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Increasing Fluosilicic Acid Evolution From Phosphate Rock by Digestion With Phosphoric Acid

UNITED STATES DEPARTMENT OF THE INTERIOR

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Increasing Fluosilicic Acid Evolution From Phosphate Rock by Digestion With Phosphoric Acid

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INCREASING FLUOSILICIC ACID EVOLUTION FROM PHOSPHATE ROCK BY DIGESTION WITH PHOSPHORIC ACID

by

Henry E. Blake, Jr.,[1] and Boyd D. Nash[1]

ABSTRACT

The Bureau of Mines has been engaged in a continuing research effort to develop processes for increasing the recovery and utilization of fluorine from low-grade resources.

This current research has shown that over 98 percent of the fluorine in phosphate rock is extracted when the ore is treated with excess phosphoric acid in the presence of water vapor at 150° to 180° C. More than 80 percent of the fluorine can be recovered as fluosilicic acid, which can then be converted to commercially useful hydrogen fluoride or fluorspar by previously developed Bureau processes. Extraction of P_2O_5 from the ore was about 98 percent in batch tests and 90 percent in semicyclic tests.

INTRODUCTION

The current annual U.S. demand for fluorspar (CaF_2) is about 1.5 million tons and is expected to increase to over 2 million tons by 1980. The steel industry uses about 40 percent of the total requirement of fluorspar, and nearly 55 percent is converted to hydrogen fluoride for use in the aluminum and fluorocarbon industries. Since domestic production supplies only about 20 percent of the fluorspar requirement, it is clear that an additional source of fluorine must be established (12).[2]

One such source of additional fluoride is phosphate rock, which contains 3 to 4 percent fluorine (F) (1-3, 15). It is possible that nearly 400,000 tons of fluorine could be recovered annually as a byproduct of processing phosphate rock into fertilizers, but current processing methods limit fluorine recovery from this source to less than 75,000 tons (12). Fertilizers are produced by reacting fluorapatite [$Ca_{10}(PO_4)_6F_2$] with wet-process phosphoric acid to form triple superphosphate (TSP) or by reacting phosphoric acid with ammonia to form ammonium phosphates (6, 8, 10-11, 14). When phosphate rock is treated with sulfuric acid, phosphoric acid is formed along with the

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[1] Research chemist.

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

precipitation of gypsum. It is during this stage of fertilizer production that most of the contained fluorine is lost to either the gypsum precipitate, the product acid, or both (15). Current commercial processes can be represented by the following general reaction equation:

$$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \longrightarrow \quad (1)$$
$$30[CaSO_4 \cdot 2H_2O]\downarrow + 18H_3PO_4 + H_2SiF_6.$$

Laboratory investigations by the Bureau of Mines have been directed toward an alternate method of acidulation of phosphate rock by which the fluorine is evolved before gypsum is precipitated. The most promising method investigated involved contacting the ore with excess phosphoric acid at temperatures of 150° to 180° C while injecting water into the reaction mass. By this technique, 80 to 90 percent of the fluorine is evolved and collected by water scrubbing. The generalized reaction equation can be represented as follows:

$$3[Ca_{10}(PO_4)_6F_2] + 42H_3PO_4 + SiO_2 \xrightarrow[H_2O]{150^\circ \text{ to } 180^\circ \text{ C}} \quad (2)$$
$$30Ca(H_2PO_4)_2 + H_2SiF_6 + 2H_2O.$$

The reaction mass is then dissolved in water, and gypsum is precipitated by addition of sulfate ion. The fluosilicic acid generated and collected can then be processed by procedures already developed by the Bureau of Mines (3, 9) to acid-grade CaF_2 or to commercially acceptable anhydrous HF. Alternatively, it may be converted to other marketable fluoride salts (2, 4-5, 7-8, 13, 16).

This investigation is part of an ongoing Bureau of Mines program in fluorine recovery. A future report will describe the work now in progress on a semicontinuous pilot plant.

RAW MATERIALS--ORE SAMPLES

Batch testing of the phosphoric acid-water vapor acidulation method was for the most part conducted on a typical western U.S. phosphate ore concentrate but was also applied to other ores and products from several sources. A list of these ores and analyses are shown in table 1.

TABLE 1. - Analyses of various phosphate ores and products[1]

