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The Removal of Fluorine from Wet Process Phosphoric Acid

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NOTE

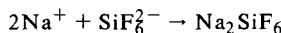
The Removal of Fluorine from Wet Process Phosphoric Acid

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Abstract

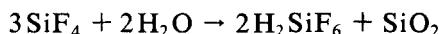
Fluorine (and silicon) can be removed from technical phosphoric acid (30% P₂O₅) and recovered quantitatively as a by-product by adding a sodium or a potassium salt, preferably the carbonate, and boiling for a few minutes. The corresponding fluorosilicates precipitate, e.g.,



can be separated by filtration. If this procedure is followed, no precipitation will take place in the evaporators during concentrating the acid to 40% P₂O₅.

INTRODUCTION

Phosphate rock contains 3 to 4% fluorine on the average. During the manufacture of phosphoric acid by treating the rock with H₂SO₄, about 20% of the fluorine is volatilized as HF and SiF₄, about 65% is lost in the gypsum residue, and 15% remains in the acid (1). The volatilized fluorine compounds are usually recovered by washing the gases with water to get a mixture of HF and H₂SiF₆:



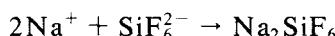
The fluorine remaining in the acid, however, not only represents a loss of this element but its presence is undesirable, especially when the acid is concentrated by evaporation, since it may cause corrosion or precipitation problems in the evaporators. Moreover, it will contaminate the fertilizer produced from such acid and therefore will lower its P_2O_5 content. Fluorine is also an undesirable element in the soil.

There have been numerous attempts to remove this remaining fluorine. The most important process is based on adding silica gel to the acid and heating under vacuum. Under these conditions silicon tetrafluoride forms and is volatilized:



It can then be scrubbed from the exist gases and recovered as fluorosilicic acid (2). In another method, the phosphoric acid is extracted by isobutyl alcohol (3), tributyl phosphate (4), or a mixture of tributyl phosphate and isopropyl alcohol (5), leaving the impurities behind in the aqueous phase.

The precipitation of sodium or potassium fluorosilicate by adding a sodium or a potassium salt, respectively, is not widely practiced although it appears to be a convenient method for eliminating not only fluorine, but also silicon, e.g. (1)



The present investigation was undertaken to study this method.

EXPERIMENTAL

Freshly produced black technical phosphoric acid, about 30% P_2O_5 , was acquired from a manufacturer in New Brunswick, Canada, by treating Florida phosphate rock by sulfuric acid. After storage in the laboratory for a few weeks, the crystalline gypsum deposit formed was filtered. The acid contained 6.4 g/L silicon as determined by atomic absorption. Samples of the acid were reacted with concentrated solutions of sodium and potassium salts under different conditions; any precipitated crystals were filtered, washed with a small amount of water, dried at 80°C for 2 h, weighed, and then examined by X-ray diffraction and scanning electron microscopy.

RESULTS AND DISCUSSION

Quantitative precipitation of fluorosilicates at room temperature necessitated the addition of about three times the stoichiometric amount of the sodium or potassium salt. However, it was possible to achieve the same yield with the stoichiometric amounts if precipitation was conducted hot, preferably for a few minutes at the boiling point. Table 1 shows the solubilities of some alkali fluorosilicates in water. It can be seen that only the sodium and the potassium (cubic form) salts have a low solubility and therefore can be precipitated; potassium fluorosilicate in the cubic form precipitates under these conditions. Although the solubility in water increases with increased temperature, the reverse is true in H_3PO_4 .

When the volume of acid was reduced to three-fourth by evaporation, i.e., a 30% P_2O_5 technical acid was concentrated to 40% P_2O_5 , a small amount of sodium fluorosilicate precipitated, apparently due to the presence of a small amount of sodium ions in the acid. For example, 1 L of acid on evaporation yields about 1 g of Na_2SiF_6 as compared to 42 g obtained when the stoichiometric amount of Na_2CO_3 is added. Once fluorosilicate ion is precipitated by the addition of Na_2CO_3 and separated, the remaining acid can be evaporated without yielding any precipitate.

A trace amount of colloidal silica usually coprecipitates with the fluorosilicates. This remains suspended in the acid and can be separated by decantation. X-ray diffraction analysis revealed that no other products are coprecipitated. Scanning electron micrographs of K_2SiF_6 and Na_2SiF_6 obtained from technical H_3PO_4 are shown in Figs. 1 and 2, respectively.

