RI 8205

Bureau of Mines Report of Investigations/1977

Fluorine Recovery From Phosphate Rock Concentrates

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8205

Fluorine Recovery From Phosphate Rock Concentrates

By B. D. Nash and H. E. Blake, Jr.

UNITED STATES DEPARTMENT OF THE INTERIOR
Thomas S. Kleppe, Secretary
BUREAU OF MINES
Thomas V. Falkie, Director

This publication has been cataloged as follows:

Nash, Boyd D

Fluorine recovery from phosphate rock concentrates / by B. D. Nash and H. E. Blake, Jr. [Washington] : Bureau of Mines, 1977.

16 p. : diagrams ; 26 cm. (Report of investigations - Bureau of Mines ; 8205)

Bibliography: p. 15-16.

1. Fluorine. 2. Fluosilicic acid. 3. Phosphate rock. I. Blake, Henry E., joint author. II. United States. Bureau of Mines. III. Title. IV. Series: United States. Bureau of Mines. Report of investigations - Bureau of Mines ; 8205.

TN23.U7 no. 8205 622.06173

U.S. Dept. of the Int. Library

CONTENTS

ILLUSTRATION

TABLES

FLUORINE RECOVERY FROM PHOSPHATE ROCK CONCENTRATES

by

B. D. Nash[1] and H. E. Blake, Jr.[1]

ABSTRACT

The Bureau of Mines continued its research into the recovery of fluorine by the phosphoric acid acidulation defluorination of phosphate rock concentrates. A small process development unit with a capacity of about 10 kilograms of charge per hour was operated, and concentrates from both Idaho and Florida were processed. Over 80 percent of the fluorine was evolved and recovered as a dilute fluosilicic acid solution. Phosphate extraction from the concentrates always exceeded 98 percent.

The fluorine was converted to a synthetic fluorspar product ($3CaF_2 \cdot SiO_2$) suitable for use as a slag conditioner in electric furnace steelmaking operations.

INTRODUCTION

World needs for fluorine continue to increase as the developing nations expand their industrial bases. Foreign imports, mainly in the form of fluorspar (CaF_2), accounted for nearly 80 percent of the 700,000 to 800,000 tons of fluorine consumed in the United States in the early 1970's. Not only are foreign imports becoming less dependable, but prices are also increasing, making it desirable for the United States to find alternate or secondary domestic sources of this commodity.

Fortunately, this country possesses large reserves of fluorine in the phosphate deposits of Florida and in the Western United States. Phosphate concentrates contain from 3 to 4 percent fluorine in the mineral fluorapatite $Ca_{10}(PO_4)_6F_2$ (1-2, 4-5, 7, 11, 16).[2] If the fluorine contained in phosphate ores currently being processed for fertilizers in this country were recovered, nearly half of the Nation's needs for fluorine could be met. At present, roughly 20 percent of this fluorine is being recovered during the manufacture of phosphate fertilizers; the rest is lost in waste products (11).

---

[1] Research chemist, Albany Metallurgy Research Center, Albany, Oreg.

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

When fluorapatite is treated with strong mineral acids, as in the manufacture of fertilizers, soluble phosphates are formed and fluorine is released as HF. The HF in turn reacts with silica, present in most ores as an impurity, forming the volatile gas SiF_4. As SiF_4 is formed and scrubbed from the gas stream it hydrolyzes, forming fluosilicic acid and silica. These reactions are represented in the following equations:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \longrightarrow 6\ H_3PO_4 + 10\ CaSO_4 \cdot H_2O + 2\ HF, \quad (1)$$

$$Ca_{10}(PO_4)_6F_2 + 14\ H_3PO_4 \longrightarrow 10\ Ca(H_2PO_4)_2 + 2\ HF, \quad (2)$$

$$4\ HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O, \quad (3)$$

and

$$3\ SiF_4 + 2\ H_2O \longrightarrow 2\ H_2SiF_6 + SiO_2. \quad (4)$$

Equation 1 represents what is currently called the "wet-acid process" for making fertilizer acid from phosphate rock. Equation 2 represents the formation of solid "triple superphosphate," an enriched phosphate fertilizer. In the wet-acid process about 41 percent of the fluorine in the phosphate rock is volatilized, 13 percent remains in the concentrated acid, and 46 percent is discarded with the gypsum filter cake. Overall recovery of fluorine from the volatile fluorides is unlikely to exceed 50 percent, with the remainder joining other dilute wastes in the cooling water recirculation pond (15). During the manufacturing of triple superphosphate essentially all of the fluorine is retained in the solid product.