Sample	Phosphate ore or product	Composition, percent								
		P_2O_5	SiO_2	CaO	F	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O
1	Dry Valley, low grade.......	15.6	33.5	25.5	1.88	2.30	2.22	0.55	0.76	1.75
2	Dry Valley, medium grade....	20.8	28.0	28.8	2.27	2.14	1.90	.60	.51	1.80
3	Dry Valley, high grade......	29.8	19.4	38.8	3.23	1.75	1.15	.39	.27	.98
4	Dry Valley, concentrate No. 1.....................	33.0	12.5	44.1	3.44	1.25	.81	.18	.41	.71
5	Dry Valley, concentrate, run 17..................	36.3	3.9	51.3	4.16	.84	.52	<.10	.36	.22
6	Conda unaltered rock........	27.0	15.1	44.4	3.00	2.13	1.33	-	-	-
7	Conda washing plant product.	31.0	11.7	46.0	3.55	1.12	.58	1.05	.62	.57
8	British Columbia composite..	10.9	35.5	27.5	1.46	4.75	3.72	-	-	-
9	Australian No. 1............	24.3	35.7	34.4	2.46	.87	1.07	-	-	-
10	Australian No. 2............	19.1	40.8	29.4	2.12	2.82	4.89	-	-	-
11	Saudi Arabian ore...........	20.5	.55	61.6	2.54	.62	.29	-	-	-
12	Saudi Arabian concentrate...	30.8	.80	57.1	3.29	.05	.65	.24	-	-
13	Fort Hall mill shale........	26.6	21.4	38.8	2.74	3.02	1.69	-	-	-
14	Chamasari (India) No. 1.....	35.2	9.11	49.0	4.02	.88	1.79	-	-	-
15	Chamasari (India) No. 2.....	16.6	49.4	22.4	1.84	2.37	5.58	-	-	-
16	Chamasari (India) No. 3.....	31.9	8.10	43.3	3.26	1.30	11.4	-	-	-
17	IMC (Florida) concentrate...	33.0	2.91	51.4	3.99	1.01	3.41	-	-	-

[1] Material calcined at 800° C for 2 hours.

SINGLE-STAGE TESTS

Acidulation

Preliminary acidulation tests were conducted in open vessels in which phosphate rock was contacted with phosphoric acid. The purpose of these tests was to determine the conditions at which maximum fluoride evolution and phosphate solubilization occurred. The very earliest tests were made using 50 grams of minus 65-mesh concentrate and reagent-grade phosphoric acid (H_3PO_4) at 100 percent of stoichiometry calculated from the phosphorous pentoxide content (P_2O_5), which was assumed to be all fluorapatite.

At reaction temperatures of 120° C, it was expected that the fluoride would be evolved as HF, which will react with the SiO_2 present in the ore to form gaseous SiF_4. The SiF_4 is recovered as H_2SiF_6 by water scrubbing. During the acidulation reaction, the apatite is converted to water-soluble monocalcium phosphate, which can be treated with sulfate ion ($SO_4^{=}$) to precipitate gypsum and form H_3PO_4. The reaction equations can be represented as follows:

$$3[Ca_{10}(PO_4)_6F_2] + 42H_3PO_4 \xrightarrow{120^\circ\ C} 6\ HF + 30[Ca(H_2PO_4)_2], \qquad (3)$$

$$4\ HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O, \qquad (4)$$

$$3\ SiF_4 + 2\ H_2O \longrightarrow 2\ H_2SiF_6 + SiO_2 \qquad (4a)$$

and

$$30[Ca(H_2PO_4)_2] + 30H_2SO_4 + 60H_2O \xrightarrow{75^\circ\ C} \qquad (5)$$

$$30[CaSO_4 \cdot 2H_2O] \downarrow + 60H_3PO_4.$$

However, when this procedure was followed, the reaction mass became very viscous, and mixing or stirring became impossible. Furthermore, fluorine evolution rarely exceeded 40 percent. Therefore, a series of tests were run, using 100-gram samples, in which excess H_3PO_4 was used and water was injected into the acidulated mass at reaction temperatures maintained between 150° to 180° C for 1 hour. The water flow rate was held at 3.5 milliliters per minute in each test. These tests were run in a closed system that had provision for injection of water as well as stirring and temperature control. The vapors were collected in scrubbers by water aspiration. A more complete description of the apparatus is given later in this report.

The data in table 2 shows that under the test conditions, a minimum of 250 percent stoichiometric H_3PO_4 was required to volatilize at least 80 percent of the fluoride present. In all tests, the total extraction of both fluoride and phosphate exceeded 98 percent. Since the ore contained about 78 percent fluorapatite (33 percent P_2O_5), 100 grams of this ore would require 106 grams of H_3PO_4 at 100 percent stoichiometry, if impurities are neglected. This means that about 265 grams of H_3PO_4 were needed for 100 grams of ore to maintain a manageable and effective acidulation. Put another way, the test data indicate that 265 grams of H_3PO_4 are required for each 45.5 grams of potential green-acid product or a ratio of about 5.8 to 1.

TABLE 2. - Fluorine evolution and phosphate extraction by H_3PO_4 acidulation of phosphate rock[1]

Test	Stoichiometric H_3PO_4, percent	Fluorine distribution, percent			Total fluorine extracted, percent[2]	Total P_2O_5 extracted, percent[2]
		Scrubber	Solution	Residue		
1	600	83.8	15.1	1.09	98.9	99.2
2	450	85.2	13.7	1.14	98.9	99.9
3	350	83.9	15.1	1.00	99.0	99.9
4	300	88.8	10.4	.78	99.2	99.9
5	250	81.2	17.0	1.84	98.2	99.9
6	250	81.0	17.7	1.33	98.7	99.8
7	200	46.9	51.9	1.14	98.9	99.8

[1] Analysis of ore was 33.0 percent P_2O_5, 3.72 percent F, and 44.1 percent CaO.
[2] Based on analysis of acid-insoluble residue.

