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# ALUMINUM REMOVAL FROM PHOSPHORIC ACID AS CHUKHROVITE

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# INTRODUCTION

Phosphate rock is mined throughout the world as the main source of the plant nutrient,  $P_2O_5$ . To concentrate the phosphate as phosphoric acid, finely ground phosphate ore is digested with sulfuric acid at about  $90^\circ C$  which produces the “wet-process acid” and the by-product calcium sulfate dihydrate or gypsum which is generally filtered from the 25-30%  $P_2O_5$  acid. The wet-process acid (WPA) is commonly concentrated to 40-55%  $P_2O_5$  to merchant-grade acid (MGA) and serves as the feed material for fertilizer products.

Commercial phosphate rock contains a few tenths of a percent to 3% aluminum, typically between 0.4-1.0%. From 75 to 90% of the aluminum is transferred to the WPA acid during digestion with other metallic impurities, such as iron and magnesium, and affects the composition and characteristics of the phosphoric acid.

Some aluminum in a WPA promotes well-formed gypsum crystals improving filtration rates. However, as the aluminum concentration increases there is an increase in the viscosity and density of the WPA. As the WPA is concentrated the metallic impurities can affect the MGA quality by forming compounds such as ralstonite, the so-called X compounds of  $\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$  and  $\text{Al}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$  as well as  $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  if the phosphate ore is also high in iron. The precipitation of solids can continue from days to months forming a sludge that is difficult and costly to remove. The precipitates contain valuable  $\text{P}_2\text{O}_5$  that cannot be effectively recovered. Further precipitation can occur when the concentrated acid is neutralized with ammonia to formulate fertilizer products. The nitrogen grade for diammonium phosphate may not be met because too much  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  does not leave enough of the first phosphoric acid valence to combine ammonia. Furthermore, it overloads the fertilizer through the dead weight of these elements:

Aluminum and iron are generally considered to belong to the same impurity category. The general designation  $R_2O_3$  refers to  $(Al_2O_3 + Fe_2O_3)$ . When the  $R_2O_3/P_2O_5$  weight ratio reaches 0.09 or 0.1, some of the common finished products manufactured with the phosphoric acid start to show serious quality weaknesses. A usual merchant-grade limit in the acid is the weight relationship  $0.02 > R_2O_3/P_2O_5 < 0.08$ .

Producers avoid the potential problems of high aluminum values in the acid by refusing to process ores with high aluminum contents, leaving a substantial amount of potential phosphate reserve unavailable.

Chukhrovite, an aluminum-containing mineral, can appear naturally during WPA production and is most often encountered during filtration where it crystallizes and plugs the filter cloth during the very low P<sub>2</sub>O<sub>5</sub> concentration phases of the filter tail washes. Chukhrovite is less soluble in water than phosphoric acid and solubility decreases with increasing pH and lower temperature.

Chukhrovite was discovered in Central Kazakhstan and was described with the formula  $\text{Ca}_3\text{Al}_2(\text{RE})\text{SO}_4\text{F}_{13} \cdot 10\text{H}_2\text{O}$ , where RE is a mixture of rare earths (Yermilova et al., *Zap. Vsesoyuzn. Miner. Obshch*, 89, 15, 1960). Its octahedral crystal habit and XRD pattern were matched to crystals found in gypsum cake produced at Fisons Fertilizers in Suffolk with the formula  $\text{Ca}_{3.33}\text{Ba}_{0.03}\text{X}_{0.06}\text{AlSi}_{0.62}(\text{SO}_4)_{0.83}\text{F}_{10.74} \cdot 8.26\text{H}_2\text{O}$ , where X could be lanthanides or rare earths (Coates et al., *Nature*, 212, 392, 1966). Later the crystal habit and XRD pattern were matched to a solid in raw WPAs but not in MGAs with formulation  $\text{Ca}_4\text{SO}_4\text{AlSiF}_{13} \cdot 12\text{H}_2\text{O}$  (Lehr et al., *Agricultural and Food Chemistry*, 14, No. 1, 1966).

# PURPOSE

The purpose of this study is to determine the effectiveness of chukhrovite precipitation in removing aluminum from WPA. A secondary consideration was whether iron and/or magnesium was capable of incorporating into the chukhrovite structure under treatment conditions.

