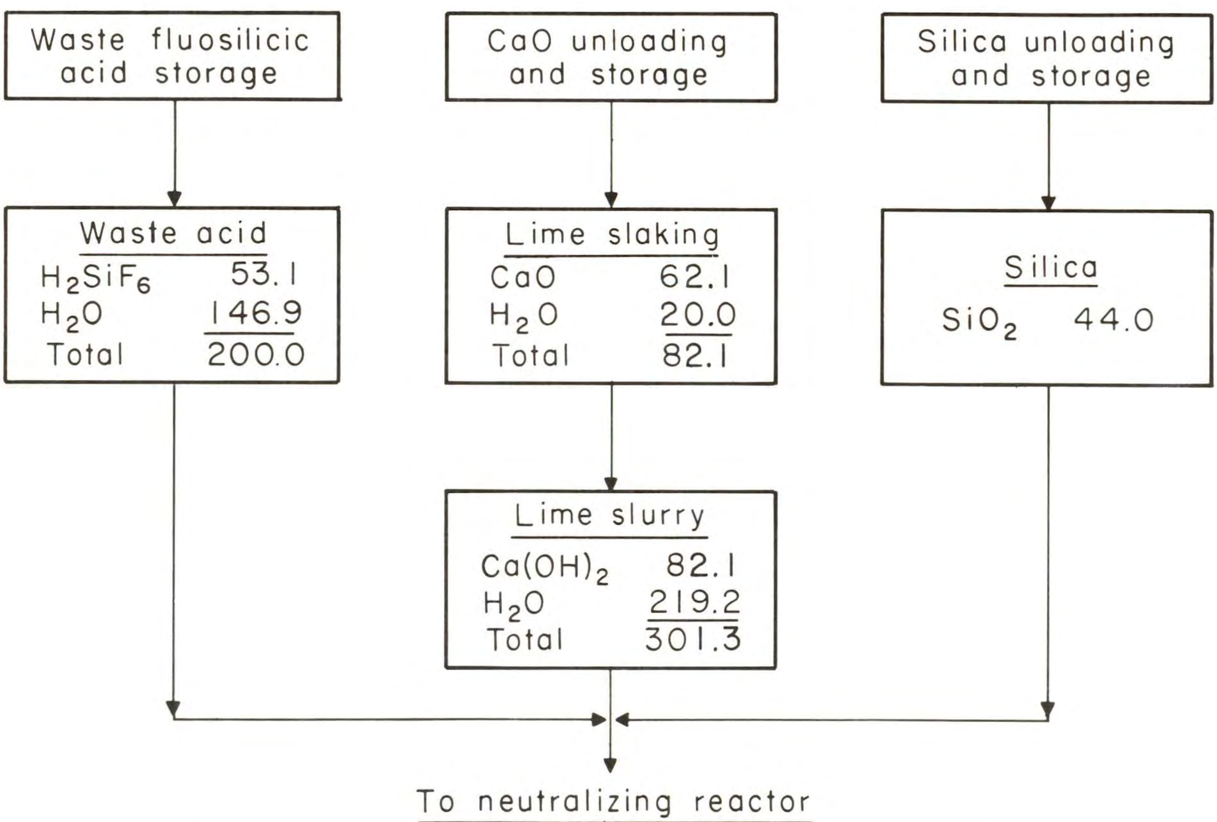

FIGURE 7. - Material Balance, Raw Materials Preparation and Storage Operation, Hydrogen Fluoride Process Without Recycle of Calcine (Tons Per Day).

process are shown in table 30. A detailed material balance and fixed capital cost are shown in figures 7 to 11 and tables 31 to 35, respectively. The operating costs for each of the units are tabulated for comparison in table 36. The annual operating costs for the integrated plant are shown in table 37, and the summary of costs and operating personnel are shown in table 38.

TABLE 30. - Major equipment for hydrogen fluoride process without recycle of calcine

Item	Number	Horsepower	Size	Capacity, each	Purpose
Rubber-lined tank.......	1	-	21 by 16 ft	40,000 gal	H_2SiF_6 storage.
Storage silo............	1	-	16 by 32 ft	4,210 cu ft	SiO_2 storage.
Storage silo............	1	-	30 by 60 ft	15,000 cu ft	CaO storage.
Lime slaker.............	1	11.5	-	95 tpd	-
Agitated tank, stainless	6	12	5 ft dia, 7 ft deep	1,000 gal	H_2SiF_6-SiO_2-CaO reactor.
Cooling tower...........	1	10	-	365 gpm	Reactor cooling.
Thickener...............	1	1.0	14 ft dia.	1,235 cu ft	PPT separation.
Disk filter.............	2	120	500 sq ft	7.0 tph	PPT dewatering.
Pelletizer dryer........	1	40.0	7 by 120 ft	15.0 tph	-
Boiler..................	1	35	-	17.0 mmBtu/hr	Steam generator.
Multiple hearth furnace.	3	225	23½ dia, 10 hearth	6.00 tpd	Defluorinating.
Barometric condenser....	1	15	5½ by 8 ft	11.0 tph	HF condenser.
Cooling tower...........	1	60	-	1,300 gpm	HF condensate cooler.
Agitated tank, stainless	2	3.0	5 by 4½ ft	660 gal	NaF-HF reactor.
Thickener...............	1	1	12 ft	905 cu ft	$NaHF_2$ separation.
Disk filter.............	1	60	500 sq ft	5.0 tph	$NaHF_2$ dewatering.
Dryer...................	1	25	5 by 48 ft	5.00 tph	$NaHF_2$ dryer.
Rotary kiln.............	1	35	5 by 35 ft	5.0 tph	$NaHF_2$ decomposition kiln.
Agitated tank, stainless	3	4.5	5 by 4½ ft	660 gal	Cryolite reactor.
Thickener...............	1	1.0	14 ft	1,235 cu ft	Cryolite separation.
Disk filter.............	1	13	200 sq ft	0.75 tph	Cryolite dewatering.
Rotary dryer............	1	5	2 by 16 ft	0.75 tph	Cryolite dryer.

Raw Materials Preparation and Storage

The raw materials for this process include the crude fluosilicic acid which is stored in a 40,000 gallon rubber-lined tank, a finely sized silica and pebble lime, which are received by rail and elevated to 4,210 cubic feet and 15,000 cubic feet storage silos, respectively. The pebble lime is fed from this silo and slaked at the rate of 62.1 tons per day to produce a calcium hydroxide slurry.

TABLE 31. - Fixed capital cost summary for raw material preparation and storage operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
UNLOAD HOPPER		2	6300.	800.	7100.
BUCKET ELEVATOR		2	8500.	1900.	10400.
LIME STORAGE BIN		1	9000.	1100.	10100.
FEED-O-WEIGHT		2	6600.	700.	7300.
BELT CONVEYOR		1	5300.	1200.	6500.
LIME SLAKER		1	22100.	2700.	24800.
SLAKED LIME MIXER		1	12900.	1500.	14400.
LIME FEED SYSTEM		1	300.	0.	300.
LIME SLURRY PUMP		1	1100.	100.	1200.
STORE TANK H2SIF6		1	27900.	1700.	29600.
STORE BIN SILICA		1	4600.	600.	5200.
TOTAL			104600.	12300.	116900.
FOUNDATIONS	.050				5200.
STRUCTURES	.060				6300.
BUILDINGS	.100				10500.
INSULATION	.000				0.
INSTRUMENTATION	.040				4200.
ELECTRICAL WORK	.140				14600.
PIPING	.150				15700.
PAINTING	.020				2100.
MISCELLANEOUS	.100				10500.
TOTAL	.660				69100.
TOTAL DIRECT CONSTRUCTION COST					186000.
INDIRECT COST, CONTINGENCY, AND FEE			.400		74400.
INTEREST DURING CONSTRUCTION			.018		4700.
TOTAL FIXED CAPITAL COST					265100.

Acid Neutralization and Balling

The crude fluosilicic acid solution and calcium hydroxide slurry are pumped to six 133-cubic-foot enclosed agitator reactors and mixed with silica fed from the storage silo. The reactors are operated in series and provide a 1-hour retention time. This reaction is exothermic and the temperature is maintained at 200° F by circulating cooling water through internal lead coils. The circulating water is cooled in a 152,000 Btu minute cooling tower. The reactors are discharged into a thickener whose primary function is to absorb surges. Thickener underflow is processed with two 500-square-foot disk filters. The filtrate is discarded and the cake is conveyed to a storage bin from which it is further conveyed to a combination balling and drying kiln. This unit removes approximately 70 percent of the moisture and agglomerates the solids into balls suitable for feed to the defluorination furnace.