This H_3PO_4 acidulation-water vapor dissolution technique was applied to all the ores and products listed in table 1. Examination of the data in table 3 shows that when the ratio of percent CaO versus percent P_2O_5 in the material (1.31 in pure fluorapatite) is from about 1.3 to 1.4, high extraction of P_2O_5 and fluoride evolution can be expected regardless of the P_2O_5 content. The reason is that any excess CaO present as calcite ($CaCO_3$) will react with the acid first, which decreases the amount of acid available to react with the apatite. Since 2 moles of H_3PO_4 are required for 1 mole of CaO as calcite compared with about 4 moles of H_3PO_4 for 3 moles CaO as apatite, the calcite content of the material is a critical factor.

TABLE 3. - Phosphoric acid-water vapor dissolution of calcined phosphate ores and products[1]

Sample	Phosphate ore or product	Fluorine volatilized, percent	P_2O_5 solubilized, percent	CaO/P_2O_5
1	Dry Valley, low grade...........	64.0	75.4	1.63
2	Dry Valley, medium grade........	69.5	95.8	1.38
3	Dry Valley, high grade..........	93.8	98.8	1.30
4	Dry Valley, concentrate No. 1...	95.0	97.4	1.33
5	Dry Valley, concentrate, run 17.	99.7	99.8	1.41
6	Conda unaltered rock............	87.2	62.3	1.64
7	Conda washing plant product.....	99.8	99.7	1.48
8	British Columbia composite......	69.5	67.6	2.52
9	Australian No. 1................	98.1	99.7	1.41
10	Australian No. 2................	85.0	94.7	1.54
11	Saudi Arabian ore...............	46.1	83.2	3.00
12	Saudi Arabian concentrate.......	53.2	84.6	1.85
13	Fort Hall mill shale............	89.3	98.7	1.46
14	Chamasari (India) No. 1.........	99.5	99.8	1.39
15	Chamasari (India) No. 2.........	87.2	96.7	1.35
16	Chamasari (India) No. 3.........	95.4	96.1	1.36
17	IMC (Florida) concentrate.......	96.3	98.2	1.56

[1] 100 grams of ore reacted with 250 stoichiometric percent H_3PO_4 at 180° C for 1 hour.

Although only preliminary data are presented, H_3PO_4 acidulation of materials as coarse as 20 mesh seemed to present no difficulty except that reaction times may be increased. Current wet-acid processes using sulfuric acid (H_2SO_4) generally require materials of 200 mesh or finer. Data are shown in table 4.

TABLE 4. - Acidulation of coarse samples of phosphate ore[1]

Ore size	Reaction time, hours	P_2O_5 extracted, percent	Fluorine volatilized, percent
Minus 10 plus 20........	1	83.2	69.4
Do....................	2	96.3	88.3
Do....................	3	98.2	91.4
Minus 20 plus 28........	1	90.3	76.4
Do....................	2	95.8	87.6
Do....................	3	98.4	93.6
Minus 28 plus 35........	1	90.6	80.4
Do....................	2	96.4	90.1
Do....................	3	99.1	94.4

[1] 100 gram samples reacted with 250 percent stoichiometric H_2PO_4 at 180° C in presence of water vapor.

Gypsum Precipitation

The monocalcium phosphate-phosphoric acid solutions obtained from the previous acidulation tests were collected and mixed together to make a sufficient volume of a solution having a uniform composition for subsequent gypsum precipitation and filtration tests. The composition of this "master-mix" solution was as follows, in grams per liter: 24 CaO, 368 total P_2O_5, and 463 free H_3PO_4 (335 P_2O_5) plus minor amount of other salts.

Aliquot portions of this solution were then depleted of calcium by the addition of varying amounts of H_2SO_4 at variable time-temperature conditions. The amount of $SO_4^=$ used ranged from 90 to 120 percent of stoichiometry, according to the following general equation:

$$Ca(H_2PO_4)_2 + H_2SO_4 + 2H_2O \longrightarrow [CaSO_4 \cdot 2H_2O] + 2H_3PO_4 . \qquad (6)$$

After the addition of $SO_4^=$ as H_2SO_4, the gypsum precipitate was filtered off, and the filtrates were analyzed for Ca^{++} and $SO_4^=$ remaining in solution. The data listed in table 5 show that the best results were attained at 100 percent of stoichiometry when the reaction was allowed to proceed for a period of at least 12 hours at 25° C. However, if this acidulation process is to be made cyclic, the precipitation time will have to be reduced.

