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THE EFFECT OF EXTRANEOUS SOLUBLE IONS IN IGNEOUS ROCK PHOSPHATE ON CRYSTALLOGRAPHY OF GYPSUM DIHYDRATE AND THUS PHOSPHORIC ACID PRODUCTION¹

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SUMMARY

At present, Foskor produces 3 million tons per annum of igneous origin rock phosphate. Three grades are produced, namely, 88 BPL pyroxenite (88P), 88 BPL foskorite (88S) and 80 BPL (80M). Approximately two thirds (mostly 80M product) are used locally for phosphoric acid production and the higher grades are exported mainly to Asian and European markets. The 88 grade consists predominantly of fluoroapatite (greater than 39 percent P_2O_5) and therefore contains only trace amounts of minerals and thus chemical impurities.

By nature, igneous rock behaves somewhat differently to sedimentary rock and as such, the influence of impurities would have a measurable effect in a wet process acid (WPA) environment. Notably, the effects of aluminium and silica (and other trivalent cations) have a positive influence on the morphology and filterability of the gypsum by-product. Sodium and potassium have deleterious effects on filterability.

RESUME

Actuellement, Foskor est le seul producteur de phosphate en Afrique du Sud (3 millions de t/an). Trois titres sont produits, à savoir la pyroxénite 88 BPL (88P), la foskorite 88 BPL (88S) et le 80 BPL (80M). Deux tiers environ (essentiellement le produit 80M) sont utilisés localement pour produire l'acide phosphorique et les titres plus élevés sont principalement exportés sur les marchés asiatiques et européens. Le titre 88 consiste surtout en fluoapatite (avec plus de 39 % P_2O_5) et ne contient par conséquent que des traces de minéraux donc d'impuretés chimiques.

Par nature, le phosphate igné se comporte différemment du phosphate sédimentaire et par là l'influence des impuretés doit avoir un effet mesurable dans le procédé d'acide phosphorique de voie humide. En particulier, les effets de l'aluminium et de la silice (et d'autres cations trivalents) ont une influence favorable sur la morphologie et la filtrabilité du gypse sous-produit. Le sodium et le potassium ont un effet défavorable sur la filtrabilité.



1. INTRODUCTION

As the availability of high grade and good quality sedimentary phosphate rock diminishes, the utilisation of igneous rock for all types of phosphoric acid production will progressively increase. This fact, together with its inherent advantages, such as the by-production of high quality gypsum, will see the introduction of igneous rock phosphate, either in a blend or singularly on many plants throughout the world.

Igneous rock, however, is currently not widely utilised on its own, but in blends with other sedimentary rock. This is often due to logistic reasons, but sometimes there is a preference to use sedimentary rock based on the misconception that igneous origins are more difficult to process. This paper attempts to readdress this misapprehension and show that by using high-grade igneous rock under controlled conditions, the benefits of igneous rock can be enjoyed.

¹ L'influence d'ions solubles dans le phosphate igné sur la cristallographie du dihydrate de gypse et donc sur la production de l'acide phosphorique

1.1 Gypsum crystallography

The crystallography of gypsum dihydrate produced from igneous rock is very often quite different to the cluster type crystals produced from sedimentary rock sources. Normally, the crystals are flat, needle-like in appearance and are affected by factors such as uncomplexed ("free") sulphate variations, phosphoric acid concentration, temperature, and soluble impurities. Such impurities may be present in low grade (low P₂O₅ content) material since lower grades will contain contaminating minerals other than quartz which may be soluble in a phosphoric and sulphuric acid environment. In some instances, the impurities may originate from other rock sources used in a blend. Depending on the level of the impurity, the rate of crystal growth and morphology may be affected such that filtration rates are retarded and production capacity hindered. Alternatively, the ions produced upon dissolution may have a positive effect on crystallography by increasing the size and thickness of the crystal.

In addressing this issue, a significant amount of work has been published on specific impurities and their effects. Most work has been done on pure reagents, that is, pure phosphoric acid and calcium phosphate, but little work has been done in the area of using actual plant raw materials and simulation of plant conditions. This is presumably, because it is difficult to duplicate dihydrate crystallisation processes in a laboratory environment. Novel apparatus design has however, allowed investigations of the effect of impurities under plant conditions.

In this exercise, therefore, studies have been conducted on some common contaminants, using this apparatus, to quantify its effect in a phosphoric acid production environment. All studies were carried out on Foskor's pyroxenitic rock phosphate (88P) since this will become Foskor's chief product in the future.