TABLE 32. - Fixed capital cost summary for acid neutralization and balling operation

	NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST				
PUMP, MECH SEAL SS	1	600.	0.	600.
REACTOR, AGIT, SS	6	18600.	2800.	21400.
COOLING TOWER	1	8000.	1600.	9600.
WATER PUMP	2	2500.	100.	2600.
THICKENER	1	5100.	800.	5900.
PUMP, RUBBER LINED	1	1300.	100.	1400.
DIAPHRAGM PUMP	1	1900.	100.	2000.
CENTRIFUGAL PUMP	1	300.	0.	300.
DISC FILTER	2	42800.	4300.	47100.
PUMP	2	2100.	100.	2200.
VACUUM PUMP	1	22600.	2300.	24900.
BLOWER	1	1400.	100.	1500.
BELT CONVEYOR FC	1	6100.	1200.	7300.
STORAGE BIN	1	2700.	300.	3000.
TABLE FEEDER	1	2600.	200.	2800.
BELT FEED	1	7900.	1600.	9500.
KILN ROTARY	1	144200.	28800.	173000.
BELT CONVEYOR	1	3200.	600.	3800.
BELT CONVEYOR	1	16400.	3300.	19700.
TOTAL		290300.	48300.	338600.
FOUNDATIONS	.080			23200.
STRUCTURES	.070			20300.
BUILDINGS	.400			116100.
INSULATION	.000			0.
INSTRUMENTATION	.030			8700.
ELECTRICAL WORK	.120			34800.
PIPING	.250			72600.
PAINTING	.010			2900.
MISCELLANEOUS	.100			29000.
TOTAL	1.060			307600.
TOTAL DIRECT CONSTRUCTION COST				646200.
INDIRECT COST, CONTINGENCY, AND FEE		.400		258500.
INTEREST DURING CONSTRUCTION		.018		16300.
TOTAL FIXED CAPITAL COST				921000.

TABLE 33. - Fixed capital cost summary for defluorination operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
BELT CONVEYOR		4	22600.	4500.	27100.
STEAM BOILER		1	48300.	9700.	58000.
MULTI HEARTH FURNA		3	896200.	179200.	1075400.
MULTICLONE D.C.		1	16100.	1600.	17700.
BELT CONVEYOR		1	3300.	700.	4000.
BELT CONVEYOR		1	7900.	1700.	9600.
DUST BIN		1	600.	100.	700.
BELT FEEDER		1	1300.	100.	1400.
SCREW CONVEYOR		3	3400.	700.	4100.
BUCKET ELEVATOR		1	4100.	900.	5000.
STORAGE BIN + GATE		1	3200.	400.	3600.
TOWER COOLING		1	13300.	2700.	16000.
PUMP WATER		2	3100.	600.	3700.
TANK PLASTIC LINE		3	44400.	5300.	49700.
SOLUTION PUMP		3	5600.	300.	5900.
PACKED TOWER,PB L.		1	3800.	800.	4600.
TOTAL			1077200.	209300.	1286500.
DUMP TRUCK		1	17700.	0.	17700.
TOTAL			17700.	0.	17700.
FOUNDATIONS	.080				86200.
STRUCTURES	.060				64600.
BUILDINGS	.150				161600.
INSULATION	.000				0.
INSTRUMENTATION	.050				53900.
ELECTRICAL WORK	.050				53900.
PIPING	.070				75400.
PAINTING	.015				16200.
MISCELLANEOUS	.100				107700.
TOTAL	.575				619500.
TOTAL DIRECT CONSTRUCTION COST					1923700.
INDIRECT COST, CONTINGENCY, AND FEE			.400		769500.
INTEREST DURING CONSTRUCTION			.018		48500.
TOTAL FIXED CAPITAL COST					2741700.

TABLE 34. - Fixed capital cost summary for anhydrous HF production operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
REACTOR, AGIT. SS		2	4200.	600.	4800.
THICKENER		1	5000.	700.	5700.
DISC FILTER		1	21400.	2100.	23500.
VACUUM PUMP		1	14500.	1400.	15900.
BLOWER		1	900.	100.	1000.
ROTARY KILN		1	37400.	7500.	44900.
FAN		1	700.	100.	800.
WET CYCLONE D.C.		1	1000.	200.	1200.
ROTARY KILN		1	43100.	21600.	64700.
FAN		1	700.	100.	800.
ELECTROSTATIC PPTR		1	3700.	400.	4100.
HEAT EXCHANGER		1	3900.	500.	4400.
HEAT EXCHANGER		1	1500.	200.	1700.
REFRIG UNIT		1	9000.	1300.	10300.
BINS AND HOPPERS		5	10600.	1300.	11900.
MATERIALS HANDLING		13	49900.	9300.	59200.
PUMPS		7	4900.	300.	5200.
TOTAL			212400.	47700.	260100.
FORK LIFT		1	6200.	0.	6200.
TOTAL			6200.	0.	6200.
FOUNDATIONS	.080				17000.
STRUCTURES	.070				14900.
BUILDINGS	.400				85000.
INSULATION	.000				0.
INSTRUMENTATION	.040				8500.
ELECTRICAL WORK	.080				17000.
PIPING	.160				34000.
PAINTING	.015				3200.
MISCELLANEOUS	.100				21200.
TOTAL	.945				200800.
TOTAL DIRECT CONSTRUCTION COST					467100.
INDIRECT COST, CONTINGENCY, AND FEE		.400			186800.
INTEREST DURING CONSTRUCTION		.018			11800.
TOTAL FIXED CAPITAL COST					665700.

TABLE 35. - Fixed capital cost summary for cryolite recovery operation

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
UNLOAD HOPPER		1	3200.	400.	3600.
BUCKET ELEVATOR		1	4200.	900.	5100.
STORAGE BIN		1	2700.	300.	3000.
FEED-O-WEIGHT		1	3300.	300.	3600.
BELT CONVEYOR		1	7800.	1700.	9500.
REACTOR, SS		3	6200.	900.	7100.
STORAGE TANK		1	1100.	100.	1200.
GEAR PUMP		1	200.	0.	200.
THICKENER		1	5000.	700.	5700.
DIAPHRAGM PUMP		1	1300.	100.	1400.
CENTRIFUGAL PUMP		1	300.	0.	300.
DISC FILTER		1	7700.	800.	8500.
VACUUM PUMP		1	3900.	400.	4300.
BLOWER		1	300.	0.	300.
FILTRATE PUMP		1	300.	0.	300.
BELT CONVEYOR		1	5300.	1200.	6500.
STORAGE BIN		1	2700.	300.	3000.
TABLE FEEDER		1	2600.	200.	2800.
BELT CONVEYOR		1	3500.	800.	4300.
ROTARY KILN		1	11200.	2200.	13400.
FAN		1	200.	0.	200.
ELECTROSTATIC PPTR		1	3700.	400.	4100.
BUCKET ELEVATOR		1	3500.	400.	3900.
STORAGE BIN		1	1000.	100.	1100.
BAGGING MACHINE		1	5000.	500.	5500.
TOTAL			86200.	12700.	98900.
FORK LIFT		1	6200.	0.	6200.
TOTAL			6200.	0.	6200.
FOUNDATIONS	.080				6900.
STRUCTURES	.070				6000.
BUILDINGS	.400				34500.
INSULATION	.000				0.
INSTRUMENTATION	.040				3400.
ELECTRICAL WORK	.080				6900.
PIPING	.160				13800.
PAINTING	.015				1300.
MISCELLANEOUS	.100				8600.
TOTAL	.945				81400.
TOTAL DIRECT CONSTRUCTION COST					186500.
INDIRECT COST, CONTINGENCY, AND FEE	.400				74600.
INTEREST DURING CONSTRUCTION	.018				4700.
TOTAL FIXED CAPITAL COST					265800.

TABLE 36. - Annual operating cost of unit operations for HF process

	RAW MATERIAL PREP, STORE	ACID NEUT. + BALLING	DEFLUORINATE	ANHYDROUS HF PRODUCTION	CRYOLITE RECOVERY
DIRECT COST					
MATERIALS					
CA O	388100.	0.	0.	0.	0.
SILICA	677600.	0.	0.	0.	0.
AL2O3.3H2O	0.	0.	0.	0.	127700.
NAF	0.	0.	0.	0.	1037400.
(TOTAL MATERIALS)	(1065700.)	(0.)	(0.)	0.)	(1165100.)
UTILITIES					
ELECTRICITY, 440 V.(LOW)	2100.	21900.	34100.	13600.	3400.
NATURAL GAS, CONSUMED	0.	34800.	130900.	15700.	1400.
WATER	13000.	4600.	14500.	2600.	0.
(TOTAL UTILITIES)	(15100.)	(61300.)	(179500.)	31900.)	(4800.)
TOTAL	1080800.	61300.	179500.	31900.	1169900.
DIRECT LABOR					
LABOR 3.600/MAN HOUR	15700.	63600.	86100.	62900.	78600.
SUPERVISION .150	2400.	9500.	12900.	9400.	11800.
TOTAL	18100.	73100.	99000.	72300.	90400.
PLANT MAINTENANCE					
LABOR	5200.	27100.	80800.	19600.	7800.
SUPERVISION .200	1000.	5400.	16200.	3900.	1600.
MATERIALS	5200.	27100.	80800.	19600.	7800.
TOTAL	11400.	59600.	177800.	43100.	17200.
PAYROLL OVERHEAD .250	6100.	26400.	49000.	24000.	25000.
OPERATING SUPPLIES .200	2300.	11900.	35600.	8600.	3400.
TOTAL DIRECT COST	1118700.	232300.	540900.	179900.	1305900.
INDIRECT COST					
ADMINISTRATION AND OVERHEAD					
UNITS .45719	14500.	66100.	143000.	56700.	50700.
FIXED COST					
TAXES AND INSURANCE .020	5200.	18100.	53900.	13100.	5200.
DEPRECIATION 12.500 YR	21200.	73700.	219300.	53300.	21300.
TOTAL	26400.	91800.	273200.	66400.	26500.
TOTAL ANNUAL COST	1159600.	390200.	957100.	303000.	1383100.