A series of tests was made to determine the amount of washing necessary to remove entrapped P_2O_5 from the gypsum. The procedure was to take large aliquots from the "master-mix" solution and divide each aliquot into two equal fractions. To one fraction stirred at room temperature, the stoichiometric amount of H_2SO_4 was added dropwise, which should just react with the calcium present in the solution. Heat of dilution of the acid raised the temperature of the solution to about 30° C. The other fraction was heated to about 65° C and was stirred while a like amount of acid was added dropwise. All solutions were filtered at or near room temperature, followed by an initial 100-milliliter water wash to displace the bulk of the phosphoric acid retained in the filter cake.

Table 6 shows the results of subsequent washing of the gypsum filter cake with 100-milliliter portions of cold water. The variations in the volumes and concentrations are the result of filtering until the gypsum cake was just free of standing liquid.

One normally thinks that gypsum will form larger, more easily filtered crystals if the precipitation occurs in a hot (60° to 70° C) solution that is then allowed to cool slowly. However, in washing the precipitate, it was found that the gypsum obtained from precipitation at room temperature could be washed free of acid more rapidly and with less water than was needed to wash the "hot solution" gypsum. One possible explanation is that the gypsum crystals precipitated at room temperature are smaller and less uniform so that the wash water encounters smaller void channels during passage through the filter cake. This would mean a more initmate contact with the solids, hence a more efficient washing.

TABLE 5. - Calcium precipitation from $Ca(H_2PO_4)_2$ solutions by $SO_4^=$

Test	Stoichiometric $SO_4^=$, percent	Temperature, ° C	Time, hours, approximate	Remaining in filtrate, g/l	
				Ca^{++}	$SO_4^=$
1	90	25	2	13.2	0.91
2	100	25	2	9.6	4.2
3	110	25	2	4.3	6.4
4	120	25	2	2.6	8.3
5	90	60	2	16.6	1.15
6	100	60	2	11.6	6.20
7	110	60	2	8.1	7.9
8	120	60	2	4.6	9.9
9	90	90	2	16.5	1.08
10	100	90	2	12.0	5.95
11	110	90	2	8.5	8.0
12	120	90	2	4.7	9.8
13	90	25	6	9.3	.65
14	100	25	6	4.7	1.32
15	110	25	6	2.6	4.85
16	120	25	6	1.42	6.25
17	90	60	6	11.3	1.23
18	100	60	6	8.6	2.94
19	110	60	6	6.2	3.88
20	120	60	6	4.4	7.18
21	90	90	6	11.6	1.36
22	100	90	6	9.4	3.05
23	110	90	6	7.1	4.61
24	120	90	6	4.6	8.22
25	90	25	12	6.26	.88
26	100	25	12	.83	1.02
27	110	25	12	.60	2.96
28	120	25	12	.35	4.03
29	90	90	12	5.33	.90
30	100	90	12	1.88	1.36
31	110	90	12	.66	3.22
32	120	90	12	.43	4.60

TABLE 6. - Precipitation and washing of gypsum

Room temperature precipitation			Precipitation at 65° to 70° C		
Wash	Volume, ml	Free acid content, g/l H_3PO_4	Wash	Volume, ml	Free acid content, g/l H_3PO_4
RUN 1			RUN 1A		
1	100	62.4	1	120	73.7
2	98	2.9	2	100	13.2
3	100	.3	3	101	2.1
4	97	0	4	96	.2
RUN 2			RUN 2A		
1	102	35.9	1	107	67.1
2	100	1.5	2	106	39.6
3	100	.38	3	104	13.0
4	152	.19	4	218	.6
RUN 3			RUN 3A		
1	100	122.9	1	107	143.6
2	103	22.3	2	106	26.8
3	109	3.6	3	130	5.5
4	143	.2	4	115	.57

A third series of tests was run to determine if $SO_4^=$ from a source other than sulfuric acid could be used to precipitate gypsum from monocalcium phosphate-phosphoric acid solutions. Again aliquots of the "master-mix" solution were used. In one set, a calcium sulfate product was precipitated by the addition of $SO_4^=$ as ammonium sulfate, and for comparison, sulfuric acid (H_2SO_4) was used as described earlier. The precipitates were washed until they were free of acid and then dried and analyzed. The data in table 7 show that the sulfate product formed by addition of ammonium sulfate retained nearly six times as much P_2O_5 as that precipitated by H_2SO_4. In addition, the product formed by the $(NH_4)_2SO_4$ was hemihydrate rather than gypsum even though conditions of temperature, time, concentration, and stoichiometry were duplicated in each pair. No explanation for this result was found.