Studies conducted by the Bureau of Mines (3) have shown that from 70 to 80 percent of the fluoride can be recovered from phosphate ores or concentrates by reacting them with an excess of phosphoric acid at elevated temperatures as shown in equations 2, 3, and 4. During the initial reaction to form monocalcium phosphate, $Ca(H_2PO_4)_2$, the fluorine is evolved and collected. The reaction is completed by liberating the phosphoric acid with the addition of sulfuric acid, as shown in equation 5:

$$Ca(H_2PO_4)_2 + H_2SO_4 + 2\ H_2O \longrightarrow 2\ H_3PO_4 + CaSO_4 \cdot 2\ H_2O. \quad (5)$$

The fluosilicic acid that is generated can be processed by procedures already developed by the Bureau of Mines either to acid-grade CaF_2 or to commercially acceptable anhydrous HF (3, 9). Alternatively it may be converted to other marketable fluoride salts such as aluminum fluoride or sodium silicofluoride (2, 4-8, 14, 17). This report describes an alternative procedure in which the fluoride is recovered as an impure calcium fluoride (equation 6) which, in preliminary evaluation tests, was found to be suitable for use as a fluorspar substitute in some iron and steelmaking operations.

$$H_2SiF_6 + 3\ Ca(OH)_2 \longrightarrow [3\ CaF_2 \cdot SiO_2] + 4\ H_2O. \quad (6)$$

Research discussed in this report is an extension of earlier Bureau of Mines work which investigated fluorine recovery from phosphate ores (3) and describes the design and operation of a semicontinuous acidulation-defluorination process development unit. A materials flow diagram is presented in figure 1.

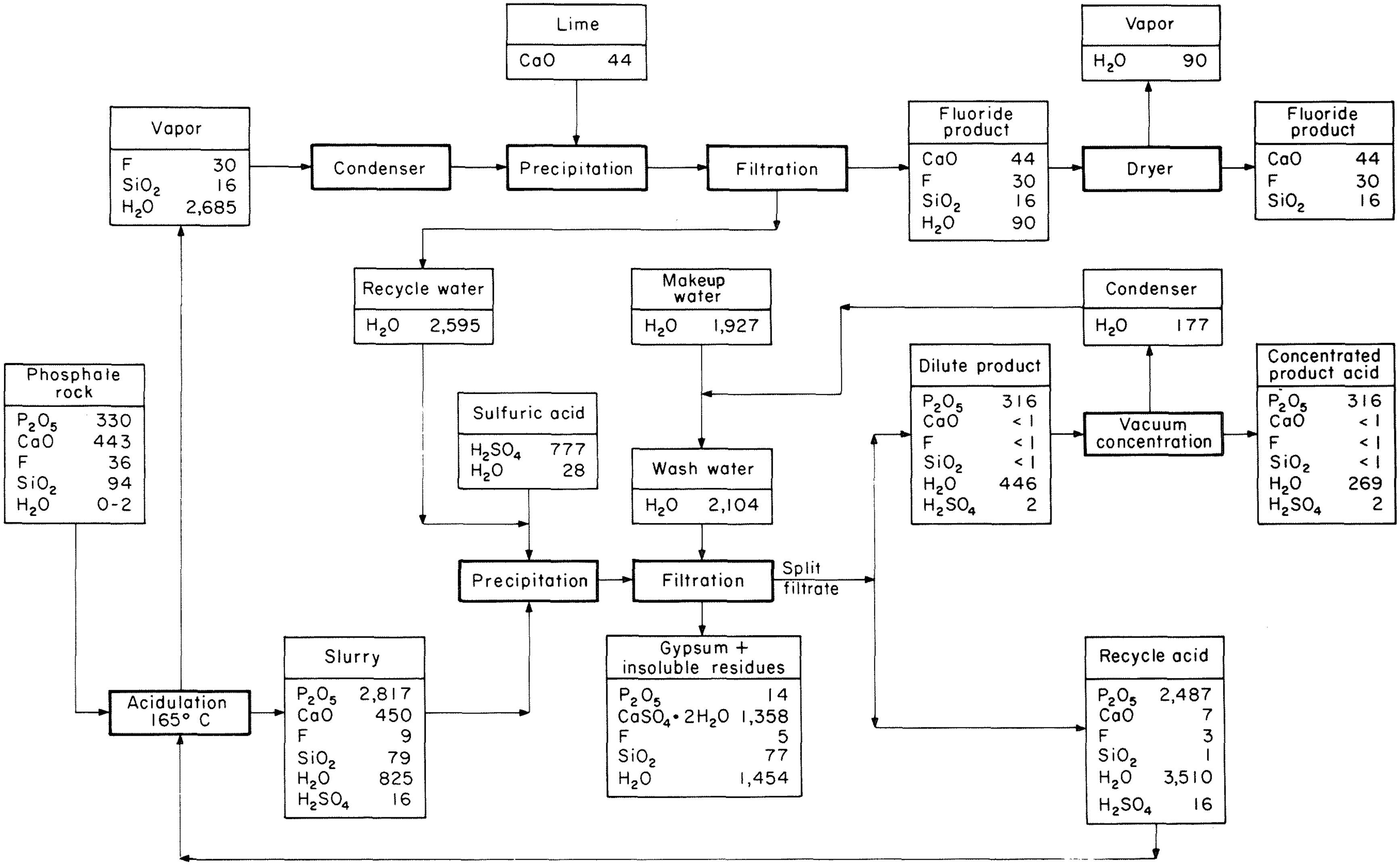

FIGURE 1. - Approximate material-flow diagram for acidulation of phosphate rock concentrates by recycle phosphoric acid, kilograms.