TABLE 37. - Annual operating cost for HF process

	ANNUAL CONSUMPTION	UNIT COST	TOTAL OPERATION DOLLARS	PERCENT
DIRECT COST				
MATERIALS				
CA O	21560.0TON	18.00	388100.	9.25
SILICA	15400.0TON	44.00	677600.	16.16
AL2O3.3H2O	1645.0TON	77.60	127700.	3.05
NAF	2660.0TON	390.00	1037400.	24.74
(TOTAL MATERIALS)		(	2230800.	53.20)
UTILITIES				
ELECTRICITY	5304.9966 MKWHR	10.00	53000.	1.26
NATURAL GAS, CONSUMED	438360.0 MCF	.40	175300.	4.18
(TOTAL UTILITIES		(	228300.	5.44)
TOTAL			2459100.	58.64
DIRECT LABOR				
LABOR 3.600/MAN HOUR			306900.	7.32
SUPERVISION .150			46000.	1.10
TOTAL			352900.	8.42
PLANT MAINTENANCE				
LABOR			140500.	3.35
SUPERVISION .200			28100.	.67
MATERIALS			140500.	3.35
TOTAL			309100.	7.37
PAYROLL OVERHEAD .250			130500.	3.11
OPERATING SUPPLIES .200			61800.	1.47
TOTAL DIRECT COST			3313400.	79.01
INDIRECT COST				
ADMINISTRATION AND OVERHEAD				
OVERALL .400			289500.	6.90
FIXED COST				
TAXES AND INSURANCE .020			115800.	2.76
DEPRECIATION 12.500 YR			474300.	11.33
TOTAL			590100.	14.07
TOTAL ANNUAL OPERATING COST			4193000.	100.00

TABLE 38. - Summary of costs and operating personnel for HF process

	NUMBER OF OPERATORS	CAPITAL COST	ANNUAL OPERATING COST	PERCENT ANNUAL OPERATING COST	UNIT PRODUCTION COST,$/LB HF
RAW MATERIAL PREP, STORE	2.1	265100.	1159600.	27.66	.05226
ACID NEUT. + BALLING	8.5	921000.	390200.	9.31	.01758
DEFLUORINATE	11.5	2741700.	957100.	22.83	.04313
ANHYDROUS HF PRODUCTION	8.4	665700.	303000.	7.23	.01365
CRYOLITE RECOVERY	10.5	265800.	1383100.	32.99	.06233
FACILITIES, 10.PCT		485900.			
UTILITIES, 12.PCT		582800.			
TOTAL FIXED CAPITAL		5928000.			
WORKING CAPITAL		1195000.			
TOTAL	41.0	7123000.	4193000.	100.00	.18896
BYPRODUCTS			1260000.		
OPERATING COST LESS BYPRODUCT CREDIT, OB			2933000.		.13218
OB LESS DEPRECIATION, OD			2458800.		
RATE OF RETURN = .200000					
CASH FLOW = 1559800., OD + CASH FLOW =			4018600.		.18110
RATE OF RETURN = .250000					
CASH FLOW = 1877800., OD + CASH FLOW =			4336600.		.19543
RATE OF RETURN = .300000					
CASH FLOW = 2206500., OD + CASH FLOW =			4665300.		.21024
RATE OF RETURN = .350000					
CASH FLOW = 2543000., OD + CASH FLOW =			5001800.		.22541
SELLING PRICE, $ 490.000/TON					
RATE OF RETURN = .413433					
CASH FLOW = 2977700., OD + CASH FLOW =			5436500.		.24500

Defluorination

The agglomerated feed from the previous unit is conveyed directly to a distributor that feeds three multiple-hearth defluorination furnaces. These furnaces are 23.5 feet in diameter with 10 hearths and are heated by gas-fired radiation tubes. All metal parts are constructed of 446 stainless steel. A multiple hearth furnace was selected for this commercial defluorination operation because an indirect fixed rotary kiln such as used in the laboratory could not be scaled to satisfy the needs of the operation. The feed is heated by a combination of radiant heat from the kiln's radiation tubes and direct heat from the superheated steam injected into the bottom hearth. Under these conditions, the fluorides in the feed are hydrolyzed and hydrogen fluoride is vaporized and ducted out of the kiln. The residual calcine is trucked to a disposal area for discard.

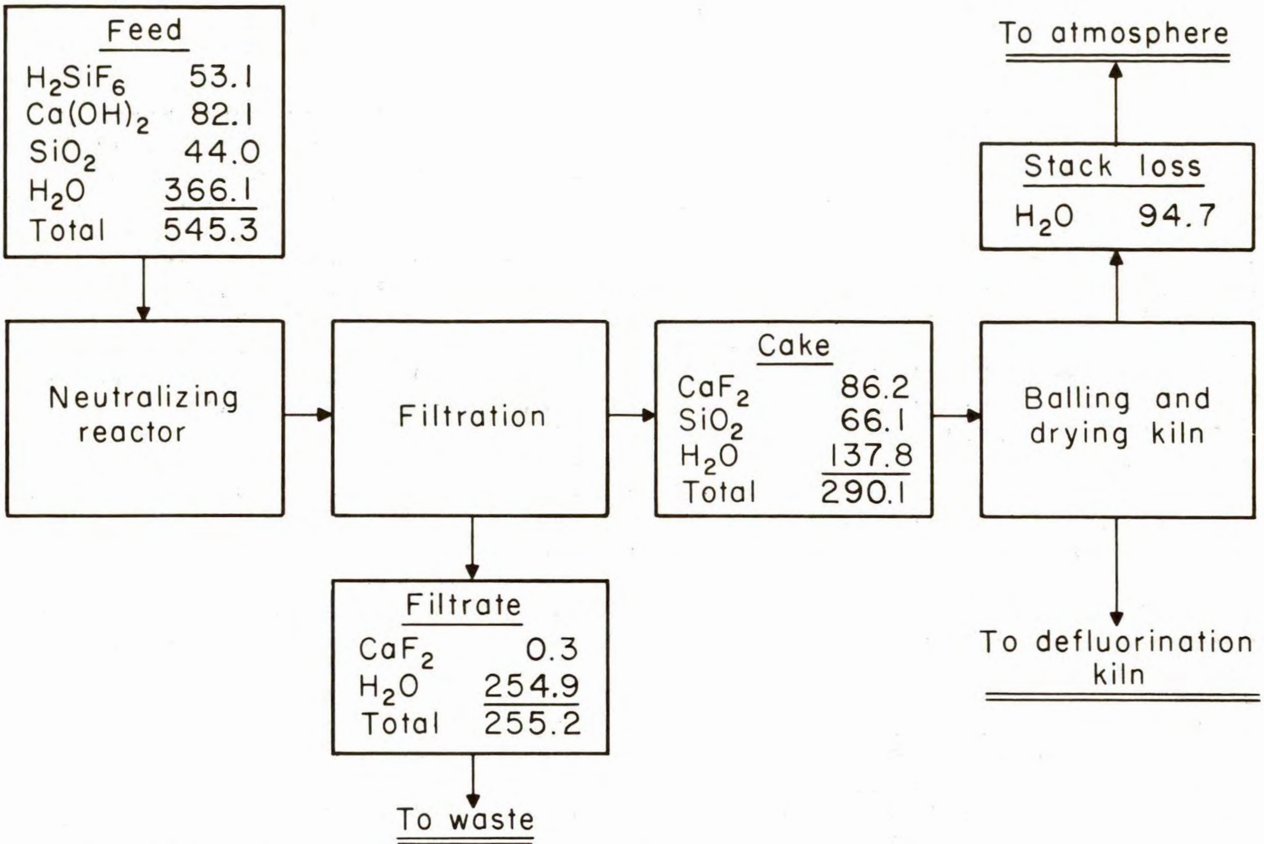

FIGURE 8. - Material Balance, Acid Neutralization and Balling Operation, Hydrogen Fluoride Process Without Recycle of Calcine (Tons Per Day).

Vapors from the furnaces, consisting of steam and hydrogen fluoride, are ducted to a barometric condenser and cooled with recirculating condensate, which in turn is cooled in a heat exchanger in conjunction with a 321,000-Btu/minute cooling tower. Condensate from this operation is a silica-free solution containing 12 to 15 percent hydrogen fluoride.

Anhydrous Hydrogen Fluoride Production

The condensate from the defluorination operation is pumped to two enclosed agitated reactors where it is combined with recycle and makeup sodium fluoride. These reactors are operated in series to provide a 20-minute retention time. Reactor discharge is settled in a 14-foot thickener, which serves primarily as a reserve surge reservoir. Thickener underflow is pumped to a 500-square-foot disk filter. Filtrate, together with thickener overflow, is pumped to the cryolite operation for recovery of the soluble sodium bifluoride. Filter cake is conveyed to a storage bin, from which it is fed to a 5- by 48-foot rotary dryer operated at approximately 150° C. The dried product is conveyed to another storage bin from which it is fed to a 5- by 35-foot indirect-fired rotary kiln operated at 400° C to decompose the sodium bifluoride.