TABLE 7. - Precipitation of gypsum from monocalcium phosphate solutions[1]

Test	$SO_4^=$ added as	Stoichiometric $SO_4^=$, percent	CaO precipitated, percent	Analysis, percent				X-ray[2] diffraction
				F	Fe	SiO_2	P_2O_5	
1	$(NH_4)_2SO_4$..	100	87.2	<0.1	<0.05	<0.1	7.4	$2CaSO_4 \cdot H_2O$
2	$(NH_4)_2SO_4$..	125	88.5	<.1	<.05	<.1	6.8	$2CaSO_4 \cdot H_2O$
3	$(NH_4)_2SO_4$..	150	89.0	<.1	<.05	<.1	6.3	$2CaSO_4 \cdot H_2O$
4	H_2SO_4......	100	94.7	<.1	<.05	<.1	.53	$CaSO_4 \cdot 2H_2O$
5	H_2SO_4......	125	95.9	<.1	<.05	<.1	1.08	$CaSO_4 \cdot 2H_2O$
6	H_2SO_4......	150	96.3	<.1	<.05	<.1	1.58	$CaSO_4 \cdot 2H_2O$

[1] Precipitations made at 70° C for 2 hours.
[2] Product dried at 75° C for 8 hours.

CYCLIC TESTS

Information generated during single-stage testing led to attempts to recycle the phosphoric acid generated in such tests. Earlier work had indicated that there was a possibility that some of the impurity ions (Fe, Al, etc.) increased in the acid during a recycling process, thereby decreasing the extraction and recovery of both P_2O_5 and fluorine. To determine whether there was such an impurity buildup and its effects, and also to establish recoveries of these products, the phosphoric acid of a single-stage test was recycled for up to five additional cycles. Table 8 and table 9 show the chemical analysis and particle size determination of the ore used in this study, respectively. It is a western U.S. phosphate ore obtained from southeastern Idaho.

TABLE 8. - Chemical analysis of a western U.S. phosphate ore

	Percent
P_2O_5	33.0
F	3.59
Al_2O_3	2.83
MgO	.60
SiO_2	9.4
CaO	48.0
Na_2O	.60
K_2O	.36
Fe_2O_3	.72
$CO_3^{=}$	1.85
$S^{=}$	.80

TABLE 9. - Screen analysis of a western U.S. phosphate ore

Mesh size	Percent of sample	Fluorine content, percent
Plus 48	5.9	3.55
Minus 48 plus 65	6.1	4.20
Minus 65 plus 100	8.8	3.69
Minus 100 plus 150	13.5	3.15
Minus 150 plus 200	18.1	3.72
Minus 200	47.6	3.43
Total	100.0	[1]3.55

[1]Calculated fluorine content.

The reactions of phosphoric acid with those substances found on the phosphate ore are shown in table 10. To insure that a stoichiometric amount of acid would be available for reaction in those cases where more than one reaction is possible, the reaction that would give the maximum consumption of phosphoric acid is shown. Although there may be some errors involved in using these equations, they served as a guide in the reactions involving acid and ore. Based on the results obtained, the equations appear to be satisfactory, and no serious buildup of impurities occurred.

TABLE 10. - Possible reactions of phosphoric acid with phosphate ore

Reactions							H_3PO_4, grams[1]
$Ca_{10}(PO_4)_6F_2$	+	$14H_3PO_4$	$\longrightarrow$	$10Ca(H_2PO_4)_2$	+	$2HF$........	106.25
Al_2O_3	+	$2H_3PO_4$	$\longrightarrow$	$2AlPO_4$	+	$3H_2O$.......	5.44
MgO	+	$2H_3PO_4$	$\longrightarrow$	$Mg(H_2PO_4)_2$	+	H_2O.......	2.92
Na_2O	+	$2H_3PO_4$	$\longrightarrow$	$2NaH_2PO_4$	+	H_2O.......	1.90
K_2O	+	$2H_3PO_4$	$\longrightarrow$	$2KH_2PO_4$	+	H_2O.......	.75
Fe_2O_3	+	$2H_3PO_4$	$\longrightarrow$	$2FePO_4$	+	$3H_2O$.......	.88
$3CO_3^{=}$	+	$2H_3PO_4$	$\longrightarrow$	$3CO_2 + 2PO_4^{-3}$	+	$3H_2O$.......	2.01
$3S^{=}$	+	$2H_3PO_4$	$\longrightarrow$	$3H_2S + 2PO_4^{-3}$	+	$3H_2O$.......	1.63

[1] Values are for the number of grams of 100 percent H_3PO_4 required to react with 100 grams of phosphate ore. (See table 8.)

Apparatus

Reactions were carried out in a stainless steel vessel 5 inches in diameter and 9 inches high heated in a resistance furnace. The capacity was sufficient for a 200-gram charge of ore. A stainless steel "O" ring provided the seal with the metal top plate. The top plate contained openings to accomodate a thermocouple, lines for addition of reagents and for an aspirator, and a Teflon[3] bearing for the stirrer shaft. The stirrer was powered by a 1/40-hp variable-speed motor. A slight negative pressure generated by a water aspirator swept vapors into two ice-cooled scrubbing flasks to collect the fluorine-bearing water vapor.