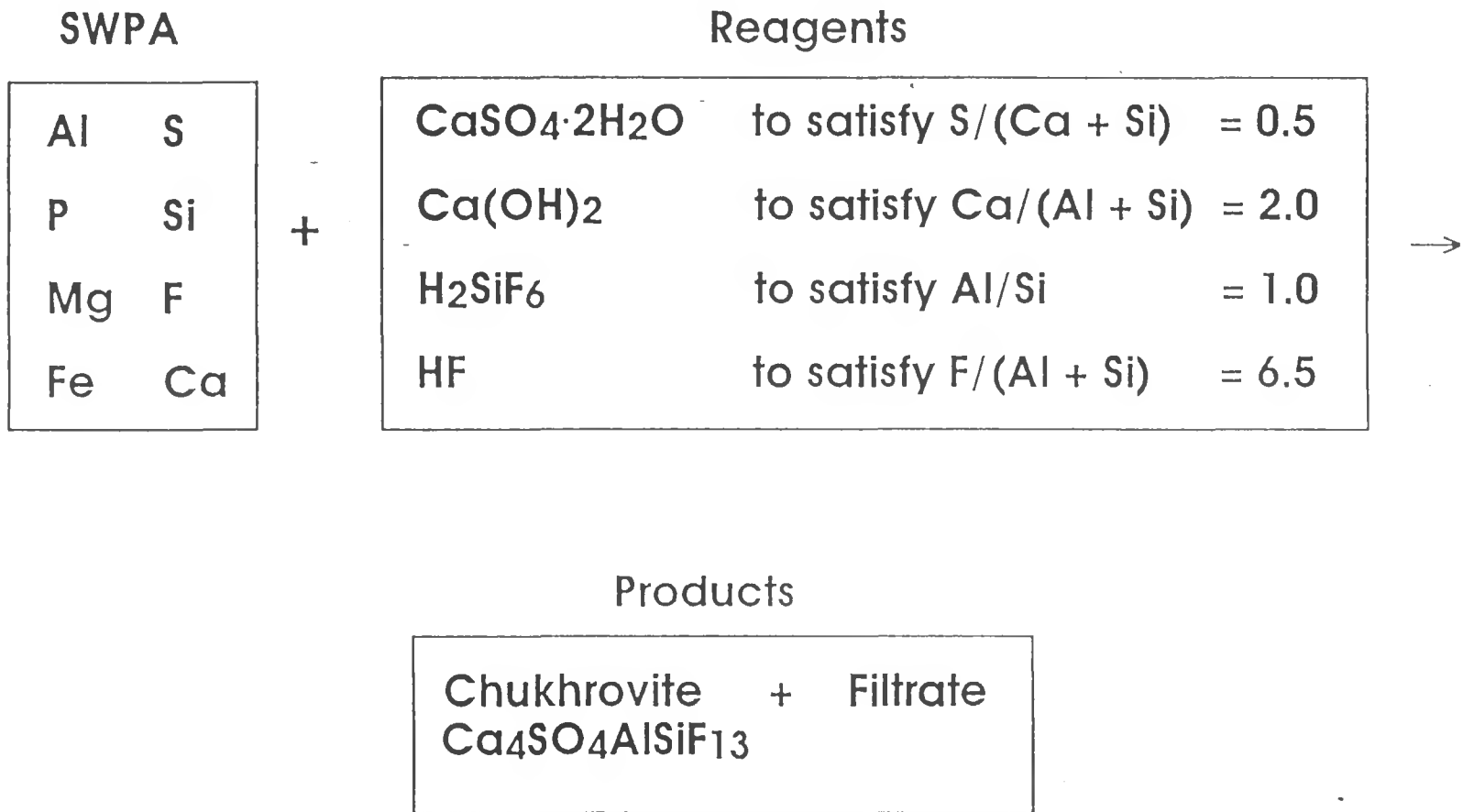
# EXPERIMENTAL

Simulated wet-process acids (SWPA) were prepared as follows. Calcium sulfate and magnesium oxide are mixed with a diluted phosphoric acid, shaken and warmed for 2 hours on a Lab-Line Orbit Environ-Shaker until dissolved. Sulfuric acid is added to the cooled mixture, followed by the addition of an iron-phosphoric acid stock solution, an aluminum-phosphoric acid stock solution, the hydrofluoric and fluorosilicic acids, and finally any water required to prepare 1000 g of each SWPA.

The reactants were added to 250 g of the SWPA in a 500 mL polypropylene wide-mouth bottle according to the treatment scheme for the experiment. The reaction mixture was heated to 65 °C, and shaken at 180 revolutions per minute for 2 hours in a Lab-Line Orbit Environ-Shaker. The hot mixture was vacuum-filtered at 25 in Hg and the precipitate washed with ~200 mL of distilled water and ~50 mL of acetone and air-dried.

## EXPERIMENT 1

Analysis data of 16 Florida phosphoric acids produced in 1988 guided the preparation of the 16 SWPAs in this experiment. The P<sub>2</sub>O<sub>5</sub> concentrations ranged from 26.6 to 45.8% P<sub>2</sub>O<sub>5</sub> (11.6 to 20.0% P). The assumption was made that aluminum would precipitate in chukhrovite as Ca<sub>4</sub>SO<sub>4</sub>AlSiF<sub>13</sub> · 12H<sub>2</sub>O. Consequently treatment of each SWPA consisted of satisfying the following mole ratios, Si/Al=1, Ca/(Al+Si)=2.0, S/(Al+Si)=0.5, F/(Al+Si)=6.5, as shown in Figure 1.