ACKNOWLEDGMENTS

The authors wish to thank the J. R. Simplot Co. of Pocatello, Idaho, and International Minerals Corp. of Bartow, Fla., for providing the phosphate concentrates used in this investigation.

EQUIPMENT

Materials of Construction

Because of the corrosive nature of nearly all fluorine-containing compounds, and especially the HF and H_2SiF_6 formed during reaction of phosphate ore and phosphoric acid at elevated temperatures, it was necessary to find construction materials that would withstand the heat, corrosion, and abrasion anticipated in such a reaction vessel. Tests in solutions similar to those expected to be encountered were made on a number of standard stainless steels in addition to some of the newer alloys presently produced by industry. While several of the alloys tested had good resistance to corrosion and abrasion (13), the alloy chosen for reactor construction was series 316 stainless steel (SS). Advantages of 316 SS included availability, cost, familiarity of fabrication properties, and acceptability for the job. Tests showed that 304 SS was not a suitable material because the corrosion rate was from 3 to 4 times that of 316 SS. High-temperature plastic pipe was found to be satisfactory for the condenser and scrubber systems.

Reactor for Acidulation and Defluorination

The design of a semicontinuous acidulation-defluorination unit, or process development unit, requires a reaction vessel in which the mixing and initial feed digestion can occur, followed by a heated defluorination section which allows for the continuous withdrawal of the defluorinated monocalcium phosphate, fluosilicic acid condensers and scrubbers, a gypsum filtration unit, and an acid concentrator.

The acidulation unit was a cylindrical vessel 12 inches in diameter and 29 inches high, made from 316 SS and heated by a resistance furnace. The top plate contained a 3/8-inch acid inlet line and a 1-inch high-temperature plastic offgas line leading to a condenser and scrubber system. A side port contained a 3/4-inch screw feeder for the addition of dry feed, while opposite it was a 1-inch overflow pipe for discharge of the acid slurry. A later modification of the system provided for the separate premixing of dry feed with acid at room temperature and the pumping of the premixed slurry into the reactor through the top plate. A 1-hp electric mixer stirred the contents. A baffle inside the reactor blocked the direct opening to the overflow port to prevent any short circuiting of the reactants, forcing the slurry to enter the overflow pipe from below the baffle. The defluorinated monocalcium phosphate was discharged from the reactor into a receiving vessel for subsequent processing.

The partially cooled defluorinated monocalcium phosphate was converted to phosphoric acid by slowly adding it to dilute sulfuric acid with constant stirring in a plastic-lined 55-gallon steel drum. The temperature was maintained at or below 65° C to assure the formation of gypsum ($CaSO_4 \cdot 2\ H_2O$). The gypsum was filtered and washed on a stainless steel tilting-pan vacuum filter.

Condensers and Scrubbers

Fluorine-bearing gases and water vapor were collected by passing them through a water-cooled surface condenser and/or a packed column recirculating water scrubber. A slight negative pressure on the acidulation-defluorination vessel, created by water aspiration, pulled air into the vessel through the discharge port and effectively swept all gases and vapors into the condenser-scrubber section for recovery of fluosilicic acid. Cleanout ports were provided in the cooler sections of the condensing system to remove the silica deposits which formed during the hydrolysis of volatile SiF_4 to H_2SiF_6 (equation 4).

Vacuum Concentrator

A vacuum concentrator, constructed to concentrate the recycle acid used during this investigation, consisted of a tank 28 inches high and 19 inches in diameter made from 316 SS. The tank was equipped with six 316 SS 3-kilowatt immersion heaters and operated at 75° to 85° C, with a vacuum of 24 to 25 inches Hg supplied by a water aspirator. The unit handled about 50 kilograms of 28 percent P_2O_5 acid and concentrated it to about 28 kilograms of 50 percent P_2O_5 acid during an 8-hour period.

RAW MATERIALS

Phosphate Rock Concentrates

Although small-scale acidulation-defluorination tests had been run on phosphate samples obtained from various parts of the world (3), this study was limited to two phosphate concentrates obtained in the United States. Principal deposits for phosphate ores in the United States are located in Florida, North Carolina, and Tennessee in the Southeast, and in the western Mountain States of Montana, Idaho, Wyoming, and Utah (10). Concentrates for this study were obtained from Florida and Idaho. Analyses of these concentrates are given in table 1.