Procedure

The first run in a recycle series was made by mixing 200 grams of phosphate ore with a 250-percent stoichiometric amount of phosphoric acid (54 percent P_2O_5). This mixture was stirred in the reaction vessel at room temperature while a slight negative pressure from the aspirator was maintained. After one-half hour the temperature was raised to 110° to 115° C and held another one-half hour. This caused the decomposition of the carbonates and sulfides present in the ore without causing excessive foaming. It also helped to reduce the water content of the mixture, allowing the boiling point to increase. The mixture was then heated rapidly to 160° C. As the water evaporated and the temperature reached 135° to 140° C, the material became quite viscous, but after going beyond 140° C, the slurry was easily stirred. After the temperature reached 160° C, water was added dropwise at the rate of 4 to 5 milliliters per minute for 1 hour. The water helped to control the temperature between 160° to 170° C and served as a carrier vapor to help sweep out the fluorine compounds that formed. The vapors were condensed in the ice-cooled scrubbers. At the end of the hour, 1 liter of water was added to the reactor to dissolve the monocalcium phosphate, $Ca(H_2PO_4)_2$. About 10 percent of the ore remained in the monocalcium phosphate solution as an insoluble residue. Analyses showed that the residue consisted mainly of quartz. These

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[3] Reference to specific brands, equipment, or trade names does not imply endorsement by the Bureau of Mines.

residues made filtrating the monocalcium phosphate solutions extremely difficult, and they were left in the solutions for separation in the next step, that is, the precipitation of gypsum.

Precipitation of Gypsum

The monocalcium phosphate solution, still containing the insoluble residue, was stirred at room temperature while a slight stoichiometric excess (about 2 percent) of concentrated sulfuric acid was added dropwise. This caused the formation of gypsum and phosphoric acid, based on the following equation:

$$Ca(H_2PO_4)_2 + H_2SO_4 + 2H_2O \longrightarrow [CaSO_4\ 2H_2O] + 2H_3PO_4. \qquad (7)$$

There does not seem to be any advantage in filtering the solution to remove the impurities because at the present time in the United States there is little or no use for synthetic gypsum. The gypsum formed in this process, whether from filtered monocalcium phosphate or not, has extremely small crystals. Based on information from a major gypsum consumer, it cannot be used for the manufacture of wallboard, the largest market for gypsum. Modification of the precipitation step may physically change the gypsum sufficiently to be of some potential value in industry.

The gypsum slurry was stirred after addition of the sulfuric acid for another one-half hour and then was filtered through a Buchner funnel on coarse filter paper. Vacuum was maintained until the filter cake was just free of liquid. Wash water was then added in 200- to 300-milliliter aliquots and sucked through the filter cake to wash it free of acid. The gypsum retained a large amount of acid, and the first wash solutions collected were nearly as concentrated as the initial filtrate. It required a volume of water about equal to the volume of the initial filtrate to wash the acid from the gypsum to the point that the wash solution analyzed less than 1 gram per liter of free acid. After the filter cake had been washed free of acid, it was dried at 60° C to remove the remaining water. The moist filter cake contained about 50 percent water by weight, even after vacuum filtering as dry as possible. After drying the cake for 24 hours it was analyzed for fluorine and P_2O_5. The average P_2O_5 content was 2.27 percent, and fluorine, 0.26 percent.

A quantity of filtrate, equivalent to the 66 grams of P_2O_5 charged in the ore, was removed, and the remaining acid containing about 25 percent P_2O_5 was concentrated to less than half the initial volume to obtain a filtrate solution containing 50 to 55 percent P_2O_5. This was returned to the reactor with fresh ore to begin the next cycle. Dilute wash solutions containing 8 to 10 percent of the total P_2O_5 were collected and added to the next cycle as leach solution. In this way, all the soluble P_2O_5 was accounted for.

Table 11 shows results of three cyclic test series, series 1, series 2, and series 3, of 5, 4, and 6 cycles, respectively. The initial acid used in series 1 was reagent-grade phosphoric acid diluted to approximately 54 percent P_2O_5. The initial acid used for series 2 and 3 was a merchant-grade acid listed as being 54 percent P_2O_5. It also contained 8.95 grams per liter fluorine. The losses indicated in table 11 resulted from the P_2O_5 retained in the discarded gypsum. Most of the losses probably result from the isomorphous substitution of the phosphate ion for the sulfate ion in the gypsum crystal lattice. The data in table 11 also show that about 75 to 85 percent of the fluorine in the ore was recovered in the water scrubber. From 15 to 25 percent of the fluorine remained in the acid at a concentration of 0.8 to 1 gram per liter after removal of the gypsum. If this dilute acid were concentrated to a commercial grade (54 percent P_2O_5), more of the fluorine could probably be stripped from the acid.