Sodium or potassium fluorosilicates can be the starting material for numerous industrially important fluorine compounds. For example:

TABLE I
Solubilities of Some Alkali Fluorosilicates in Water

Salt	Structure	Solubility, g/100 mL H_2O	
		At 17°C	At 100°C
$Li_2SiF_6 \cdot 2H_2O$	Monoclinic	73	
Na_2SiF_6	Hexagonal	0.065	2.46
K_2SiF_6	Cubic	0.12	0.95
K_2SiF_6	Hexagonal	6.9	
$(NH_4)_2SiF_6$	Octagonal hexagonal	18.6	55.5

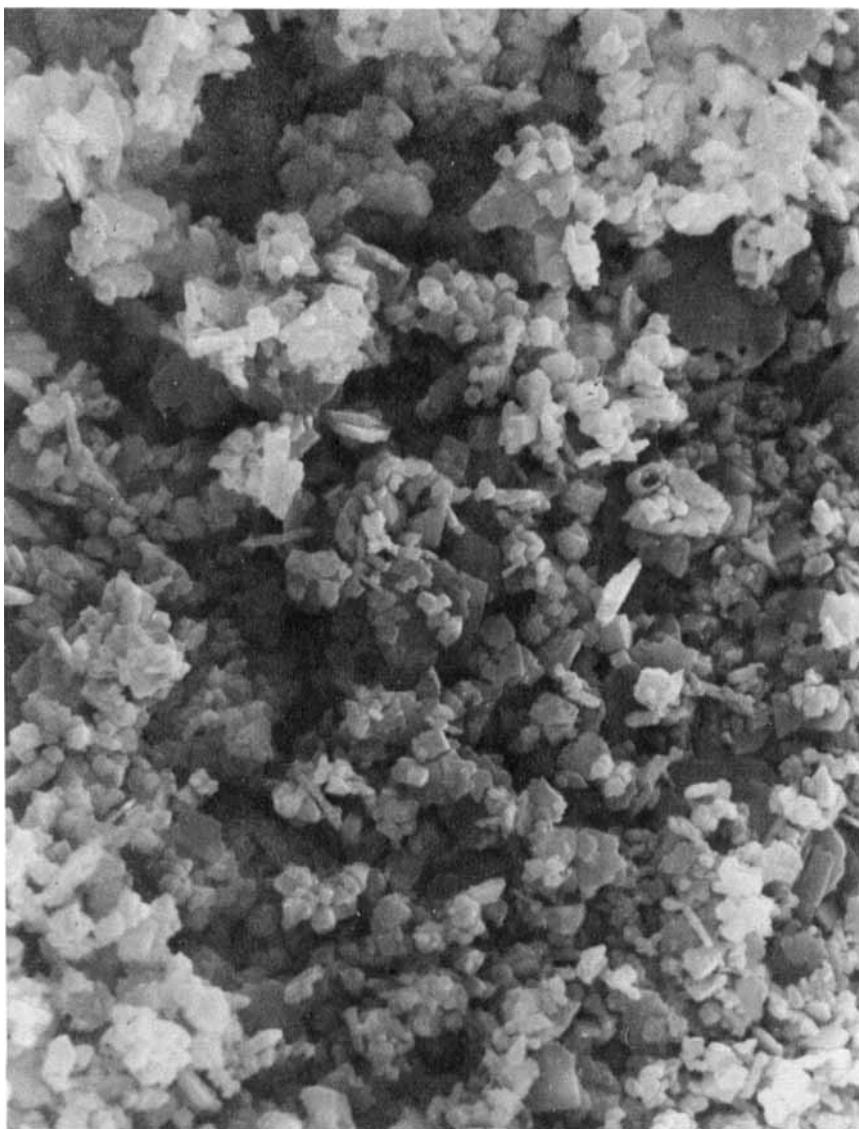


FIG. 1. Scanning photomicrograph of K_2SiF_6 (cubic) (4000 \times) obtained from technical phosphoric acid by precipitation with potassium carbonate.