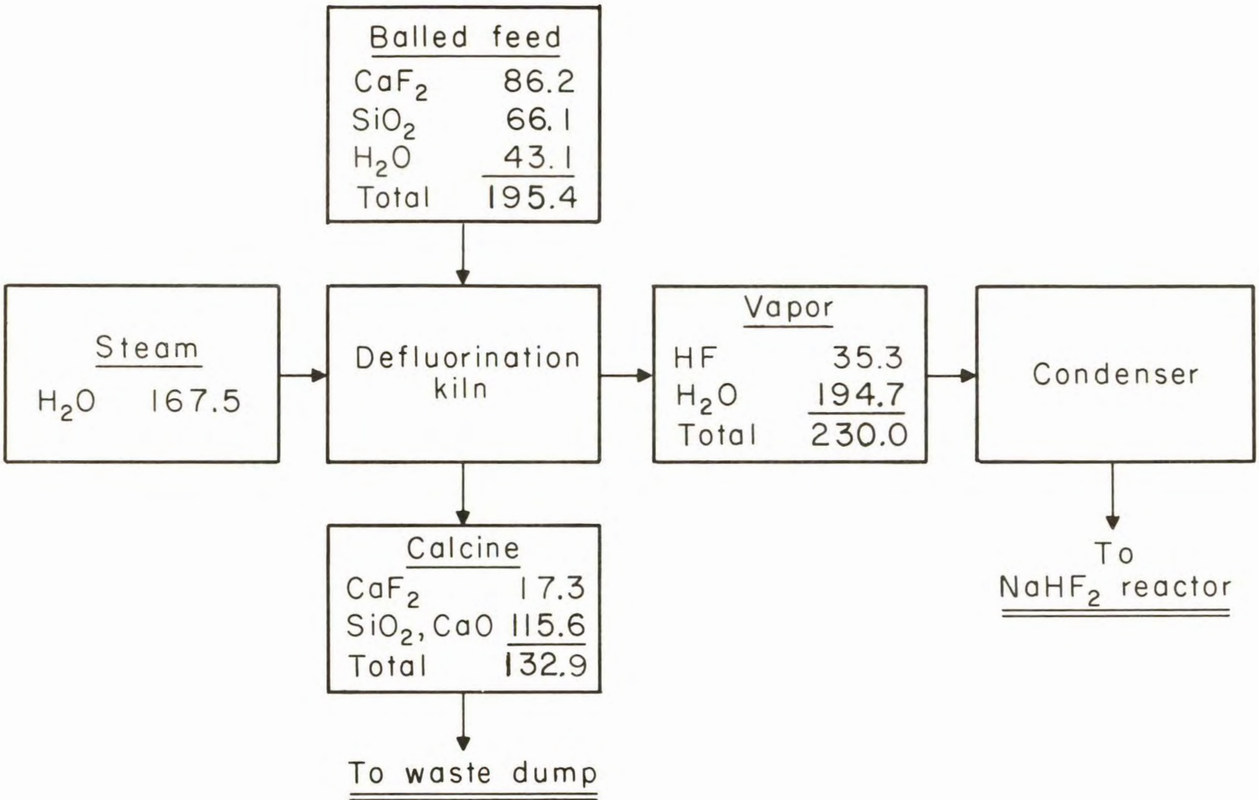

FIGURE 9. - Material Balance, Defluorination Operation, Hydrogen Fluoride Process Without Recycle of Calcine (Tons Per Day).

The decomposition products from this kiln are sodium fluoride and anhydrous hydrogen fluoride. The sodium fluoride is recycled to a storage bin, from which is is fed to the sodium bifluoride reactors, and the anhydrous hydrogen fluoride is liquified by a 6-ton refrigeration unit and loaded into steel bottles for marketing.

Cryolite Recovery

The fluorine values contained in the filtrate from the sodium bifluoride filtration are recovered by mixing this filtrate with hydrated alumina to form insoluble cryolite. This reaction is accomplished in three enclosed agitated reactors, which are operated in series to provide a 30-minute retention time. These reactors are charged continuously with filtrate, pumped from the sodium bifluoride operation, and hydrated alumina, conveyed from a storage bin. Reactor discharge slurry is settled in a 14-foot thickener whose main purpose is to provide reserve storage capacity. Cryolite in the thickener underflow is dewatered with a 200-square-foot disk filter. Filtrate joins the overflow from the thickener and is pumped to a waste disposal area. Cryolite filter cake is conveyed to a storage bin from which it is fed to a 2- by 16-foot rotary dryer operated at approximately 150° C. Dried cryolite is conveyed to a storage bin from which it is fed to a weighing and bagging machine.

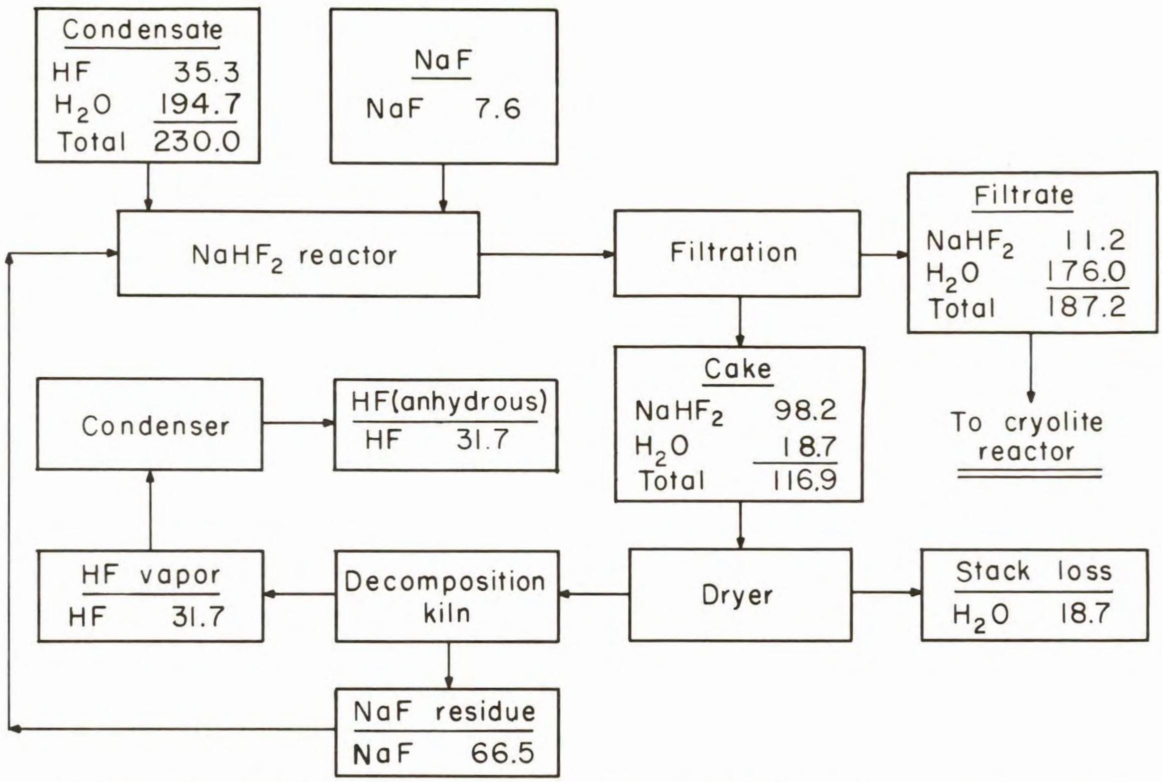

FIGURE 10. - Material Balance, Anhydrous Hydrogen Fluoride Operation, Hydrogen Fluoride Process Without Recycle of Calcine (Tons Per Day).

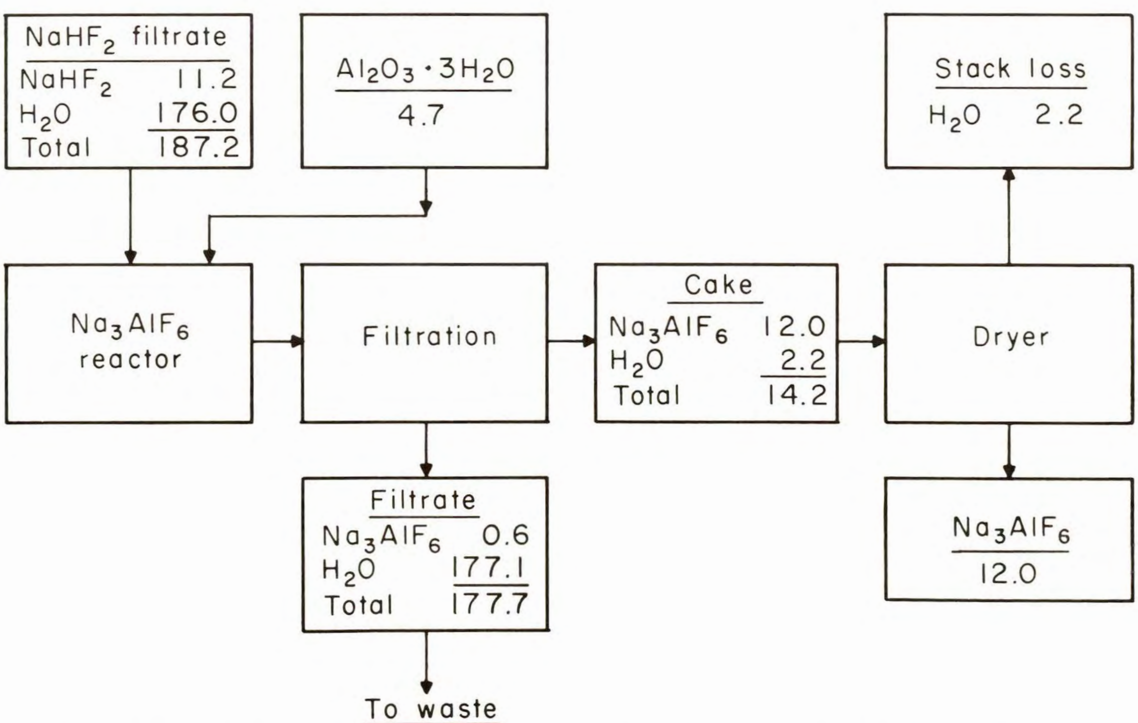

FIGURE 11. - Material Balance, Cryolite Operation, Hydrogen Fluoride Process Without Recycle of Calcine (Tons Per Day).