1.2 The crystallisation process

In order to understand and define the mechanism of crystallisation of gypsum dihydrate from phosphoric acid, it is necessary to highlight certain aspects of the theory of crystallisation. Crystallisation in this case pertains to the growth of CaSO₄.2H₂O units in an ordered pattern.

Crystallisation takes place according to two models:

- i) Homogeneously (crystals form around aggregates of ions)
- ii) Heterogeneously (crystals form around foreign particles e.g. dust)

It is likely that a precipitation will involve both of these mechanisms.

The forces, which draw ions from solutions to nucleation sites, are both electrostatic and chemical in nature.

There are varying degrees of supersaturation, depending on the concentration of solute and temperature of the solution. When an equilibrium condition exists the solution is called a saturated solution. Solutions with temperature and concentration values above saturation are supersaturated solutions until critical supersaturation is reached. The solutions are then unstable and precipitation will occur from such solutions.

The degree of supersaturation in a solution influences the rate at which a precipitate forms. The proportionality is expressed in a semi-quantitative way by the von Weimarn equation[1].

$$\text{Rate} \propto (Q - S)/S \quad (1)$$

Where: Q = actual concentration
S = equilibrium solubility

A number of variations on this equation have been published, but all appear to adopt the basic form:

$$\text{Rate} = K(Q - S)^n/S \quad (2)$$

Where: K is a rate constant for the process of crystal growth.
n is the reaction order

Becker has described the crystallisation process as the birth of a constant number of nuclei (under supersaturation conditions) followed by growth of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on these nuclei, that is, the crystal growth rate is a function of the rate of nucleation and growth rate on these nuclei. This fundamental principle has been adopted throughout this investigation.

As it is difficult to determine the specific surface area of flat elongated crystals, as is the case with igneous rock phosphate, a simplified rate equation was adopted to determine the growth rate[2]:

$$\text{Rate} = dQ/dt \quad (3)$$

In which the concentration of dissolved calcium sulphate was monitored as a function of time (t).

1.2.1 *The mechanism of the influence of impurities on crystallisation process*

The exact mechanism by which a precipitate may become contaminated is most often complex and is governed by four processes namely[1]:

Co-precipitation by adsorption:

Contamination of colloidal surfaces involves both physical (electrostatic) and chemical interactions. There are four chemical factors which favour the adsorption of one ion rather than another of the same charge at a surface site:

- i) Solubility: The ion which forms the less soluble compound with one of the ions of the precipitate will be preferentially adsorbed. (Paneth-Fajans-Hahn rule)
- ii) Concentration: The ion that is present at higher concentration will be adsorbed
- iii) Ionic charge: The higher the charge on an ion, the more readily it is adsorbed.
- iv) Ionic size: Precipitates prefer to adsorb ions which are similar in size to those making up the precipitate crystal lattice.

Co-precipitation by occlusion:

In this form of contamination impurities (foreign ions and solvent) are trapped either in cavities within crystals or in cavities within aggregates of small crystals.

Co-precipitation by Isomorphous replacement:

Isomorphous replacement occurs when one compound is able to fit into the crystal lattice of another compound with little or no distortion of the lattice. It is necessary that the ions making up the two compounds have about the same ionic radius and that the chemical bonds of the two compounds have about the same degree of covalence. The replacement tends to be uniform throughout the precipitate, in contrast to the highly localised contamination that results from occlusion.

Post-precipitation:

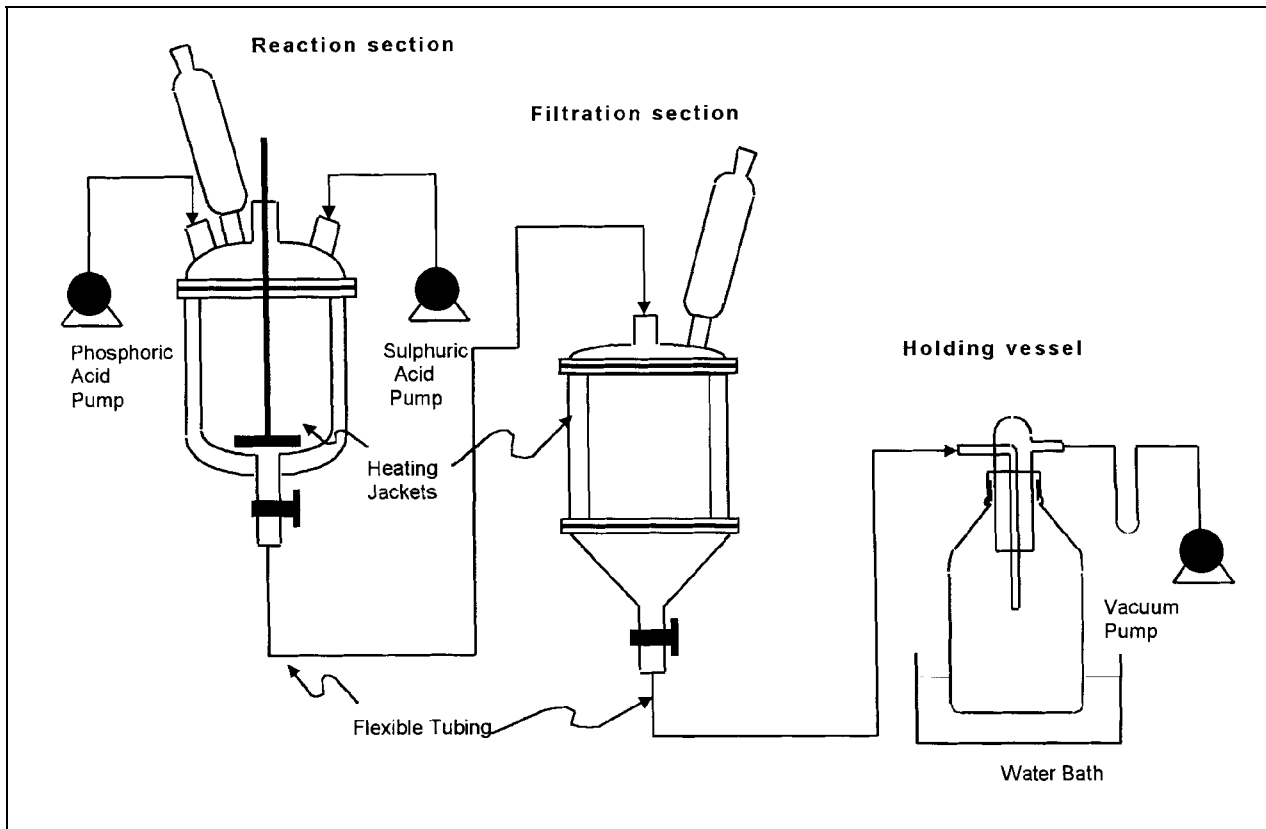
A second precipitate which develops after the first precipitation, which may have the same composition as the initial precipitation or a different composition.

2. METHODOLOGY

2.1 Crystal production and growth

The apparatus used for all crystallisation experiments is depicted in Figure 1. The apparatus consists of a reaction section, in which reagents and ingredients were allowed to react under controlled conditions; a filtration section, in which solids were separated from phosphoric acid, and a filtered acid storage unit.

Figure 1 - Schematic diagram of crystallisation test apparatus



Reagents (sulphuric acid, calcium hydroxide, 5 percent (mass per mass) gypsum and weak phosphoric acid obtained from a WPA plant) were pumped at precise, measured flow-rates into the reaction vessel which was heated to a nominal temperature (usually 80°C) and stirred at a suitable, predetermined rate. Various effects were measured at this point, such as the rate of pumping, adding the sulphuric acid to the phosphoric acid, etc. Provision was made for sampling of the slurry formed during this stage. The sampling system incorporated a vacuum drawn system through a fine, porous, glass frit into a pre-weighed container. The sample was then completely digested (since some solids would post-precipitate) with concentrated nitric acid. Sulphate, calcium, and other elements were then analysed at leisure.

The reaction to produce precipitated gypsum was as follows:



Upon complete addition of the reagents, and after a predetermined retention time was allowed, the contents of the reactor was drained into the filtration section in which the solids was totally separated from the acid. The rate of filtration was determined from the time taken till all visible liquid was removed (in reality the cake would still contain a significant amount of phosphoric acid). The weight and concentration of phosphoric acid was determined. The mass and density of the total slurry and the phosphoric acid produced was recorded and the percentage solids calculated according to equation 5:

$$\% \text{ Solids} = \left[\frac{2.32 (\text{Slurry density} - \text{acid density})}{\text{Slurry density} (2.32 - \text{acid density})} \right] \times \frac{100}{1} \quad (5)$$

Where: 2.32 is the density of gypsum dihydrate

The cake was then thoroughly washed and sampled for further analyses and tests (recording of crystal quality, size, SEM (scanning electron microscope and other characteristics). The rate of post-precipitation (and the characteristics of the precipitate) was also determined as a function of time.