**FIGURE 1**

Only 4 of the 16 precipitates were > 95% chukhrovite, although chukhrovite was present in all of the solids. The Si/Al mole ratios in the chukhrovites were about 0.7 rather than the expected value of 1. Regardless, the mole ratios of Ca, F, or S to (Al+Si) approached the expected values of 2.0, 6.5, and 0.5, as shown in Table I.

TABLE I

## CHUKHROVITE MOLE RATIOS

PLM

| No. | CHUKHROVITE MOLE RATIOS |                  |                 |                 | PLM              |
|-----|-------------------------|------------------|-----------------|-----------------|------------------|
|     | Si/Al                   | Ca/<br>(Al + Si) | F/<br>(Al + Si) | S/<br>(Al + Si) | Chukhro-<br>vite |
| 1   | 0.6                     | 2.1              | 6.5             | 0.5             | 95%              |
| 42  | 0.7                     | 2.1              | 6.6             | 0.5             | 95%              |
| 34  | 0.7                     | 2.1              | 6.6             | 0.5             | 95%              |
| 48  | 0.7                     | 2.1              | 7.0             | 0.5             | 95%              |

Table II lists the % element removed from SWPAs after precipitation of chukhrovite. From 88-97% of the aluminum was removed in these four tests. The removal of silicon, fluorine, and sulfur ranged from 25-60%, 30-52%, and 37-78%, respectively. In addition, phosphorus losses ranged from 6-11%.

TABLE II

PERCENT ELEMENT REMOVED FROM SWPA

| No. | Al   | P    | Fe   | Mg   | Ca     | Si   | F    | S    |
|-----|------|------|------|------|--------|------|------|------|
| 1   | 89.7 | 6.2  | 10.5 | -1.2 | -246.9 | 24.9 | 30.3 | 37.8 |
| 42  | 97.3 | 10.8 | 19.3 | 4.3  | -585.0 | 28.3 | 36.3 | 77.7 |
| 34  | 92.5 | 6.0  | 10.9 | 1.3  | -617.2 | 49.1 | 43.2 | 74.6 |
| 48  | 87.8 | 8.7  | 10.5 | 3.6  | -381.6 | 60.4 | 51.9 | 71.9 |

The silicon remaining in the filtrates approximated the quantity of silicon added to treat the SWPAs to satisfy the mole ratio of  $\text{Si}/\text{Al} = 1$ , therefore meeting this mole ratio may be unnecessary. Four SWPAs that did not precipitate a homogeneous chukhrovite were treated again, ignoring the  $\text{Si}/\text{Al} = 1$  mole ratio. PLM techniques confirmed > 95% chukhrovite was isolated for the four SWPAs after treatment.

## EXPERIMENT 2

In this experiment chukhrovite is assumed to precipitate as  $\text{Ca}_{2(x+y)}(\text{SO}_4)_{0.5(x+y)}\text{Al}_x\text{Si}_y\text{F}_{6.5(x+y)}$  where  $x$  and  $y$  are the moles of aluminum and silicon in the SWPA. Reagents are added to SWPA according to the reaction scheme in Figure 2.

SWPA

|    |    |
|----|----|
| Al | S  |
| P  | Si |
| Mg | F  |
| Fe | Ca |

+

Reagents

|   |                                    |            |                        |
|---|------------------------------------|------------|------------------------|
| C | SO <sub>4</sub> ·2H <sub>2</sub> O | to satisfy | $S / (Ca + Si) = 0.5$  |
|   | Ca(OH) <sub>2</sub>                | to satisfy | $Ca / (Al + Si) = 2.0$ |
|   | HF                                 | to satisfy | $F / (Al + Si) = 6.5$  |

→

Products

|  |   |          |
|--|---|----------|
| Chukhrovite  | + | Filtrate |
| $Ca_{2(x+y)}(SO_4)_{0.5(x+y)}Al_xSi_yF_{6.5(x+y)}$ |   |          |

FIGURE 2

Nineteen SWPAs were prepared according to a  $2^4$  factorial design with 3 centerpoints. The effect of P, Al, Mg, and Fe concentration on chukhrovite composition is examined. The phosphorus concentration varied from 10.5-13.1%, aluminum varied from 0.39-0.54%, iron varied from 0.47-0.83%, and magnesium from 0.18-0.29%. The SWPA concentration of silicon, fluorine, sulfur, and calcium were 0.5, 2.5, 0.5, and 0.1, respectively. Table III shows the reagent composition for each treatment.