TABLE 1. - Chemical analyses of two U.S. phosphate concentrates, percent

	Florida	Idaho		Florida	Idaho
P_2O_5	31.9	33.0	K_2O	-	0.36
F	3.7	3.6	Fe_2O_3	4.4	.72
Al_2O_3	1.0	2.8	CO_2	-	1.9
MgO	1.0	.60	S	-	.80
SiO_2	6.6	9.4	Loss on ignition (1,000° C for 1 hour)	7.0	1.6
CaO	46.7	48.0			
Na_2O	-	.60			

Acid

Reagent-grade phosphoric acid (specific gravity, 1.43, 43.4 percent P_2O_5) was used for initial testing. Later a supply of product acid was accumulated which was concentrated to a specific gravity of about 1.50 (48.3 percent P_2O_5) and recycled. This product acid was commonly referred to as "green acid" because of the green color imparted to it by dissolved impurities. Analysis of a typical green acid is given in table 2.

TABLE 2. - Chemical analysis of concentrated green acid used in acidulation-defluorination studies, grams per liter

Specific gravity	Free acid, titration	P_2O_5	F	Fe	Al	Ca	SO_4	Mg
1.51........................	991	723	1.8	5.5	5.7	3.9	51.7	1.3

TEST PROCEDURES AND RESULTS

Acidulation-Defluorination Tests

Dry Feed

The following is a description of a typical run made in the acidulation-defluorination reaction vessel. Fifty-four kilograms of recycle acid (specific gravity, 1.51, 991 g/l free acid) was charged to the reactor, stirred at 100 to 130 rpm, and heated to 100° C. Twelve kilograms of dry Florida concentrate was charged to the hot acid at the rate of 4 kg/hr. When the contents of the reactor were thoroughly mixed, the temperature of the slurry was raised to 160° C and additional dry feed and acid were added at the rate of 2 kilograms of solids and 9 kilograms of acid per hour, 270 to 280 percent of the stoichiometric amount of acid required to react with the phosphate concentrate as shown in equation 2. The initial charge filled the reactor two-thirds full of slurry, and continued addition of reactants brought the level to overflowing within 4 hours. Thereafter, until the completion of the run, the hot defluorinated material, a mixture of monocalcium phosphate and phosphoric acid, overflowed on an intermittent basis and was collected in an overflow receiver for subsequent processing. Water vapors containing the volatile fluorides were collected either by water scrubbing or by condensation of the vapors for separate processing to recover the fluoride byproducts. Runs ranged from 6 to 48 hours.

Because of a slightly different chemical composition, the Idaho concentrate did not react the same as the Florida concentrate. The procedure was modified to control excessive foaming that occurred while processing the Idaho materials. The change in startup procedure was to add the Idaho concentrate to the acid in the reactor at room temperature and allow the reactants to be stirred several hours at ambient temperature prior to heating the reactor. Additionally, 2 grams of solid $KMnO_4$ were added with each kilogram of concentrate to oxidize undesirable impurities such as sulfides and carbonaceous matter which might have caused the foaming problem. A 0.3-percent concentration of sodium oleate dispersed in water was added as needed to suppress the foaming and to help keep it within tolerable limits.

The specific gravities of the defluorinated monocalcium phosphate-phosphoric acid slurries were 1.9 to 2.0. The concentration of fluorine in the scrubber and condenser solutions ranged from 10 to as much as 100 grams of fluorine per liter of solution. Subsequent treatment of the slurries and scrubber solutions from either Idaho or Florida concentrates was the same.

Predigestion

The foaming problem associated with the Idaho concentrate was aggravated by nonuniform feed rates for this material. Phosphate concentrates ground to minus 60 mesh tended to "bridge" extensively, and made it difficult to maintain uniform feed rates. This was solved by predigesting the dry material with an excess of phosphoric acid. Dry feed and acid were mixed in a 1:6 weight ratio using recycle acid with a specific gravity of 1.40, providing 316 percent of the stoichiometric amount of acid. The mixture was stirred at room temperature for 1 to 2 hours in a separate vessel, allowing for solubilization of the concentrate. Tests indicated that almost complete solubilization occurred after 2 hours, resulting in a slightly viscous slurry with a specific gravity of 1.45 to 1.50. The slurry was added through a metering pump into the hot defluorination reactor.

In the tests using predigested material the reactor was nearly filled with defluorinated slurry collected from an earlier run and heated to the predetermined defluorination temperature (145° or 165° C) while stirring. Then the predigested material was pumped into the reactor through the top plate at a constant feed rate. This change eliminated the foaming problem encountered with the dry feed. At the end of each test involving predigested material the contents of the reactor were allowed to cool to 80° C with continued stirring. By maintaining this temperature in the reactor the contents remained in a fluid state and startup for the next test was reduced by several hours.

Results of Tests

Dry Feed

Results of eight acidulation-defluorination tests using dry feed are shown in tables 3-5. Five tests were made using Florida concentrate, and three with Idaho concentrate. In all eight tests the reactor was operated at $160°\pm5°$ C, and the temperature was maintained for an hour after the last of the feed material was added to allow for defluorination of the final feed. Then the total contents of the reactor plus the overflow material were processed to determine fluorine and P_2O_5 recoveries.