2.1 Analyses of solutions and solids

Total sulphate determinations of the three acid samples were done by titration with barium chloride and sulphonazo III indicator, while the calcium was determined with ICP analyses. Acid samples were analysed for P₂O₅ and gypsum samples for total P₂O₅ only, by the colour development – UV spectrophotometric method. Gypsum samples were dried and IR spectra were recorded between 400 and 4000 cm⁻¹ on a Bruker IFS 113V spectrophotometer in the form of pressed KBr pellets. The gypsum and acid samples were analysed for different compounds with ICP analyses and electron micrographs were taken. Electron micrograph studies were carried out with JEOL JSM-840 scanning microscope.

3. DERIVATION AND IMPORTANCE OF THERMODYNAMIC SATURATION AND SUPERSATURATION LIMITS OF CaSO₄·2H₂O

The formation of calcium sulphate dihydrate (gypsum) nuclei (see section 1.2) is primarily controlled by the level of supersaturation (a metastable concentration exceeding that of solubility product) of calcium and sulphate ions in phosphoric acid. The solubility product defines the situation in which calcium sulphate in the solid phase exist in equilibrium with calcium and sulphate ions in phosphoric acid. The saturation curve can then be calculated using the solubility product [3]:

$$\text{SO}_4^{2-} \cdot x \text{Ca}^{2+} = K \quad (7)$$

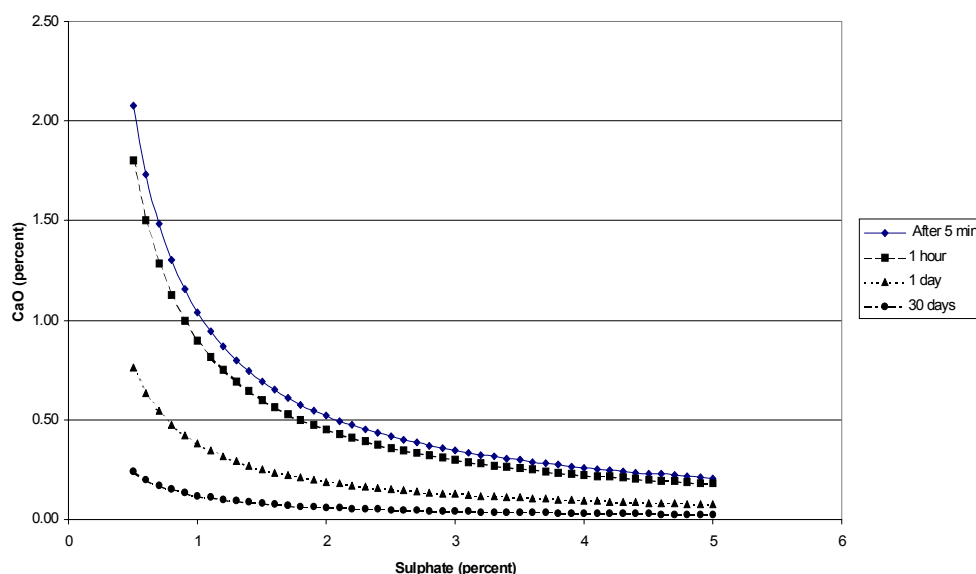
Expressing the concentration as percentages of SO₄²⁻ and CaO instead of the molar concentration, the equation can be simplified as follows:

$$K_s = \text{SO}_4^{2-\%} \times \text{CaO}\%^2 \quad (8)$$

The supersaturation curve can however, only be determined by experimentation. To achieve this, instantaneous samples of the slurry must be taken and analysed for SO₄²⁻ and CaO. These concentrations were found to be an exponential function of time and it is therefore difficult to determine the true supersaturation curve.

The saturation and supersaturation curves were determined in phosphoric acid supplied from Foskor's pilot-plant facility and used throughout as a base study. Samples of slurry were taken after 5 minutes, 1.5 hours retention time, and acid samples after 1 day and 4 weeks (30 days). The samples were analysed for SO₄²⁻ and CaO and the results were plotted graphically as presented in Figure 2.