TABLE III

| No. | SWPA ANALYSIS, WT % |      |      |      |      |      |      |      | WT RATIO                        | REACTION COMPOSITION, g |                  |                     |       |
|-----|---------------------|------|------|------|------|------|------|------|---------------------------------|-------------------------|------------------|---------------------|-------|
|     | Al                  | P    | Fe   | Mg   | Si   | F    | S    | Ca   | R <sub>2</sub> O <sub>3</sub> / | SWPA                    | Reagent Addition |                     |       |
|     |                     |      |      |      |      |      |      |      | P <sub>2</sub> O <sub>5</sub>   |                         | Gypsum           | Ca(OH) <sub>2</sub> | 48%HF |
|     | 0.36                | 10.5 | 0.48 | 0.17 | 0.50 | 2.52 | 0.49 | 0.06 | 0.06                            | 250.30                  | 0.47             | 11.90               | 9.23  |
|     | 0.39                | 13.3 | 0.45 | 0.17 | 0.48 | 2.47 | 0.46 | 0.15 | 0.05                            | 250.10                  | 0.48             | 11.88               | 9.25  |
|     | 0.39                | 10.5 | 0.82 | 0.19 | 0.51 | 2.55 | 0.47 | 0.16 | 0.08                            | 250.14                  | 0.50             | 11.88               | 9.29  |
|     | 0.39                | 13.0 | 0.93 | 0.19 | 0.51 | 2.48 | 0.50 | 0.06 | 0.07                            | 232.30                  | 0.49             | 11.88               | 9.30  |
|     | 0.37                | 10.6 | 0.45 | 0.28 | 0.47 | 2.54 | 0.42 | 0.15 | 0.06                            | 250.20                  | 0.49             | 11.90               | 9.25  |
|     | 0.39                | 13.2 | 0.45 | 0.30 | 0.50 | 2.51 | 0.46 | 0.06 | 0.05                            | 249.81                  | 0.46             | 11.78               | 9.28  |
|     | 0.38                | 10.5 | 0.81 | 0.30 | 0.50 | 2.54 | 0.48 | 0.06 | 0.08                            | 250.11                  | 0.48             | 11.88               | 9.24  |
|     | 0.37                | 13.2 | 0.82 | 0.28 | 0.46 | 2.52 | 0.42 | 0.15 | 0.06                            | 249.73                  | 0.47             | 11.90               | 9.24  |
|     | 0.62                | 9.7  | 0.47 | 0.18 | 0.49 | 2.49 | 0.47 | 0.06 | 0.08                            | 249.81                  | 2.38             | 14.37               | 15.38 |
|     | 0.61                | 13.2 | 0.45 | 0.18 | 0.50 | 2.49 | 0.46 | 0.16 | 0.06                            | 250.60                  | 2.40             | 14.35               | 15.34 |
|     | 0.59                | 10.5 | 0.84 | 0.17 | 0.47 | 2.48 | 0.43 | 0.15 | 0.10                            | 250.70                  | 2.40             | 14.38               | 15.35 |
|     | 0.62                | 13.1 | 0.88 | 0.19 | 0.51 | 2.48 | 0.47 | 0.06 | 0.08                            | 249.85                  | 2.37             | 14.31               | 15.35 |
|     | 0.58                | 10.2 | 0.45 | 0.29 | 0.47 | 2.53 | 0.42 | 0.15 | 0.07                            | 250.14                  | 2.37             | 14.35               | 15.40 |
|     | 0.59                | 13.1 | 0.45 | 0.30 | 0.48 | 2.48 | 0.46 | 0.06 | 0.06                            | 250.11                  | 2.40             | 14.40               | 15.38 |
|     | 0.62                | 10.5 | 0.84 | 0.29 | 0.50 | 2.50 | 0.47 | 0.06 | 0.10                            | 250.00                  | 2.37             | 14.36               | 15.34 |
|     | 0.59                | 13.2 | 0.84 | 0.29 | 0.47 | 2.51 | 0.42 | 0.14 | 0.08                            | 250.32                  | 2.38             | 14.36               | 15.33 |
|     | 0.49                | 10.9 | 0.66 | 0.23 | 0.47 | 2.54 | 0.44 | 0.10 | 0.07                            | 250.28                  | 1.44             | 12.89               | 13.00 |
|     | 0.49                | 11.8 | 0.66 | 0.23 | 0.48 | 2.53 | 0.44 | 0.11 | 0.07                            | 250.00                  | 1.44             | 12.89               | 12.28 |
|     | 0.49                | 11.9 | 0.68 | 0.24 | 0.48 | 2.52 | 0.45 | 0.11 | 0.07                            | 250.32                  | 1.42             | 12.88               | 12.31 |

From the chukhrovite analysis data, Table IV, the Si/Al mole ratios in the chukhrovites ranged from 0.5 to 1.0 while the mole ratios of Ca/(Al+Si), S/(Al+Si), and F/(Al+Si) varied less than 3% around expected values of 2.0, 0.5, and 6.5, respectively.