TABLE 11. - Results of cyclic acidulation tests on a western phosphate ore

Cycle	P_2O_5					Fluorine		
	Charged, grams		Lost in solids[2]			Charged in ore, grams[1]	Recovered in scrubbers	
	H_3PO_4	Ore[1]	Grams	Percent of total	Percent of ore		Grams	Percent
				SERIES 1				
1...............	437.8	66	5.4	1.07	8.18	7.18	6.10	84.9
2...............	429.2	66	6.2	1.25	9.39	7.18	5.29	73.7
3...............	412.8	66	4.8	1.00	7.27	7.18	5.34	74.4
4...............	432.4	66	3.8	.66	5.00	7.18	5.71	79.5
5...............	418.4	66	3.5	.72	5.30	7.18	5.06	70.5
Total or average.....	2,130.6	330	23.2	.94	7.03	35.9	27.50	76.6
				SERIES 2				
1...............	438.3	66	6.8	1.35	10.3	7.18	5.81	80.9
2...............	438.9	66	10.8	2.14	16.4	7.18	5.53	77.0
3...............	441.9	66	8.6	1.69	13.0	7.18	5.91	82.3
4...............	404.2	66	9.9	2.10	15.0	7.18	5.63	78.4
Total or average.....	1,723.3	264	36.1	1.81	13.7	28.7	22.88	79.7
				SERIES 3				
1...............	417.8	66	4.3	0.89	6.5	7.18	6.21	86.5
2...............	461.4	66	9.9	1.88	15.0	7.18	5.98	83.3
3...............	479.1	66	9.2	1.69	13.9	7.18	5.92	82.5
4...............	448.2	66	7.2	1.40	10.9	7.18	6.41	89.3
5...............	466.4	66	7.4	1.40	11.2	7.18	5.73	79.8
6...............	435.6	66	6.4	1.28	9.7	7.18	6.26	87.2
Total or average.....	2,708.5	396	44.4	1.64	11.2	43.1	36.51	84.7

[1] 200 grams of ore (33 percent P_2O_5 and 3.59 percent F) per cycle.
[2] Includes P_2O_5 not extracted from the ore and P_2O_5 losses trapped in gypsum.

A conceptual flowsheet and weight-unit material balance is shown in figure 1.