HYDROGEN FLUORIDE PROCESS WITH PARTIAL RECYCLE OF CALCINE

This process is identical to the first hydrogen fluoride process except that a portion of the calcine from the defluorination operation is used in the neutralization of the crude fluosilicic acid. This change eliminates 55.4 percent of the calcium hydroxide and all of the silica previously required for this operation. It increases the recovery of fluorine from the crude fluosilicic acid from 79.0 to 92.3 percent. Total fluorine recovery, including the fluorine contained in the makeup sodium fluoride is increased from 80.6 to 92.9 percent. Distribution of total fluorine in each product is as follows: 76.6 percent as HF, 16.3 percent as Na_3AlF_6, 5.8 percent as waste calcine, and 1.2 percent as waste solutions.

Implementation of this process increases the bulk of solids handled in the neutralization and defluorination operations and necessitates an increase in the size of the processing equipment. Also, increased fluoride recovery necessitates larger equipment in the fluorine recovery operations. The major equipment items required for this process are shown in table 39. Changes in the equipment size can be determined by comparing this table with the one from the previous hydrogen fluoride process. The detailed material balance and fixed capital cost estimates for each of the 5-unit operations are shown sequentially in figures 12 to 16, and tables 40 to 44, respectively. The unit

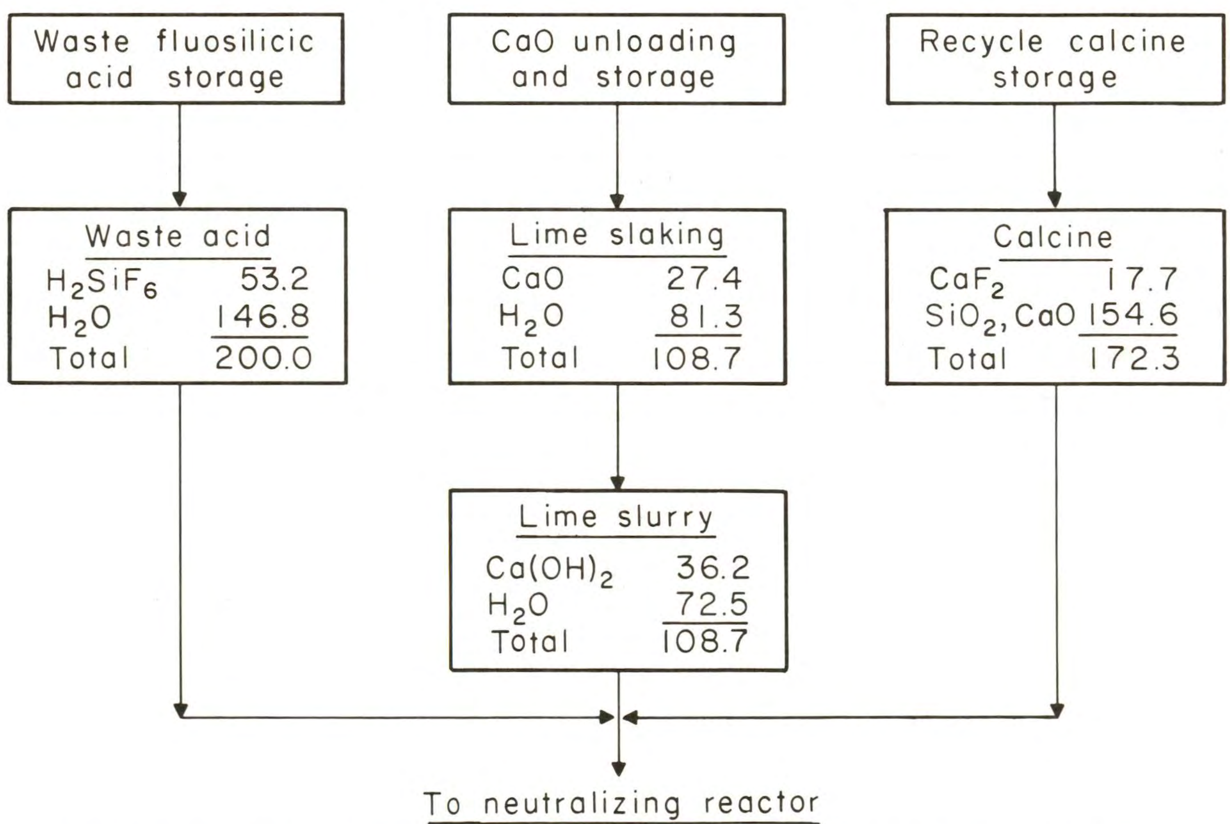

FIGURE 12. - Material Balance, Raw Materials Storage Operation, Hydrogen Fluoride Recovery Process-Calcine Recycle Alternate (Tons Per Day).

operating costs are tabulated for comparison in table 45. The annual operating costs are summarized in table 46, and the summary of costs and operating personnel is shown in table 47.

TABLE 39. - Major equipment for HF process with partial recycle of calcine

Item	Number	Horsepower	Size	Capacity, each	Purpose
Rubber-lined tank.......	1	-	21 by 16 ft	40,000 gal	H_2SiF_6 storage.
Storage silo............	1	-	14 by 28 ft	3,000 cu ft	Slag storage.
Storage silo............	1	-	30 by 60 ft	15,000 cu ft	CaO storage.
Lime slaker.............	1	6	-	36 tpd	-
Hammer mill.............	1	50	30 by 24 in	8.0 tph	Recycle residue pulverizer.
Agitated tank, stainless	10	20	5 ft dia, 7 ft deep	1,000 gal	H_2SiF_6-CaO-$CaSiO_3$ reactor.
Cooling tower...........	1	30	-	700 gpm	Reactor cooling.
Thickener...............	1	1.0	14 ft dia	1,235 cu ft	PPT separation.
Disk filter.............	3	180	500 sq ft	7.0 tph	PPT dewatering.
Pelletizer dryer........	1	55	8 by 140 ft	20.0 tph	-
Boiler..................	1	55	-	31 mmBtu/hr	Steam generator.
Multiple hearth furnace.	5	325	21½ ft dia, 10 hearth	5.0 tpd	Defluorinating.
Barometric condenser....	2	22.5	5½ by 8 ft	8.0 tph	HF condenser.
Cooling tower...........	1	90	-	1,870 gpm	HF condensate cooler.
Agitated tank, stainless	2	4.0	5 by 7 ft	1,000 gal	NaF-HF reactor.
Thickener...............	1	1.0	16 ft	1,640 cu ft	$NaHF_2$ separation.
Disk filter.............	1	60.0	500 sq ft	6.0 tph	$NaHF_2$ dewatering.
Dryer...................	1	35	5 by 55 ft	6.0 tph	$NaHF_2$ dryer.
Rotary kiln.............	1	40	5 by 40 ft	5.0 tph	$NaHF_2$ decomposition kiln.
Agitated tank, stainless	3	6.0	5 by 5 ft	700 gal	Cryolyte reactor.
Thickener...............	1	1.0	18 ft	2,000 cu ft	Cryolyte separation.
Disk filter.............	1	20.0	300 sq ft	0.75 tph	Cryolyte dewatering.
Rotary dryer............	1	6	2 by 20 ft	0.75 tph	Cryolyte dryer.

TABLE 40. - Fixed capital cost summary for raw material preparation and storage operation, alternate HF process

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
HOPPER, UNLOADING		1	3200.	400.	3600.
BUCKET ELEVATOR		1	4300.	900.	5200.
BIN CAOH STORAGE		1	9000.	1100.	10100.
FEED O WEIGHT		2	6600.	700.	7300.
SLAKER, LIME		1	12300.	1500.	13800.
MIXER SLAKED LIME		1	7200.	900.	8100.
PUMP LIME SLURRY		1	1100.	100.	1200.
LIME FEED SYSTEM		1	300.	0.	300.
STORE TANK H2SIF6		1	27900.	1700.	29600.
PUMP S.S.1.5X1.5I		1	600.	0.	600.
BELT CONVEYOR		1	5300.	1100.	6400.
HAMMER MILL 30X24		1	10200.	2000.	12200.
BELT CONVEYOR		1	9800.	2000.	11800.
BIN SLAG STORAGE		1	4600.	600.	5200.
TOTAL			102400.	13000.	115400.
FOUNDATIONS	.050				5100.
STRUCTURES	.060				6100.
BUILDINGS	.100				10200.
INSULATION	.000				0.
INSTRUMENTATION	.040				4100.
ELECTRICAL WORK	.140				14300.
PIPING	.150				15400.
PAINTING	.020				2000.
MISCELLANEOUS	.100				10200.
TOTAL	.660				67400.
TOTAL DIRECT CONSTRUCTION COST					182800.
INDIRECT COST, CONTINGENCY, AND FEE			.400		73100.
INTEREST DURING CONSTRUCTION			.018		4600.
TOTAL FIXED CAPITAL COST					260500.