The phosphorus in the chukhrovite is not lattice incorporated. Evidence of (Fe,Mg,Al)PO<sub>4</sub> in the chukhrovite suggests co-precipitation of metal-phosphate with the chukhrovite and is supported by the relatively linear relationship of Fe and Mg concentration with that of P. Neither is there evidence that iron and magnesium incorporate into the chukhrovite lattice.

TABLE IV

## CHUKHROVITE ANALYSIS, WT %

PLM  
Chukhro-  
vite

## CHUKHROVITE MOLE RATIOS

| Al   | P    | Fe   | Mg   | Si   | F     | S    | Ca    | PLM<br>Chukhro-<br>vite | Si/<br>Al | Ca/<br>(Al+Si) | F/<br>(Al+Si) | S/<br>(Al+Si) |
|------|------|------|------|------|-------|------|-------|-------------------------|-----------|----------------|---------------|---------------|
| 3.48 | 1.04 | 0.16 | 0.08 | 3.47 | 30.30 | 3.93 | 22.20 | 90%                     | 1.0       | 2.2            | 6.3           | 0.5           |
| 3.38 | 0.98 | 0.03 | 0.05 | 3.59 | 29.40 | 3.91 | 21.00 | 95%                     | 1.0       | 2.1            | 6.1           | 0.5           |
| 3.94 | 1.05 | 0.05 | 0.04 | 3.18 | 30.20 | 4.00 | 21.10 | 95%                     | 0.8       | 2.0            | 6.1           | 0.5           |
| 3.70 | 1.02 | 0.03 | 0.03 | 3.23 | 30.00 | 4.02 | 21.00 | 95%                     | 0.8       | 2.1            | 6.3           | 0.5           |
| 3.91 | 1.08 | 0.04 | 0.06 | 3.10 | 29.10 | 3.92 | 21.00 | 95%                     | 0.8       | 2.1            | 6.0           | 0.5           |
| 3.17 | 1.08 | 0.02 | 0.04 | 3.18 | 30.20 | 3.92 | 21.20 | 95%                     | 1.0       | 2.1            | 6.3           | 0.5           |
| 4.01 | 0.96 | 0.05 | 0.05 | 2.91 | 29.70 | 3.94 | 21.20 | 95%                     | 0.7       | 2.1            | 6.2           | 0.5           |
| 3.88 | 1.00 | 0.05 | 0.03 | 3.05 | 29.80 | 3.97 | 20.70 | 95%                     | 0.8       | 2.0            | 6.2           | 0.5           |
| 4.13 | 1.76 | 0.31 | 0.18 | 2.62 | 30.00 | 3.56 | 21.20 | 95%                     | 0.6       | 2.1            | 6.4           | 0.5           |
| 3.83 | 0.86 | 0.04 | 0.07 | 3.19 | 31.10 | 3.60 | 19.60 | 95%                     | 0.8       | 1.9            | 6.4           | 0.4           |
| 4.22 | 0.91 | 0.07 | 0.05 | 3.04 | 31.50 | 3.83 | 21.40 | 90%                     | 0.7       | 2.0            | 6.3           | 0.5           |
| 4.14 | 0.86 | 0.05 | 0.05 | 2.91 | 30.90 | 3.75 | 20.80 | 95%                     | 0.7       | 2.0            | 6.3           | 0.5           |
| 4.22 | 0.89 | 0.05 | 0.07 | 2.58 | 29.70 | 3.69 | 21.20 | 95%                     | 0.6       | 2.1            | 6.3           | 0.5           |
| 4.06 | 0.89 | 0.03 | 0.09 | 3.17 | 29.80 | 3.82 | 21.40 | 95%                     | 0.8       | 2.0            | 6.0           | 0.5           |
| 4.43 | 0.87 | 0.08 | 0.06 | 2.38 | 30.70 | 3.92 | 21.50 | 95%                     | 0.5       | 2.2            | 6.5           | 0.5           |
| 3.77 | 1.63 | 0.33 | 0.17 | 3.04 | 29.10 | 3.74 | 21.20 | 95%                     | 0.8       | 2.1            | 6.2           | 0.5           |
| 3.81 | 1.19 | 0.11 | 0.08 | 3.02 | 30.00 | 3.72 | 21.80 | 95%                     | 0.8       | 2.2            | 6.3           | 0.5           |
| 3.87 | 0.94 | 0.03 | 0.04 | 2.80 | 29.60 | 3.76 | 21.20 | 95%                     | 0.7       | 2.2            | 6.4           | 0.5           |
| 4.08 | 0.98 | 0.03 | 0.04 | 3.09 | 29.60 | 3.98 | 21.40 | 95%                     | 0.7       | 2.0            | 6.0           | 0.5           |

Comparing the SWPA (Table III), to filtrate concentration data (Table V), essentially complete removal of aluminum occurred, averaging 98%. Consequently the design variables showed no significant effect on the aluminum removed. In contrast silicon removal ranged from 48% to a maximum of 81%. Maximum removal was associated with high concentrations of aluminum and phosphorus and an Si/Al mole ratio of about 0.8 in the SWPA.