TABLE 3. - Extraction of F and P_2O_5 from phosphate concentrates, dry feed

Concentrate and run	Inputs, kilograms			Outputs, kilograms			Extraction, percent	
	Feed	F	P_2O_5	Insoluble residue	F	P_2O_5	F	P_2O_5
Florida:								
1.............	20.0	0.74	6.36	4.69	0.016	0.270	97.8	95.8
2.............	31.4	1.16	9.98	1.70	.016	.126	98.6	98.7
3.............	31.0	1.15	9.86	1.52	.005	.044	99.6	99.6
4.............	31.5	1.17	10.0	1.26	.004	.031	99.7	99.7
5.............	45.0	1.69	14.35	6.61	.021	.424	98.8	97.0
Idaho:								
6.............	14.6	.52	4.92	3.64	.006	.204	98.9	95.9
7.............	26.5	.95	8.93	1.92	.006	.226	99.4	97.5
8[1]............	100.0	3.60	33.72	130.0	.351	.658	90.2	98.0

[1] In test 8 the insoluble residues were not separated prior to gypsum precipitation.

TABLE 4. - P_2O_5 recovery from phosphate concentrates, dry feed

Concentrate and run	Input, P_2O_5, kilograms			Output, P_2O_5, kilograms				Accountability, percent P_2O_5
	Feed	Acid	Total	Filter acid	Solids	Scrubber	Total	
Florida:								
1........	6.36	50.6	56.96	55.1	0.34	1.27	56.71	99.5
2........	9.98	64.3	74.28	72.9	.61	1.36	74.87	100.8
3........	9.86	62.5	72.36	71.6	.33	.88	72.81	100.6
4........	10.0	74.2	84.2	87.0	.21	.33	87.54	104.0
5........	14.35	95.6	109.95	107.0	1.29	1.49	109.78	99.8
Idaho:								
6........	4.92	38.9	43.82	42.9	.51	.02	43.43	99.1
7........	8.93	68.3	77.23	76.6	.58	.04	77.22	100.0
8........	33.72	237.1	270.82	269.9	.66	1.41	271.97	100.4

TABLE 5. - Fluorine recovery from phosphate concentrates, dry feed

Concentrate and run	Input, F, kilograms			Output, F, kilograms				F in scrubber, percent	F accountability, percent
	Feed	Acid	Total	Filter acid	Residues	Scrubber	Total		
Florida:									
1........	0.74	0.08	0.82	0.11	0.05	0.64	0.80	78.0	97.6
2........	1.16	-	1.16	.15	.06	.92	1.13	79.3	97.4
3........	1.15	-	1.15	.17	.05	.96	1.18	83.5	102.6
4........	1.17	.18	1.35	.44	.04	.82	1.30	60.7	96.3
5........	1.68	.29	1.97	.71	.08	1.27	2.06	64.5	104.6
Idaho:									
6........	.52	.06	.58	.11	.06	.42	.59	72.4	101.7
7........	.95	.18	1.13	.29	.07	.80	1.16	70.8	102.7
8........	3.60	.76	4.36	1.51	.35	3.19	5.05	73.2	115.8

In seven of the tests the defluorinated material was dissolved in water and filtered to isolate the insoluble residues, thereby allowing for the determination of fluorine and phosphate extracted from the concentrates. In test 8, the insoluble residues were not separated prior to precipitation of the gypsum. In this case the analyses showed significant retention of fluorine but little retention of P_2O_5 in the filter cake. In general, more than 97 percent of the fluorine and more than 95 percent of the P_2O_5 were extracted, with an average of only 1 percent of the fluorine and 2.3 percent of the P_2O_5 left in the insoluble residues. Fluorine recovery in the scrubber solutions ranged from 60 to 83 percent, with an average of 73 percent recovered in the eight tests.

Predigestion

Eight acidulation-defluorination tests were made using predigested Idaho phosphate concentrates. Feed rates, temperatures, and water content of the feed materials were varied. Temperature appears to be the critical variable with higher temperatures favoring more complete defluorination of the feed. Based on fluorine inputs the average fluorine recovery was 72 percent at 145° C and 85 percent at 165° C. Table 6 contains details of the tests.

TABLE 6. - Fluorine recovery from Idaho phosphate concentrate, predigested feed

Run	Temperature, ° C	Inputs, g/min				Outputs, g/min				F in scrubber,[2] percent	F accountability, percent[3]
		Feed	Acid[1]	Water	F, total	Scrubber Liquid	Scrubber F	Overflow Slurry	Overflow F		
1....	145	22.2	77.7	66.6	0.97	60.8	0.79	102.2	0.29	81.4	111.3
2....	145	27.8	97.3	111.2	1.23	99.7	.96	134.4	.37	78.0	108.1
3....	145	27.8	97.3	83.4	1.25	72.0	.81	141.3	.38	64.8	95.2
4....	145	22.2	77.7	88.8	.94	68.2	.61	76.6	.22	64.9	88.3
5....	165	27.8	97.3	83.4	1.50	74.3	1.18	130.7	.33	78.7	100.6
6....	165	22.2	77.7	88.8	1.02	85.5	.94	104.0	.20	92.2	111.7
7....	165	22.2	77.7	66.6	.98	61.9	.81	100.0	.21	82.7	104.1
8....	165	27.8	97.3	111.2	1.18	104.3	1.04	121.4	.28	88.1	111.8

[1] Based on 100 percent H_3PO_4. The actual acid used was a green acid with a specific gravity of 1.50 and was diluted with the appropriate amount of water.