TABLE 41. - Fixed capital cost summary for acid neutralization and balling operation, alternate HF process

	NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST				
REACTOR SS	10	31000.	4600.	35600.
TOWER COOLING	1	8000.	1600.	9600.
PUMP 6X5 IN WATER	2	2500.	100.	2600.
PUMP SLURRY	1	2300.	100.	2400.
THICKENER 14X8 FT	1	5100.	800.	5900.
PUMP CENTRIFUGAL	1	300.	0.	300.
PUMP 5 IN DUPLEX	1	3600.	200.	3800.
DISC FILTER 10.5X7	3	65000.	6500.	71500.
PUMP FILTRATE	3	3200.	200.	3400.
VACUUM PUMP	1	28800.	2900.	31700.
BLOWER	2	2800.	300.	3100.
BELT CONVEYOR FC	1	6100.	1200.	7300.
BIN STORAGE	1	2700.	300.	3000.
TABLE FEEDER	1	2600.	200.	2800.
BELT FEED	1	7900.	1600.	9500.
KILN ROTARY 8X140	1	197100.	39400.	236500.
BELT DUST 25FTX14	1	3200.	600.	3800.
BELT CONVEYOR	1	16400.	3300.	19700.
TOTAL		388600.	63900.	452500.
FOUNDATIONS	.080			31100.
STRUCTURES	.070			27200.
BUILDINGS	.400			155400.
INSULATION	.000			0.
INSTRUMENTATION	.030			11700.
ELECTRICAL WORK	.120			46600.
PIPING	.250			97200.
PAINTING	.010			3900.
MISCELLANEOUS	.100			38900.
TOTAL	1.060			412000.
TOTAL DIRECT CONSTRUCTION COST				864500.
INDIRECT COST, CONTINGENCY, AND FEE		.400		345800.
INTEREST DURING CONSTRUCTION		.018		21800.
TOTAL FIXED CAPITAL COST				1232100.

TABLE 42. - Fixed capital cost summary for defluorination operation, alternate HF process

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
BELT CONVEYOR		6	33900.	6800.	40700.
STEAM BOILER		1	61200.	12200.	73400.
MULTI HEARTH FURN		5	1397000.	279400.	1676400.
SCREW CONVEYOR		5	15500.	3400.	18900.
BUCKET ELEVATOR		1	4100.	900.	5000.
BIN STORAGE		1	3200.	400.	3600.
FEEDER VIBRATING		1	1100.	100.	1200.
MULTICLONE		1	23200.	2300.	25500.
BELT CONVEYOR		1	3300.	700.	4000.
BELT CONVEYOR		1	7900.	1600.	9500.
BIN DUST		1	600.	100.	700.
BELT FEEDER		1	800.	100.	900.
TOWER COOLING		1	16600.	3300.	19900.
PUMP WATER		2	4000.	200.	4200.
TANK PLASTIC LINE		3	60200.	7200.	67400.
PUMP S.S.		3	9700.	600.	10300.
TOWER PB LINED		2	10400.	2100.	12500.
TOTAL			1652700.	321400.	1974100.
DUMP TRUCK		1	22800.	0.	22800.
TOTAL			22800.	0.	22800.
FOUNDATIONS	.080				132200.
STRUCTURES	.060				99200.
BUILDINGS	.150				247900.
INSULATION	.000				0.
INSTRUMENTATION	.050				82600.
ELECTRICAL WORK	.050				82600.
PIPING	.070				115700.
PAINTING	.015				24800.
MISCELLANEOUS	.100				165300.
TOTAL	.575				950300.
TOTAL DIRECT CONSTRUCTION COST					2947200.
INDIRECT COST, CONTINGENCY, AND FEE				.400	1178900.
INTEREST DURING CONSTRUCTION				.018	74300.
TOTAL FIXED CAPITAL COST					4200400.

TABLE 43. - Fixed capital cost summary for anhydrous HF production operation, alternate HF process

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
REACTOR S.S.		2	5100.	800.	5900.
THICKENER		1	5700.	900.	6600.
DISC FILTER		1	21400.	2100.	23500.
VACUUM PUMP		1	14500.	1400.	15900.
BLOWER		1	900.	100.	1000.
KILN ROTARY		1	41200.	8200.	49400.
FAN DRAFT		1	800.	100.	900.
WET CYCLONE, DUST		1	1000.	200.	1200.
KILN ROTARY		1	46900.	23500.	70400.
FAN DRAFT		1	800.	100.	900.
ELECT DUST COLLECT		1	3700.	400.	4100.
HEAT EXCHANGER		1	4100.	500.	4600.
HEAT EXCHANGER		1	1500.	200.	1700.
REFRIGERATION UNIT		1	9000.	1300.	10300.
BINS AND HOPPERS		6	11000.	1300.	12300.
MATERIALS HANDLING		13	49900.	7900.	57800.
PUMPS		6	5000.	200.	5200.
TOTAL			222500.	49200.	271700.
FORK LIFT		1	6200.	0.	6200.
TOTAL			6200.	0.	6200.
FOUNDATIONS	.080				17800.
STRUCTURES	.070				15600.
BUILDINGS	.400				89000.
INSULATION	.000				0.
INSTRUMENTATION	.040				8900.
ELECTRICAL WORK	.080				17800.
PIPING	.160				35600.
PAINTING	.015				3300.
MISCELLANEOUS	.100				22200.
TOTAL	.945				210200.
TOTAL DIRECT CONSTRUCTION COST					488100.
INDIRECT COST, CONTINGENCY, AND FEE			.400		195200.
INTEREST DURING CONSTRUCTION			.018		12300.
TOTAL FIXED CAPITAL COST					695600.

TABLE 44. - Fixed capital cost summary for cryolite recovery operation, alternate HF process

		NUMBER	MATERIAL	LABOR	TOTAL
DIRECT CONSTRUCTION COST					
TANK STORAGE		1	1500.	300.	1800.
PUMP GEAR		1	200.	0.	200.
HOPPER		1	3200.	400.	3600.
BUCKET ELEVATOR		1	4200.	900.	5100.
BIN STORAGE		1	2700.	300.	3000.
FEED O WEIGHT		1	3300.	300.	3600.
BELT CONVEYOR		1	7800.	1600.	9400.
REACTOR S.S.		3	6600.	1000.	7600.
THICKENER		1	6500.	1000.	7500.
PUMP CENTRIFUGAL		1	300.	0.	300.
PUMP DUPLEX		1	1800.	100.	1900.
DISC FILTER VACUUM		1	9900.	1000.	10900.
VACUUM PUMP		1	5000.	500.	5500.
BLOWER		1	400.	0.	400.
PUMP FILTRATE		1	500.	0.	500.
BELT CONVEYOR		1	5300.	1100.	6400.
BIN STORAGE		1	2700.	300.	3000.
TABLE FEEDER		1	2600.	200.	2800.
BELT CONVEYOR		1	3500.	700.	4200.
KILN ROTARY'DIRECT		1	12300.	2500.	14800.
FAN DRAFT		1	300.	0.	300.
ELECT DUST COLLECT		1	3700.	400.	4100.
BUCKET ELEVATOR		1	3500.	400.	3900.
BIN STORAGE		1	1000.	100.	1100.
BAG MACHINE		1	5000.	500.	5500.
TOTAL			93800.	13600.	107400.
FORK LIFT		1	6200.	0.	6200.
TOTAL			6200.	0.	6200.
FOUNDATIONS	.080				7500.
STRUCTURES	.070				6600.
BUILDINGS	.400				37500.
INSULATION	.000				0.
INSTRUMENTATION	.040				3800.
ELECTRICAL WORK	.080				7500.
PIPING	.160				15000.
PAINTING	.015				1400.
MISCELLANEOUS	.100				9400.
TOTAL	.945				88700.
TOTAL DIRECT CONSTRUCTION COST					202300.
INDIRECT COST, CONTINGENCY, AND FEE			.400		80900.
INTEREST DURING CONSTRUCTION			.018		5100.
TOTAL FIXED CAPITAL COST					288300.

TABLE 45. - Annual operating cost of unit operations for alternate HF process

	RAW MATERIAL PREP, STORE	ACID NEUT. + BALLING	DEFLUORINATE	ANHYDROUS HF PRODUCTION	CRYOLITE RECOVERY
DIRECT COST					
MATERIALS					
CA O	172600.	0.	0.	0.	0.
SILICA	0.	0.	0.	0.	0.
AL203.3H20	0.	0.	0.	0.	146700.
NAF	0.	0.	0.	0.	1201200.
(TOTAL MATERIALS)	(172600.)	(0.)	(0.)	0.)	(1347900.)
UTILITIES					
ELECTRICITY, 440 V.(LOW)	6400.	30000.	42000.	15000.	4400.
NATURAL GAS, CONSUMED	0.	51800.	198300.	17500.	1600.
WATER	19300.	4100.	23600.	2600.	0.
(TOTAL UTILITIES)	(25700.)	(85900.)	(263900.)	35100.)	(6000.)
TOTAL	198300.	85900.	263900.	35100.	1353900.
DIRECT LABOR					
LABOR 3.600/MAN HOUR	45700.	63600.	86100.	62900.	78600.
SUPERVISION .150	6900.	9500.	12900.	9400.	11800.
TOTAL	52600.	73100.	99000.	72300.	90400.
PLANT MAINTENANCE					
LABOR	5100.	36300.	123800.	20500.	8500.
SUPERVISION .200	1000.	7300.	24800.	4100.	1700.
MATERIALS	5100.	36300.	123800.	20500.	8500.
TOTAL	11200.	79900.	272400.	45100.	18700.
PAYROLL OVERHEAD .250	14700.	29200.	61900.	24200.	25200.
OPERATING SUPPLIES .200	2200.	16000.	54500.	9000.	3700.
TOTAL DIRECT COST	279000.	284100.	751700.	185700.	1491900.
INDIRECT COST					
ADMINISTRATION AND OVERHEAD					
UNITS .46320	30600.	78300.	197700.	58500.	52200.
FIXED COST					
TAXES AND INSURANCE .020	5100.	24200.	82500.	13700.	5700.
DEPRECIATION 12.500 YR	20800.	98600.	336000.	55600.	23100.
TOTAL	25900.	122800.	418500.	69300.	28800.
TOTAL ANNUAL COST	335500.	485200.	1367900.	313500.	1572900.