The treatment effect on the  $R_2O_3/P_2O_5$  weight ratio was a reduction of 40-50%, depending on the aluminum contribution to the ratio.

TABLE V  
SWPA ANALYSIS, WT %

| No. | WT RATIO |      |      |      |      |      |      |      | R <sub>2</sub> O <sub>3</sub> /<br>P <sub>2</sub> O <sub>5</sub> |
|-----|----------|------|------|------|------|------|------|------|--|
|     | Al       | P    | Fe   | Mg   | Si   | F    | S    | Ca   |  |
| 1   | 0.01     | 10.1 | 0.48 | 0.20 | 0.22 | 1.13 | 0.18 | 0.47 | 0.03   |
| 18  | 0.01     | 13.4 | 0.47 | 0.18 | 0.17 | 0.91 | 0.14 | 0.51 | 0.02   |
| 21  | 0.01     | 10.6 | 0.84 | 0.19 | 0.26 | 1.20 | 0.16 | 0.65 | 0.05   |
| 6   | 0.01     | 13.2 | 0.91 | 0.20 | 0.17 | 0.92 | 0.13 | 0.42 | 0.04   |
| 25  | 0.01     | 10.6 | 0.47 | 0.30 | 0.26 | 1.23 | 0.17 | 0.64 | 0.03   |
| 10  | 0.01     | 13.8 | 0.45 | 0.29 | 0.18 | 0.96 | 0.13 | 0.38 | 0.02   |
| 13  | 0.01     | 10.6 | 0.81 | 0.27 | 0.24 | 1.26 | 0.16 | 0.62 | 0.05   |
| 30  | 0.01     | 10.4 | 0.86 | 0.19 | 0.25 | 1.16 | 0.15 | 0.58 | 0.05   |
| 3   | 0.01     | 10.5 | 0.49 | 0.19 | 0.20 | 0.95 | 0.19 | 0.32 | 0.03   |
| 20  | 0.01     | 13.4 | 0.48 | 0.20 | 0.15 | 0.61 | 0.13 | 0.28 | 0.02   |
| 23  | 0.01     | 10.8 | 0.87 | 0.19 | 0.22 | 0.98 | 0.17 | 0.43 | 0.05   |
| 8   | 0.01     | 13.3 | 0.86 | 0.18 | 0.12 | 0.65 | 0.14 | 0.22 | 0.04   |
| 27  | 0.01     | 10.5 | 0.46 | 0.31 | 0.21 | 1.02 | 0.19 | 0.45 | 0.03   |
| 12  | 0.01     | 13.2 | 0.46 | 0.28 | 0.12 | 0.70 | 0.18 | 0.28 | 0.02   |
| 15  | 0.01     | 10.6 | 0.87 | 0.31 | 0.23 | 1.04 | 0.18 | 0.38 | 0.05   |
| 32  | 0.02     | 14.9 | 0.96 | 0.34 | 0.16 | 0.69 | 0.12 | 0.26 | 0.04   |
| 33  | 0.01     | 12.0 | 0.65 | 0.24 | 0.20 | 0.87 | 0.13 | 0.21 | 0.03   |
| 34  | 0.01     | 12.0 | 0.62 | 0.23 | 0.16 | 0.89 | 0.14 | 0.37 | 0.03   |
| 35  | 0.01     | 12.1 | 0.63 | 0.24 | 0.21 | 0.97 | 0.13 | 0.35 | 0.03   |

Phosphorus losses from the SWPA range from 1 to 27%. No relationship between %P loss and the concentration of phosphorus, aluminum, magnesium, or iron in the SWPA was found. There was a linear relationship between the % iron and % magnesium lost with the % phosphorus lost.

Calcium concentrations in the filtrates are expected to be about 0.1-0.2% on bases of solubility products of chukhrovite and gypsum rather than the 0.4-0.6% observed. Correlation analysis of filtrate compositions show a moderate calcium, flourine, and silicon interaction and a weaker calcium and phosphorus interaction and suggest calcium fluorosilicate and calcium phosphate species. Calcium fluorosilicate could account for calcium concentration in the filtrate and may explain silicon's incomplete removal during treatment.

## EXPERIMENT 3

This experiment examines the effect of Si, F, and S concentration on % phosphorus and % silicon removed from a SWPA.

The composition of the SWPAs were significantly affected by the Si and F concentrations in the experimental design, and precipitate formation hampered preparation of some of the SWPAs. Table VI lists the SWPA analyses and the corresponding reagent compositions for each experiment.