[2] Based on fluorine input.

[3] Variations in fluorine accountability are due to difficulty in obtaining representative samples from overflow slurries.

Recovery of Phosphoric Acid

In each test, the defluorinated slurry was a mixture of monocalcium phosphate, excess phosphoric acid, and insoluble residues which consisted mainly of silica and carbonaceous material. The defluorinated slurry came from the reactor at a temperature above 120° C as a thin black liquid, but upon cooling it formed a thick dilatant (quicksandlike) suspension with a specific gravity of 1.9 to 2.0. Adding small amounts of water caused the formation of crystalline hydrates of monocalcium phosphate which solidified the entire mass. When this occurred, an amount of water approximately equal to the weight of the defluorinated slurry was required to completely dissolve the material, resulting in an aqueous solution with a specific gravity of 1.35. This solution was treated with sulfuric acid to precipitate a dirty gray gypsum and to generate green acid according to equation 5. If the solution was filtered first to remove the insolubles, a white gypsum was formed. The green acid, containing 28 to 32 percent P_2O_5, was the same in either case.

The most convenient way to clarify the aqueous monocalcium phosphate solution containing insoluble impurities was to add a flocculating agent and allow the "sludge" to settle out. This left a clarified solution, the majority of which could be decanted, leaving only a concentrated sludge which was readily filtered. Without the use of a flocculating agent very little settling occurred.

Three different methods were used to generate green acid and to precipitate the gypsum. The first method used to precipitate gypsum was to heat the clarified monocalcium phosphate solution to 55° to 60° C and while stirring to slowly add sulfuric acid containing 650 g/l of sulfate. The gypsum precipitated as small needles 30 to 50 micrometers long. These crystals were slow in filtering and contained up to 2 percent P_2O_5 by way of isomorphic substitution of phosphate for sulfate ions in the crystal lattice.

A second and better method for the crystallization of gypsum was to reverse the additions; that is, to add the clarified monocalcium phosphate solution to the sulfuric acid diluted with either weak wash acid or with water. This not only assured that an excess of sulfate ions was always present, thereby decreasing the isomorphoric substitution, but also resulted in the growth of much larger crystals with corresponding improvement in filtration and washing. Crystals 200 to 300 micrometers long with a length-to-width ratio of 15-20 to 1 were regularly prepared.

The filter acid obtained in methods 1 and 2 generally contained 28 to 32 percent P_2O_5 (specific gravity 1.25 to 1.29), the same as industrial wet-process acid. Because much of this acid is to be recycled, it is an economic necessity to recover as strong an acid as possible to avoid the high costs of concentrating the acid. It has been stated (12) that the reason 28 to 32 percent P_2O_5 phosphoric acid is currently made in the wet-acid process is that there are too many problems associated with the formation and filtration of gypsum crystallized from a more concentrated acid.

A third method was developed to overcome the aforementioned problems. Twenty kilograms of defluorinated monocalcium phosphate-phosphoric acid slurry containing 4.7 percent calcium were diluted with 2 liters of phosphoric acid having a specific gravity of 1.40 (41 percent P_2O_5) to provide a less viscous slurry for easier handling. This slurry was added at the rate of 10 kilograms per hour to a stirred solution of 2.4 kilograms of concentrated sulfuric acid diluted with 13 liters of dilute phosphoric acid having a specific gravity of 1.16 to 1.20 (18 to 23 percent P_2O_5). The sulfuric acid solution was maintained at a temperature of between 50° to 60° C. Sufficient sulfuric acid was used to allow for an excess of between 5 and 10 g/l of sulfate ion in the filtered phosphoric acid. Gypsum crystals, 200 to 300 micrometers long, were obtained which were readily filtered and washed.

The gypsum was filtered on a tilting-pan filter at a vacuum of 27 to 28 inches Hg. Filtration rates for phosphoric acid obtained with methods 2 and 3 were four times as great as in method 1 and are comparable with current industrial rates of 2 to 5 kilograms $P_2O_5/min/m^2$. However, more than 85 percent of the acid must be recycled, leaving less than 15 percent for a product acid. Method 3 appeared to be the best procedure inasmuch as the acid contained 42 to 44 percent P_2O_5, compared with the 28 to 32 percent P_2O_5 obtained in method 2; filtration data are given in table 7. In method 3 the first water wash of the gypsum yields an acid which is more concentrated than the acid recovered in either other method.