TABLE 46. - Annual operating cost for alternate HF process

	ANNUAL CONSUMPTION	UNIT COST	TOTAL OPERATION DOLLARS	PERCENT
DIRECT COST				
MATERIALS				
CA O	9590.0TON	18.00	172600.	4.23
SILICA	.0TON	44.00	0.	.00
AL2O3.3H2O	1890.0TON	77.60	146700.	3.60
NAF	3080.0TON	390.00	1201200.	29.48
(TOTAL MATERIALS)		(	1520500.	37.31)
UTILITIES				
ELECTRICITY	6906.4828 MKWHR	10.00	69100.	1.70
NATURAL GAS, CONSUMED	648190.0 MCF	.40	259300.	6.36
(TOTAL UTILITIES		(	328400.	8.06)
TOTAL			1848900.	45.37
DIRECT LABOR				
LABOR 3.600/MAN HOUR			336900.	8.27
SUPERVISION .150			50500.	1.24
TOTAL			387400.	9.51
PLANT MAINTENANCE				
LABOR			194200.	4.77
SUPERVISION .200			38900.	.95
MATERIALS			194200.	4.77
TOTAL			427300.	10.49
PAYROLL OVERHEAD .250			155200.	3.81
OPERATING SUPPLIES .200			85400.	2.10
TOTAL DIRECT COST			2904200.	71.27
INDIRECT COST				
ADMINISTRATION AND OVERHEAD				
OVERALL .400			360000.	8.83
FIXED COST				
TAXES AND INSURANCE .020			159200.	3.91
DEPRECIATION 12.500 YR			651600.	15.98
TOTAL			810800.	19.90
TOTAL ANNUAL OPERATING COST			4075000.	100.00

TABLE 47. - Summary of costs and operating personnel for alternate HF process

	NUMBER OF OPERATORS	CAPITAL COST	ANNUAL OPERATING COST	PERCENT ANNUAL OPERATING COST	UNIT PRODUCTION COST,$/LB HF
RAW MATERIAL PREP, STORE	6.1	260500.	335500.	8.23	.01292
ACID NEUT. + BALLING	8.5	1232100.	485200.	11.91	.01868
DEFLUORINATE	11.5	4200400.	1367900.	33.57	.05267
ANHYDROUS HF PRODUCTION	8.4	695600.	313500.	7.69	.01207
CRYOLITE RECOVERY	10.5	288300.	1572900.	38.60	.06057
FACILITIES, 10.PCT		667700.			
UTILITIES, 12.PCT		801400.			
TOTAL FIXED CAPITAL		8146000.			
WORKING CAPITAL		1091000.			
TOTAL	45.0	9237000.	4075000.	100.00	.15691

BYPRODUCTS	1459500.	
OPERATING COST LESS BYPRODUCT CREDIT, OB	2615500.	.10071
OB LESS DEPRECIATION, OD	1963800.	
RATE OF RETURN = .200000		
CASH FLOW = 2033200., OD + CASH FLOW =	3997000.	.15391
RATE OF RETURN = .250000		
CASH FLOW = 2442600., OD + CASH FLOW =	4406400.	.16967
RATE OF RETURN = .300000		
CASH FLOW = 2866700., OD + CASH FLOW =	4830500.	.18600
RATE OF RETURN = .350000		
CASH FLOW = 3301500., OD + CASH FLOW =	5265300.	.20275
SELLING PRICE, $ 490.000/TON		
RATE OF RETURN = .472898		
CASH FLOW = 4398800., OD + CASH FLOW =	6362600.	.24500

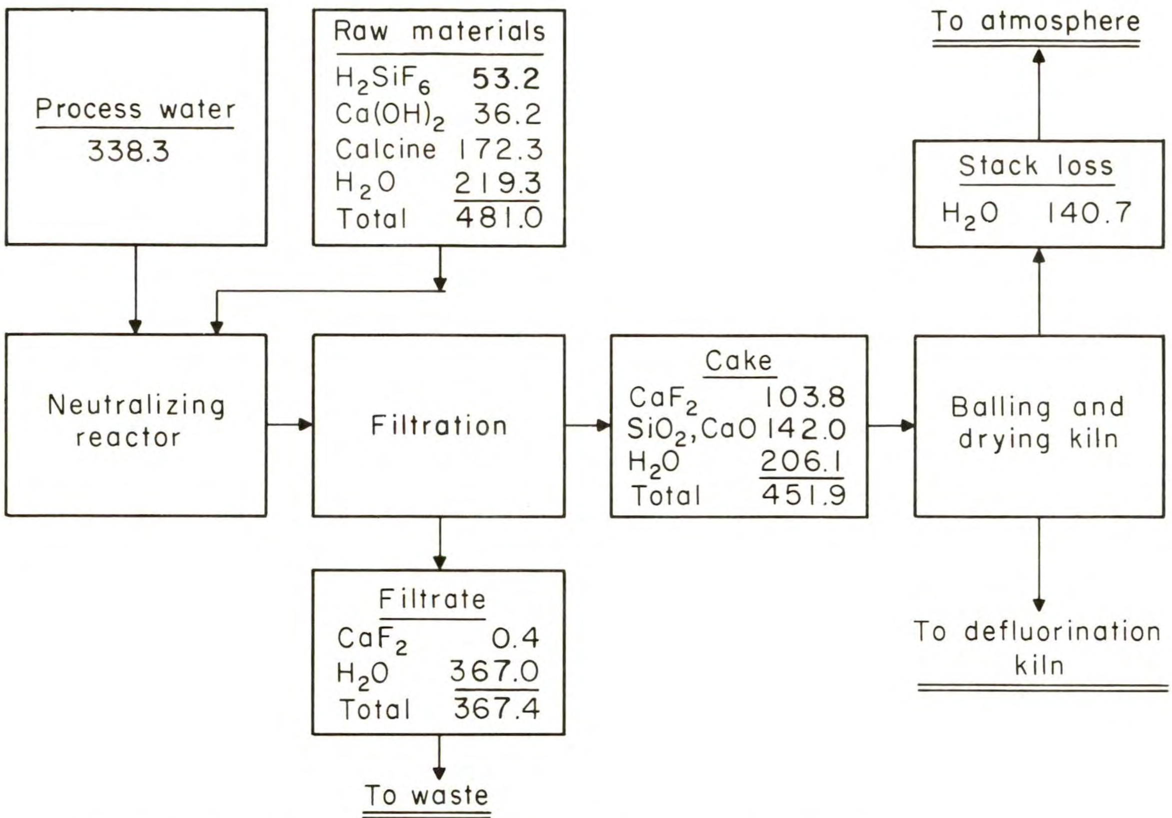

FIGURE 13. - Material Balance, Acid Neutralization and Balling Operation, Hydrogen Fluoride Recovery Process-Calcine Recycle Alternate (Tons Per Day).

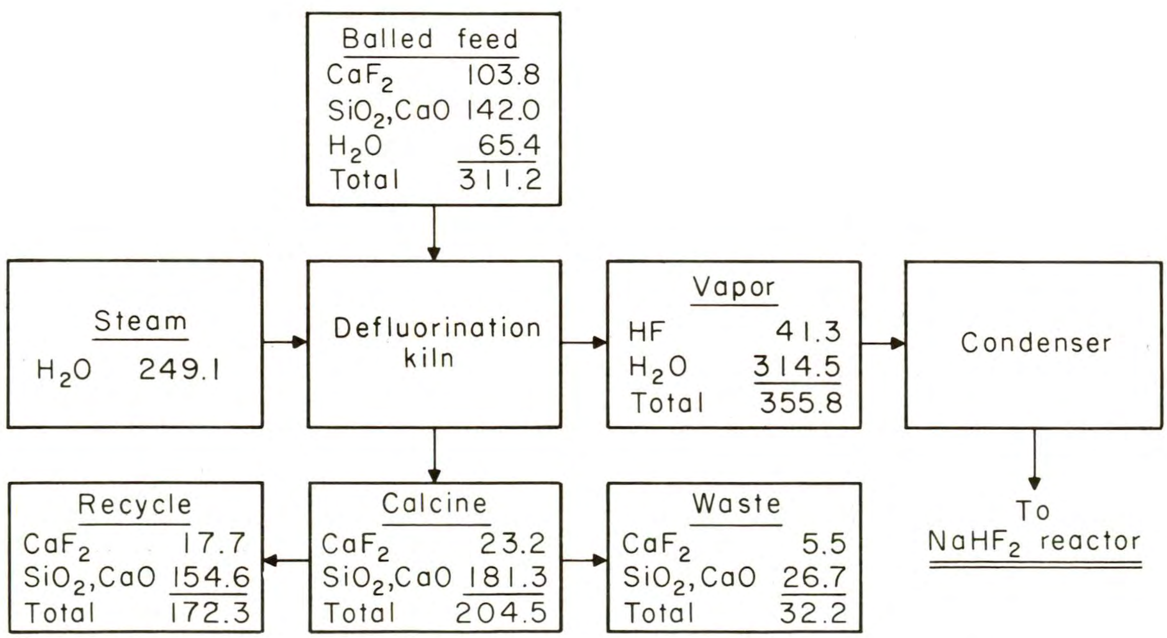

FIGURE 14. - Material Balance, Defluorination Operation, Hydrogen Fluoride Recovery Process-Calcine Recycle Alternate (Tons Per Day).