TABLE VI

SWPA ANALYSIS, WT %

REAGENT COMPOSITION, g

| Si   | F    | S    | P     | Al   | Fe   | Mg   | Ca   | Reagent Addition |                     |        |       |
|------|------|------|-------|------|------|------|------|------------------|---------------------|--------|-------|
|      |      |      |       |      |      |      |      | SWPA             | Ca(OH) <sub>2</sub> | Gypsum | 48%HF |
| 0.34 | 1.94 | 0.29 | 12.00 | 0.48 | 0.68 | 0.18 | 0.11 | 250.40           | 9.49                | 2.54   | 9.63  |
| 0.50 | 1.86 | 0.26 | 11.90 | 0.54 | 0.74 | 0.23 | 0.12 | 250.15           | 11.46               | 4.65   | 15.42 |
| 0.58 | 2.35 | 0.29 | 11.80 | 0.54 | 0.67 | 0.22 | 0.11 | 250.23           | 12.45               | 4.85   | 14.63 |
| 0.38 | 1.94 | 0.76 | 11.90 | 0.50 | 0.70 | 0.19 | 0.10 | 250.08           | 11.42               | 0.00   | 11.08 |
| 0.54 | 1.99 | 0.76 | 11.90 | 0.53 | 0.68 | 0.22 | 0.09 | 250.46           | 14.01               | 0.00   | 15.44 |
| 0.55 | 2.46 | 0.72 | 11.80 | 0.51 | 0.66 | 0.21 | 0.09 | 250.25           | 13.85               | 0.00   | 12.59 |
| 0.47 | 2.14 | 0.54 | 11.90 | 0.49 | 0.66 | 0.19 | 0.10 | 250.50           | 12.38               | 0.26   | 11.92 |
| 0.58 | 2.13 | 0.51 | 11.80 | 0.49 | 0.68 | 0.18 | 0.10 | 250.62           | 13.30               | 1.51   | 14.64 |
| 0.45 | 2.07 | 0.58 | 11.90 | 0.51 | 0.67 | 0.19 | 0.10 | 250.48           | 12.50               | 0.00   | 12.33 |

The precipitates were at least 80% chukhrovite and contaminated with one or more salts of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{AlF}_6)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{MgAl}_2\text{F}_8 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgSiF}_6$  and  $\text{CaF}_2$ . These tended to slow filtration rates from < 1 min for homogeneous chukhrovites to at least 30 min for contaminated chukhrovite.

TABLE VII

## SOLIDS ANALYSIS, WT %

## XRD

## PLM

## MOLE RATIOS IN SOLID

| No. | SOLIDS ANALYSIS, WT % |       |      |      |      |      |      |       | Wt Solids,<br>g | XRD |   |   |   |   |   | PLM         | MOLE RATIOS IN SOLID |                |               |               |
|-----|-----------------------|-------|------|------|------|------|------|-------|-----------------|-----|---|---|---|---|---|-------------|----------------------|----------------|---------------|---------------|
|     | Si                    | F     | S    | P    | Al   | Fe   | Mg   | Ca    |                 | A   | B | C | D | E | F |             | Si/<br>Al            | Ca/<br>(Al+Si) | F/<br>(Al+Si) | S/<br>(Al+Si) |
| 1   | 0.90                  | 27.80 | 3.43 | 3.07 | 5.47 | 0.19 | 1.28 | 20.50 | 18.88           | +   | + | + | + | + | + | 80% A, B, C | 0.2                  | 2.2            | 6.2           | 0.5           |
| 2   | 2.49                  | 30.10 | 3.55 | 1.10 | 4.46 | 0.07 | 0.06 | 20.50 | 30.63           | +   | + | + | - | - | - | 95% A, B    | 0.5                  | 2.0            | 6.2           | 0.4           |
| 4   | 3.14                  | 34.50 | 3.86 | 0.94 | 3.63 | 0.12 | 0.28 | 21.10 | 33.33           | +   | - | - | + | - | - | 90% A       | 0.8                  | 2.1            | 7.4           | 0.5           |
| 5   | 1.44                  | 25.80 | 4.77 | 2.37 | 4.30 | 0.18 | 0.74 | 20.10 | 24.79           | +   | + | + | + | - | + | 80% A, D    | 0.3                  | 2.4            | 6.4           | 0.7           |
| 6   | 2.63                  | 28.60 | 4.32 | 0.85 | 3.66 | 0.06 | 0.05 | 20.90 | 30.84           | +   | + | + | + | - | - | 90% A, B    | 0.7                  | 2.3            | 6.6           | 0.6           |
| 8   | 2.64                  | 30.80 | 4.00 | 0.57 | 3.66 | 0.05 | 0.34 | 20.80 | 32.35           | +   | - | - | - | - | - | 90% A, B    | 0.7                  | 2.3            | 7.1           | 0.5           |
| 9   | 2.31                  | 31.30 | 3.47 | 1.25 | 4.42 | 0.13 | 0.63 | 21.30 | 27.66           | +   | + | - | + | - | + | 90% A, G    | 0.5                  | 2.2            | 6.7           | 0.4           |
| 0   | 2.50                  | 29.50 | 3.25 | 1.10 | 3.45 | 0.20 | 0.39 | 20.60 | 33.14           | +   | - | - | + | - | + | 80% A, G    | 0.7                  | 2.4            | 7.2           | 0.5           |
| 1   | 2.49                  | 29.90 | 3.33 | 1.71 | 3.63 | 0.17 | 0.38 | 20.50 | 23.79           | +   | - | - | + | - | + | 90% A, G    | 0.7                  | 2.3            | 7.1           | 0.5           |