The gypsum cakes, 25 to 40 mm thick, were washed free of soluble phosphates and contained 50 to 55 percent moisture. Chemical analyses for the fluorine and P_2O_5 in the filter cakes are given in table 8 for each of the three methods of gypsum precipitation. For methods 2 and 3, losses were from 7 to 8 percent fluorine and 2 to 3 percent P_2O_5, which were discarded with the waste gypsum. Method 1 resulted in even higher losses of P_2O_5.

TABLE 7. - Filtration rates of phosphoric acid

Method	Run	Gypsum crystal size, micrometers	Volume, liters	P_2O_5, g/l	Total P_2O_5, kilograms	Filter time, minutes	Filter rate, kilograms P_2O_5/min/m^2
1[1].........	1....	30 to 50	27.8	336	9.3	19.9	1.26
	2....	30 to 50	27.9	356	9.9	31.2	.85
2[2].........	3....	250 to 300	28.8	352	10.1	3.8	7.15
	4....	50 to 100	40.2	371	14.9	12.0	3.34
	5....	150 to 200	36.4	362	13.2	7.5	4.73
	6....	~250	37.4	362	13.5	8.6	4.22
	7....	250 to 300	39.5	348	13.7	5.5	6.70
3[3].........	8....	200 to 300	27.2	619	16.8	8.5	5.32
	Wash[4]	-	8.4	480	4.0	3.5	3.07

[1] Addition of diluted sulfuric acid to monocalcium phosphate solution.
[2] Addition of monocalcium phosphate solution to diluted sulfuric acid.
[3] Addition of monocalcium phosphate slurry to diluted sulfuric acid.
[4] The wash for run 8wwas made with 8 liters of water.

TABLE 8. - Fluorine and phosphate content of gypsum, percent

	F	P_2O_5
Method 1:[1]		
Run 1..	0.13	2.67
Run 2..	.12	1.19
Run 3..	.09	1.34
Run 4..	.15	1.29
Run 5..	.11	1.87
Run 6..	.05	1.59
Average..................................	.11	1.66
Method 2:[2]		
Run 1..	.53	.42
Run 2..	.47	.42
Run 3..	.11	.60
Run 4..	.11	.47
Run 5..	.13	.62
Average..................................	.27	.51
Method 3[3]...................................	.17	.55

[1] Addition of diluted sulfuric acid to monocalcium phosphate solution.
[2] Addition of monocalcium phosphate solution to diluted sulfuric acid.
[3] Addition of monocalcium phosphate slurry to diluted sulfuric acid.

Recovery of Fluorine

Condenser solutions contained from 50 to 100 g/l of fluorine while scrubber solutions had from 10 to 20 g/l of fluorine. The fluorine values were recovered from these solutions by neutralizing the fluosilicic acid with hydrated lime (equation 6). The solutions were rapidly stirred in a plastic-lined barrel, and lime was slowly sprinkled onto the surface of the liquid and allowed to react with the fluosilicic acid. The liquid temperature increased during the reaction, but no attempt was made to control it. Lime was added until a pH of 8 to 9 was reached, after which the stirring was continued another hour. Solids were then allowed to settle out prior to filtration. The precipitate, designated "synthetic fluorspar," quickly settled to the bottom of the barrel and was readily filtered. In a few cases the condenser solutions were contaminated with phosphate carryover from the acidulation-defluorination step and in these tests the precipitate was difficult to filter.

As an example, 8 liters of fluosilicic acid condenser solution containing 70 g/l F, 29 g/l SiO_2, and 1 g/l P_2O_5 were vigorously stirred and hydrated lime was slowly added until a pH of 9 was reached. During the reaction period of about 30 minutes the temperature increased from room temperature to 70° C.

The precipitate was filtered on a 30-cm Buchner funnel attached to a water aspirator. The 7-cm-thick filter cake was filtered at a rate of 4 $kg/min/m^2$, and had the following analysis: 36.34 percent fluorine, 16.69 percent SiO_2, 0.48 percent P_2O_5, and 54.2 percent CaO.

SYNTHETIC FLUORSPAR--PRELIMINARY EVALUATION

Tests were conducted to evaluate the usefulness of synthetic fluorspar products as slag conditioners during electric furnace steelmaking operations. Four samples were prepared from fluosilicic acid and tested as slag conditioners. One sample was prepared by the lime addition as previously described. Preparation of the second sample was modified by adding phosphoric acid prior to the lime addition, yielding a deliberately contaminated product containing 11.2 percent P_2O_5. Two other samples were prepared by first removing the silica prior to lime treatment. This was done by treating fluosilicic acid with anhydrous ammonia till the solution was basic and then filtering the solution to remove the precipitated SiO_2. The resulting ammonium fluoride solution contained 97 percent of the initial fluoride and produced a silica-free CaF_2 product when treated with lime. One of the silica-free samples was also deliberately contaminated, but in this case finely divided Idaho concentrate was added to the dry silica-free product to yield a mixture containing 4.8 percent P_2O_5.