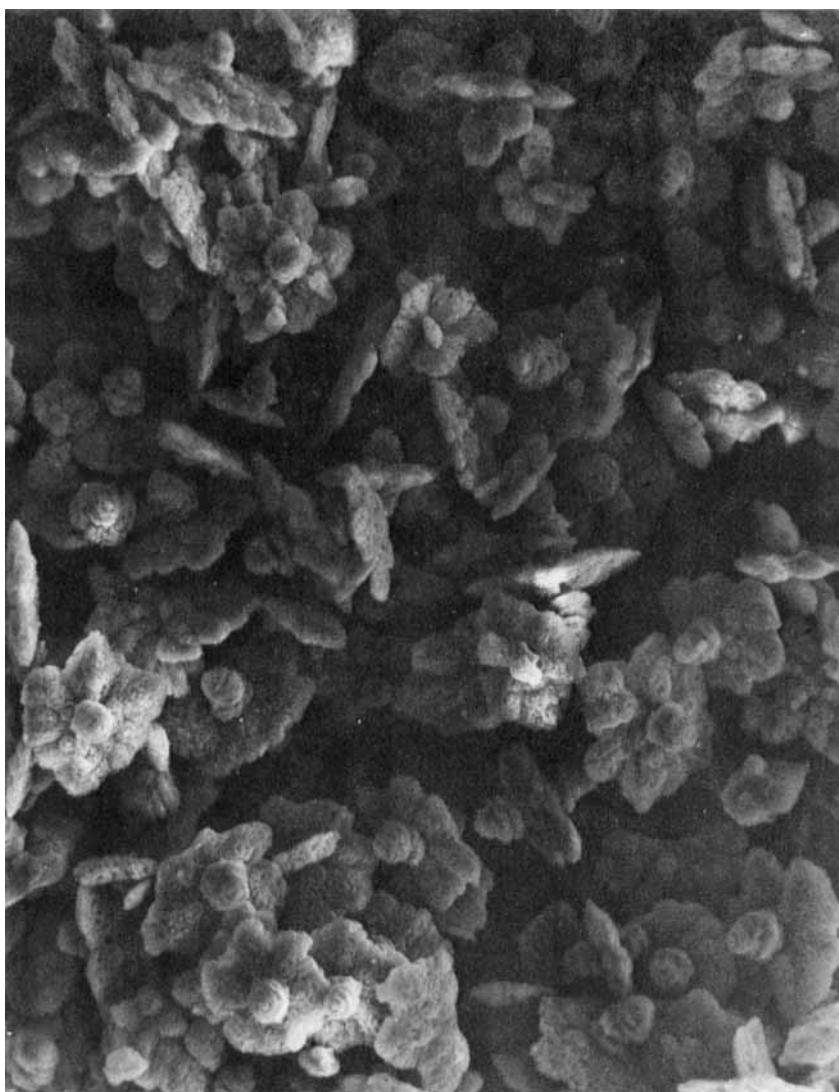
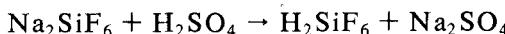


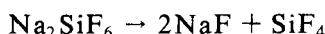
FIG. 2. Scanning photomicrograph of Na_2SiF_6 (600 \times) obtained from technical phosphoric acid by precipitation with sodium carbonate.

(1) Production of fluorosilicic acid. By heating with concentrated H_2SO_4 , fluorosilicic acid can be distilled off and recovered by condensation:

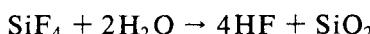


If the presence of sulfate ion can be tolerated in technical H_3PO_4 , then sodium sulfate formed by the above reaction can be recycled for precipitating Na_2SiF_6 instead of using Na_2CO_3 . Sodium carbonate has an obvious advantage when used to precipitate Na_2SiF_6 ; namely, no additional ions are added to the acid because in this case CO_2 is liberated.

(2) Formation of alkali fluoride and hydrofluoric acid. Sodium fluorosilicate, for example, can be decomposed by heating to form sodium fluoride and SiF_4 gas:



Silicon tetrafluoride can be recovered from the vapors by absorption in water to form HF and SiO_2 :



(3) Formation of synthetic cryolite. Cryolite can be prepared by reacting a mixture of HF and NaF produced by the above reaction with aluminum hydroxide:



Cryolite is used in the fused salt bath for aluminum production.

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