A = chukhrovite

B =  $\text{Ca}_3(\text{AlF}_6)_2 \cdot 4\text{H}_2\text{O}$ 

C = gypsum

D =  $\text{MgAl}_2\text{F}_8 \cdot 2\text{H}_2\text{O}$ E =  $\text{Na}_2\text{SiF}_6$ F =  $\text{CaF}_2$ 

G = unidentified

The filtrate analyses data is listed in Table VIII and the %P removed ranged from 5 to 20%. The removal was statistically related with an  $R^2=0.88$  by the coded equation:

$$\%P = 13.9 - 5.0*Si - 1.5*Si*S$$

and suggests the higher concentrations of silicon and sulfur in the SWPA minimized the loss of P. This could reflect as suggested in experiment 2 the interaction of calcium—the major cation in the treatment reaction (2-4% Ca)—with phosphate, fluorosilicate, and sulfate. The amount of phosphorus precipitated with the chukhrovite accounts for less than 2% of the total P lost; therefore it is likely the wash step leached phosphate from the precipitates.

**TABLE VIII**  
**FILTRATE ANALYSIS, WT %**

| No. | Si   | F    | S    | P     | Al   | Fe   | Mg   | Ca   | Wt<br>filtrate, g |
|-----|------|------|------|-------|------|------|------|------|-------------------|
| 1   | 0.55 | 2.24 | 0.23 | 15.50 | 0.06 | 1.00 | 0.11 | 0.80 | 153.15            |
| 2   | 0.35 | 1.44 | 0.20 | 11.70 | 0.01 | 0.71 | 0.22 | 0.35 | 222.90            |
| 4   | 0.26 | 1.31 | 0.16 | 12.10 | 0.01 | 0.78 | 0.18 | 0.25 | 219.68            |
| 5   | 0.37 | 1.42 | 0.26 | 13.10 | 0.03 | 0.81 | 0.11 | 0.28 | 169.91            |
| 6   | 0.46 | 1.84 | 0.38 | 18.00 | 0.06 | 1.11 | 0.35 | 0.44 | 148.56            |
| 8   | 0.22 | 1.02 | 0.33 | 12.30 | 0.02 | 0.77 | 0.16 | 0.30 | 221.73            |
| 9   | 0.26 | 1.05 | 0.19 | 12.30 | 0.03 | 0.75 | 0.14 | 0.32 | 212.41            |
| 10  | 0.25 | 1.06 | 0.27 | 11.90 | 0.02 | 0.75 | 0.14 | 0.22 | 219.01            |
| 11  | 0.45 | 1.77 | 0.34 | 17.00 | 0.05 | 1.09 | 0.20 | 0.38 | 149.25            |

# CONCLUSIONS

Chukhrovite,  $\text{Ca}_{2(x+y)}\text{Al}_x\text{Si}_y(\text{SO}_4)_{0.5(x+y)}\text{F}_{6.5(x+y)}$ , precipitation can remove over 90% of the aluminum in SWPAs by treating the SWPA to satisfy the mole ratios  $\text{Ca}/(\text{Al}+\text{Si}) = 2.0$ ,  $\text{F}/(\text{Al}+\text{Si}) = 6.5$ , and  $\text{S}/(\text{Al}+\text{Si}) = 0.5$ .

The chukhrovite typically incorporated < 80% of the silicon from the SWPAs which affected the % calcium, fluorine, and sulfur removed from the SWPA. The higher than expected concentration of calcium and silicon after treatment could be due to a calcium fluorosilicate interaction as suggested from regression data on the calcium, silicon, and fluorine concentrations.

# CONCLUSIONS

Iron and magnesium are not incorporated into the chukhrovite during precipitation. The reduction of the  $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)/\text{P}_2\text{O}_5$  weight ratio is reduced by aluminum's contribution, which was at least 40% in these tests.

Phosphate losses of 1-26% from SWPAs were minimized by an increase in the silicon and sulfur concentrations and could suggest that adequate fluorosilicate and sulfate concentrations are necessary to minimize phosphate-metal interactions. Since only 1% of the phosphorus lost from the SWPA was in the chukhrovite, phosphate is being leached to the wash.