Tests were carried out in a 1-ton electric furnace at fluoride levels equivalent to between 3 and 5 kilograms of CaF_2 per ton of steel. Current industrial usage is about 3 kilograms of CaF_2 per ton of steel. All four samples were visually observed to be effective as slag conditioners. Since phosphorus is an undesirable contaminant in steels, it was questionable whether phosphorus in the contaminated synthetic fluorspar would transfer into the steel. However, the steel products showed little if any phosphorus uptake from the slag conditioners, even when held as long as 47 minutes in the furnace. Results of the tests are shown in table 9 and are compared with metallurgical-grade fluorspar and reagent-grade CaF_2.

TABLE 9. - Phosphorus content of electric furnace steels using phosphate-contaminated slag conditioners

Material	Weight used, kilograms[1]	Chemical analysis, percent			Time in bath, minutes	Phosphorus in metal, percent
		CaF_2	SiO_2	P_2O_5		
Synthetic fluorspar 1[2]...	3.9	97.4	0.12	0.53	4.7	0.005
Synthetic fluorspar 2[3]...	4.3	71.2	18.3	.39	4.7	.003
Synthetic fluorspar 3[4]...	4.1	81.8	2.4	4.8	13.0	.012
Synthetic fluorspar 4[5]...	9.4	54.4	10.6	11.2	47.0	.007
Metallurgical-grade fluorspar..............	4.5	81.9	8.0	NA[6]	5.2	.011
Reagent-grade CaF_2.......	3.2	100.0	NA[6]	NA[6]	7.5	<.002

[1] Weight of slag conditioner charged to 34 kilograms of slag in a 1,800-pound steel melt.

[2] Prepared from NH_4F.

[3] Prepared from H_2SiF_6.

[4] Prepared from NH_4F, with added fluorapatite.

[5] Prepared from H_2SiF_6, with added H_3PO_4.

[6] No analysis available.

CONCLUSIONS

A small-scale process development unit for the phosphoric acid acidulation of Florida and/or Idaho phosphate concentrate, with a charge capacity of 10 kg/hr, was constructed and operated continuously for up to 48 hours. Phosphate recovery from the concentrate exceeded 98 percent, while 80 percent of the fluorine was evolved and collected as a dilute fluosilicic acid solution.

Phosphoric acid was recovered by treating the resultant monocalcium phosphate with sulfuric acid. This product phosphoric acid was suitable for concentration to merchant-grade acid (54 percent P_2O_5). The fluosilicic acid was of sufficient purity for conversion to marketable fluorspar or other usable fluorine products. One such product, a synthetic fluorspar prepared by neutralizing fluosilicic acid with lime, was found to be effective as a slag conditioner in electric furnace steelmaking operations.

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., and B. D. Nash. Increasing Fluosilicic Acid Evolution From Phosphate Rock by Digestion With Phosphoric Acid. BuMines RI 7980, 1974, 16 pp.

4. Blake, H. E., Jr., W. S. Thomas, K. W. Moser, J. L. Reuss, and H. Dolezal. Utilization of Waste Fluosilicic Acid (In Two Sections). 1. Laboratory Investigations. 2. Cost Evaluation. BuMines RI 7502, 1971, 60 pp.

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

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

7. Johnson, R. C., J. W. Sweeney, and W. C. Lorenz. Economic Availability of Byproduct Fluorine in the United States (In Two Sections). 1. Utilization of Byproduct Fluosilicic Acid in the Manufacture of Aluminum Fluoride. 2. Utilization of Byproduct Fluosilicic Acid in the Manufacture of Calcium Fluoride. 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. Legal, C. C., and O. D. Myrick, Jr. Phosphoric Acid, ed. by V. A. Slack. Marcel Dekker, Inc., New York, v. 1, pt. 1, 1968, pp. 18-19.

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

12. Noyes, R. Phosphoric Acid by the Wet Process 1967. Chem. Process Rev., Noyes Development Corp., Park Ridge, N.J., No. 9, 1967, p. 11.

13. Oden, L. L., and B. D. Nash. Corrosion of Commercial Alloys in Three Environments Simulating Phosphate Rock Acidulation. BuMines RI 7898, 1974, 10 pp.

14. Ryss, I. G. The Chemistry of Fluorine and Its Compounds (In Two Parts). U.S. Atomic Energy Commission, AEC-Tr-3927, February 1960, 840 pp.

15. Sanders, M. D. Phosphoric Acid, ed. by A. V. Slack. Marcel Dekker, Inc., New York, v. 1, pt. 2, 1968, pp. 766-767.

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

17. Weintrotter, F. Now Commercial: AlF_3 Synthesis From Super Phosphate Byproduct, Process Flowsheet. Chem. Eng., v. 71, Apr. 27, 1974, p. 132.

☆U.S. GOVERNMENT PRINTING OFFICE: 1977-703-001/21