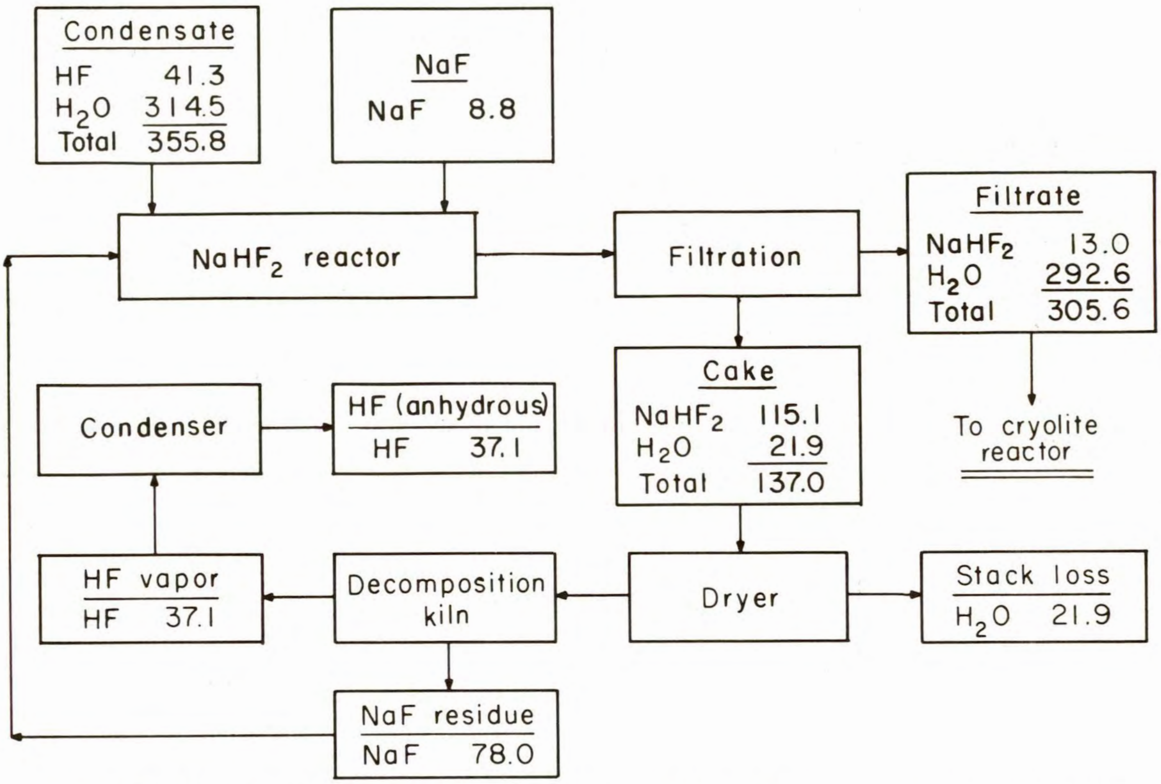

FIGURE 15. - Material Balance, Anhydrous Hydrogen Fluoride Operation, Hydrogen Fluoride Recovery Process-Calcine Recycle Alternate (Tons Per Day).

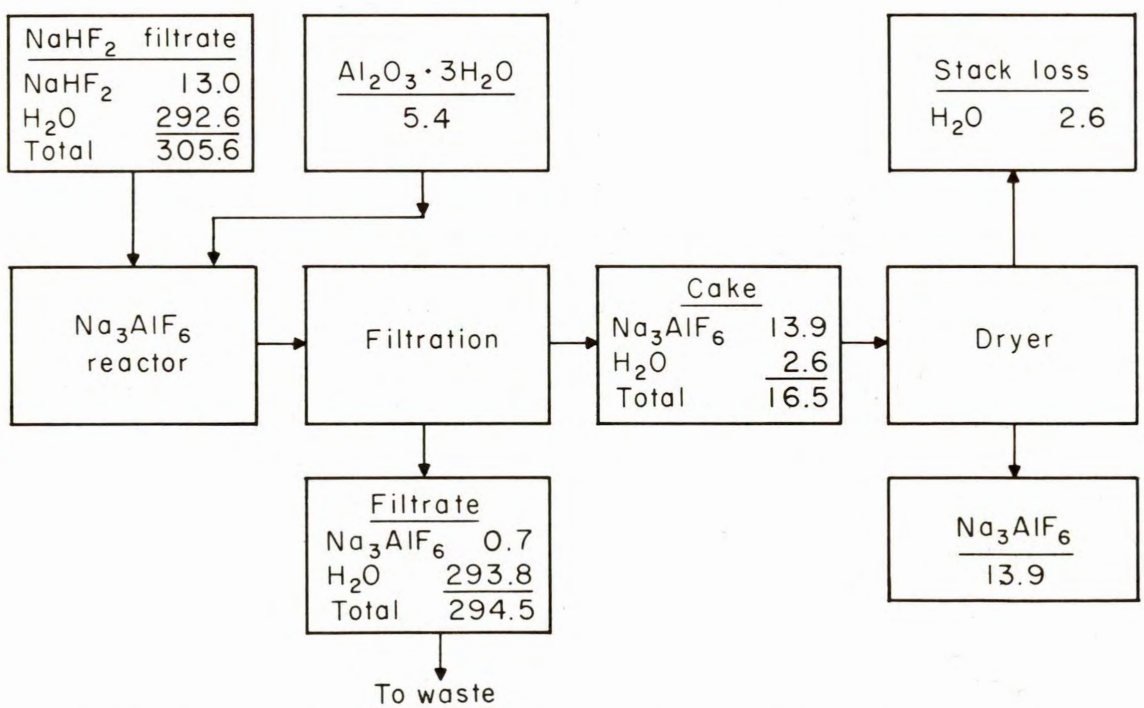

FIGURE 16. - Material Balance, Cryolite Operation, Hydrogen Fluoride Recovery Process-Calcine Recycle Alternate (Tons Per Day).

DISCUSSION AND CONCLUSIONS

When compared with current quoted prices for calcium fluoride and anhydrous hydrogen fluoride, the selling prices required to yield various rates of return on investment indicate that all processes considered could be profitable. The comparative profitability of these processes is indicated in table 48. The total capital investment and the cash flow and sales price for a 25-percent rate of return are summarized here for all processes. As another basis of comparison, the cash flow and rate of return on investment based on the current sales prices are also shown.

TABLE 48. - Comparative profitability of processes

Process	Total capital investment	Product[1] sales price, dollars per ton	Rate of return on[1] investment before taxes, pct	Cash flow	Profit before taxes, dollars per ton H_2SiF_6 processed[2]
CaF_2 process with SiO_2 recovery....	$1,642,000	$48.64	25	$431,700	$17.62
	1,642,000	[3]63.25	51	840,400	39.57
CaF_2 process with SiO_2 discard.....	1,479,000	50.64	25	388,500	15.93
	1,479,000	[3]63.25	50	741,800	34.90
HF process without calcine recycle..	7,123,000	390.86	25	1,877,800	69.16
	7,123,000	[4]490.00	41	2,997,800	129.26
HF process with calcine recycle..	9,237,000	339.34	25	2,442,600	96.19
	9,237,000	[4]490.00	47	4,398,800	201.25

[1] Data calculated with equation 1.
[2] (Cash flow - depreciation)/tons H_2SiF_6 processed.
[3] Average sales price published in Engineering and Mining Journal, July 1970.
[4] Sales price published in Oil, Paint and Drug Reporter, July 27, 1970.
[3-4] Quoted sales prices would be reduced for large volume consumers; consequently, the actual rate of return and cash flow would be less.

These tabulated costs indicate the following conclusions:

(1) The hydrogen fluoride process using calcine recycle has some advantages over that in which the calcine is discarded. The required capital investment is higher for calcine recycle; however, elimination of the silica requirement, lowering of the calcium oxide requirement, and increasing the yield of hydrogen fluoride and cryolite result in greater return on investment as well as profit per unit of fluosilicic acid treated by this process.

(2) The relative merits of the two calcium fluoride processes are not obvious from the data presented. The process with byproduct silica recovery

requires higher capital investment but this is partially compensated for through byproduct credit. In this evaluation, the byproduct credit was low because impurities in the feed result in a low-grade silica product. As a result, only a slight increase in profitability was realized. However, a premium price could be obtained for the higher grade byproduct that could be produced if pure fluosilicic acid were available at little or no added cost. This would increase the advantage of the process that recovered silica. Therefore the choice between these two processes would depend to a degree on the quality of the fluosilicic acid being treated.

(3) At the scale of operations assumed for this evaluation the hydrogen fluoride process offers a greater potential profit per unit of fluosilicic acid processed, but it also requires a much greater capital investment than the calcium fluoride process. Thus, at this scale, the calcium fluoride process with lower capital cost would be attractive only where the disposal of waste acid was of greater concern than profitability.

The availability of feed material and market demand for the product must be considered in choosing between the hydrogen fluoride and calcium fluoride processes. The rates of return on investment at current market prices for the products at the scale of operation evaluated are slightly in favor of the calcium fluoride process. However, because of the economy of size, if the same capital investment were made in the calcium fluoride process as in the hydrogen fluoride process, both the profit produced per dollar invested and rate of return on invested capital would be increased by a greater margin. Therefore, if the supply of fluosilicic acid and the market for calcium fluoride were unlimited, the calcium fluoride process would be the most economical.

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