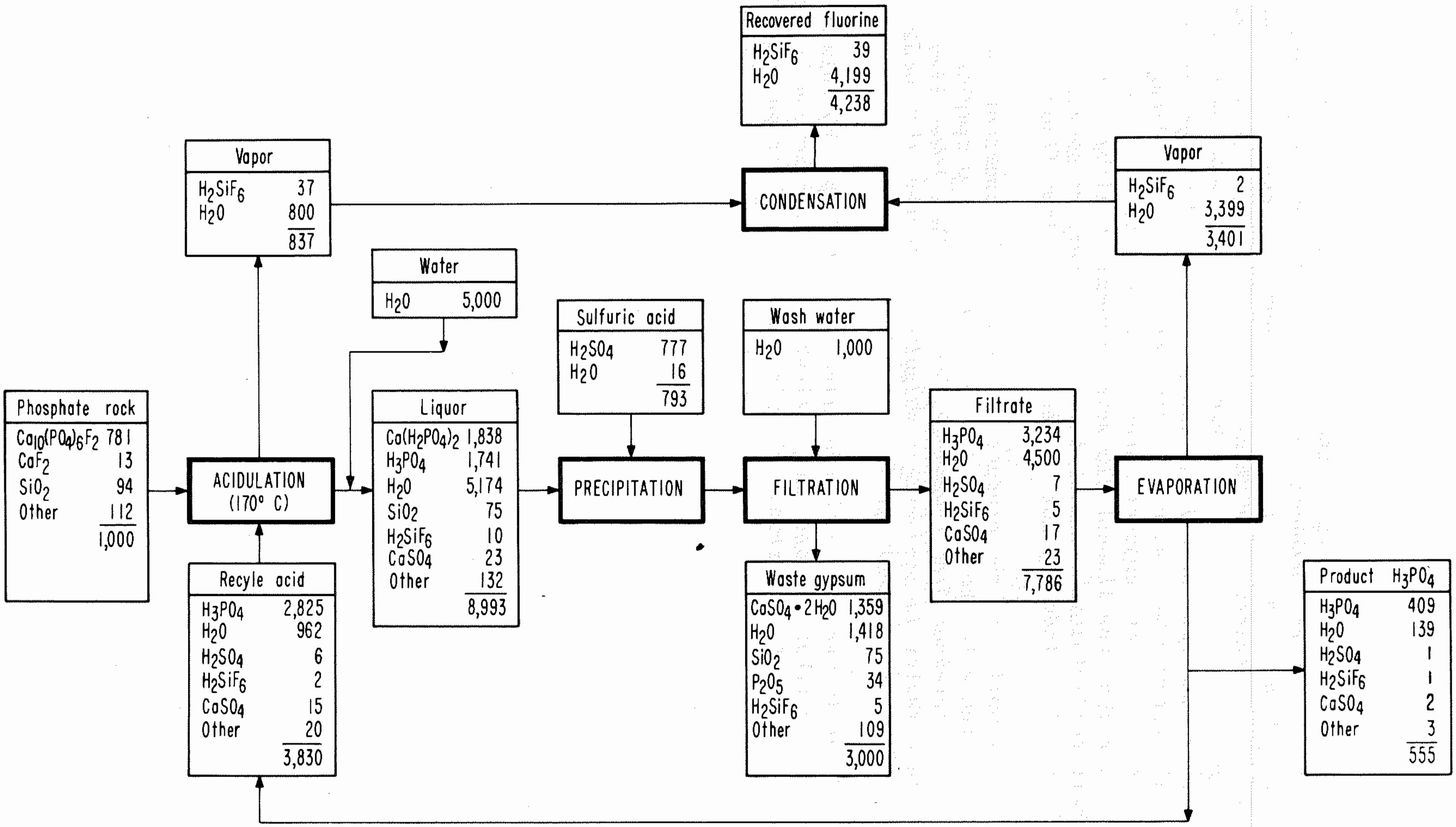

FIGURE 1. - Approximate material balance, phosphoric acid acidulation of phosphate rock.

CONCLUSIONS

The data presented in this report indicate the technical feasibility of treating phosphate rock with phosphoric acid in a cyclic process. These preliminary data indicate that the process will permit recovery of at least twice as much of the contained fluoride as current sulfuric acid processes. The data also show that although overall P_2O_5 recovery may tend to be slightly lower than current commercial practices, there are some advantages in addition to higher fluoride recoveries that would compensate for this. Among these advantages are the facts that coarser material can be acidulated, which would reduce dusting, and that the fluosilicic acid recovered will be relatively free of phosphate contamination, making it a more attractive source of fluorine to the aluminum industry for conversion to aluminum fluoride.

The level of fluoride in the product acid was on the order of 1 gram per liter or less compared with about 10 grams per liter found in samples of shipping-grade acid obtained from commercial sources. This lower level of fluoride could be a factor in producing a shipping-grade acid that would have less tendency to form unwanted sludge.

In light of the increased recovery of fluoride obtainable by this method, it is believed that further research and evaluation in a continuous larger scale miniplant is warranted, particularly since domestic fluorspar resources are limited.

REFERENCES

1. Bixby, D. W., D. L. Rucker, and S. Tisdale. Phosphatic Fertilizers. Sulphur Inst., Tech. Bull. No. 8, 1966, 85 pp.

2. Blake, H. E., Jr., and R. K. Koch. Preparation of Aluminum Fluoride From Alumina Hydrate and Dilute Fluoride Solutions. BuMines RI 6524, 1964, 17 pp.

3. Blake, H. E., Jr., W. S. Thomas, K. W. Moser, J. L. Reuss, and H. Dolezal. Utilization of Waste Fluosilicic Acid (In two sections). BuMines RI 7502, April 1971, 60 pp.

4. Byrns, A. C. (assigned to Kaiser Aluminum and Chemical Co.). Production of Cryolite. U.S. Patent No. 2,994,582, Aug. 1, 1961.

5. Fugate, A. D., and R. K. Koch. Recovery of Low-Silica Cryolite From Siliceous Fluoride Offgases. BuMines RI 6186, 1963, 14 pp.

6. Hall, M. B., and L. H. Banning. Removing and Recovering Fluorine From Western Phosphate Rock and Utilizing the Defluorinated Rock. BuMines RI 5381, 1958, 49 pp.

7. Johnson, R. C., J. Sweeny, and W. C. Lorenz. Economic Availability of Byproduct Fluorine in the United States (In two sections). BuMines IC 8566, 1973, 97 pp.

8. Kirk, O. Fluorine Compounds, Inorganic. Ch. in Encyclopedia of Chemical Technology. John Wiley & Sons, Inc., New York, v. 9, 2d ed., 1966, pp. 576-577, 622.

9. Koch, R. K., A. D. Fugate, and H. E. Blake, Jr. Separation of HF From $HF-SiF_4-H_2O$ Mixtures. BuMines RI 6877, 1966, 15 pp.

10. Lewis, R. W. Phosphorus. Ch. in Mineral Facts and Problems. BuMines Bull. 650, 1970, pp. 1139-1155.

11. MacMillan, R. T. Fluorine. Ch. in Mineral Facts and Problems. BuMines Bull. 650, 1970, pp. 989-1000.

12. National Materials Advisory Board. Trends in the Use of Fluorspar. Rept. NMAB-269, 1970, 54 pp.

13. Ryss, I. G. The Chemistry of Fluorine and Its Compounds. U.S. Atomic Energy Commission, AEC-Tr-3927 (in two parts), February 1960, 840 pp.

14. Sauchelli, V. Normal Superphosphate: Chemistry and Technology. Ch. 7 in Chemistry and Technology of Fertilizers. Reinhold Publishing Corp., New York, 1967, pp. 129-166.

15. U.S. Department of Health, Education, and Welfare. Atmospheric Emissions From Wet-Process Phosphoric Acid Manufacture. National Air Pollution Control Administration Pub. No. AP-57, 1970, 86 pp.

16. Weintrotter, F. Now Commercial: AlF_3 Synthesis From Super Phosphate Byproduct. Process Flowsheet. Chem. Eng., v. 71, Apr. 27, 1964, p. 132.

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