Figure 2. Supersaturation and saturation curves of calcium sulphate dihydrate in 29 percent P₂O₅ phosphoric acid

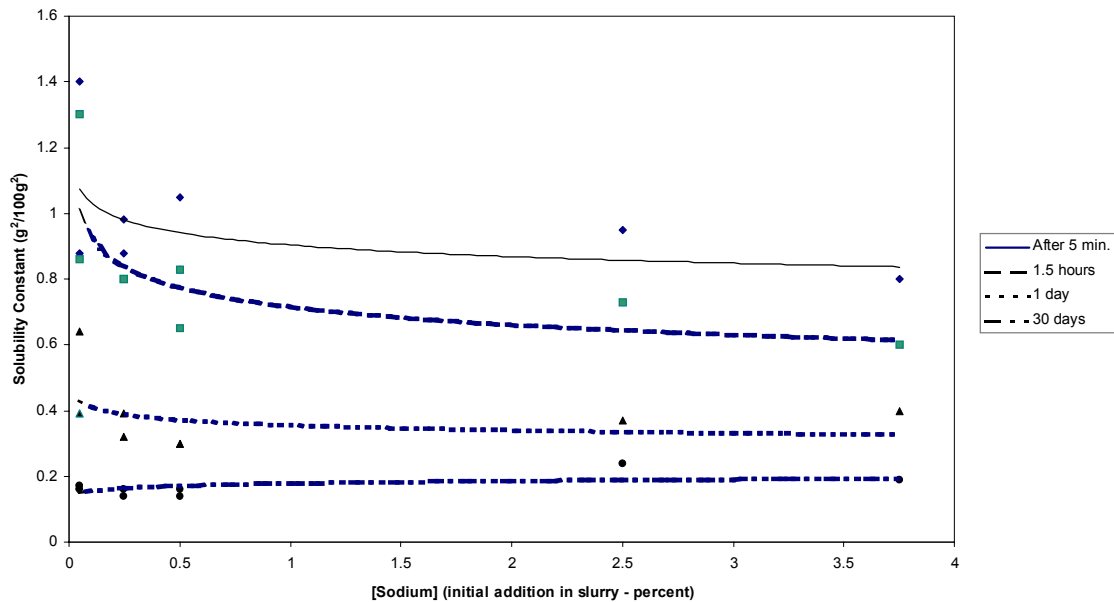


² A value of 0.83 has been quoted by Becker, but as is shown in this investigation, it varies considerably depending on factors like time, level of impurities, etc.

3.1 The effect of sodium on gypsum solubility and crystal morphology

For the study of gypsum supersaturation and saturation with increased levels of sodium, sodium hydroxide was added in differing amounts together with sulphuric acid and plotted as a function of the solubility product of dissolved calcium sulphate as is shown in Figure 3.

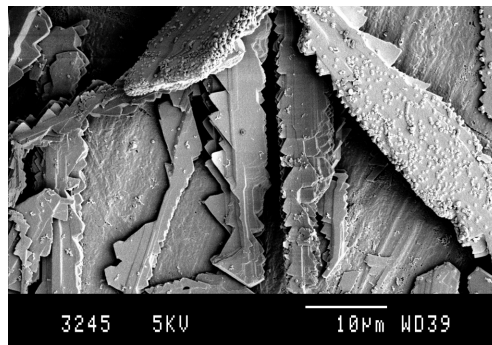
Figure 3. The effect of the increase in Sodium concentration on gypsum solubility



Sodium appears to significantly depress gypsum supersaturation at higher levels, that is, it reduces solubility, and increases the rate of crystallisation in the initial stages of reaction (after 5 minutes). This is supported by Brandse *et al* [4] who found that the addition of sodium chloride in pure solutions increased the rate of crystallisation remarkably. This would imply that gypsum crystals would be smaller and finer with increased sodium concentration leading to poorer filtration rates.

The morphology of the gypsum crystals was not significantly affected, however the morphology of the post-precipitate was indeed altered, in that twinning and a “saw tooth” appearance was observed. This is shown in electron micrographs EM1 (Figure 4). Sodium hexafluorosilicate precipitation can also be seen in the micrograph. The reason why the morphology of the gypsum crystals was not affected is probably an insufficient amount of time to reach equilibrium before the gypsum is filtered.

Figure 4 - Micrograph (EM1) of gypsum post-precipitate under the influence of sodium.



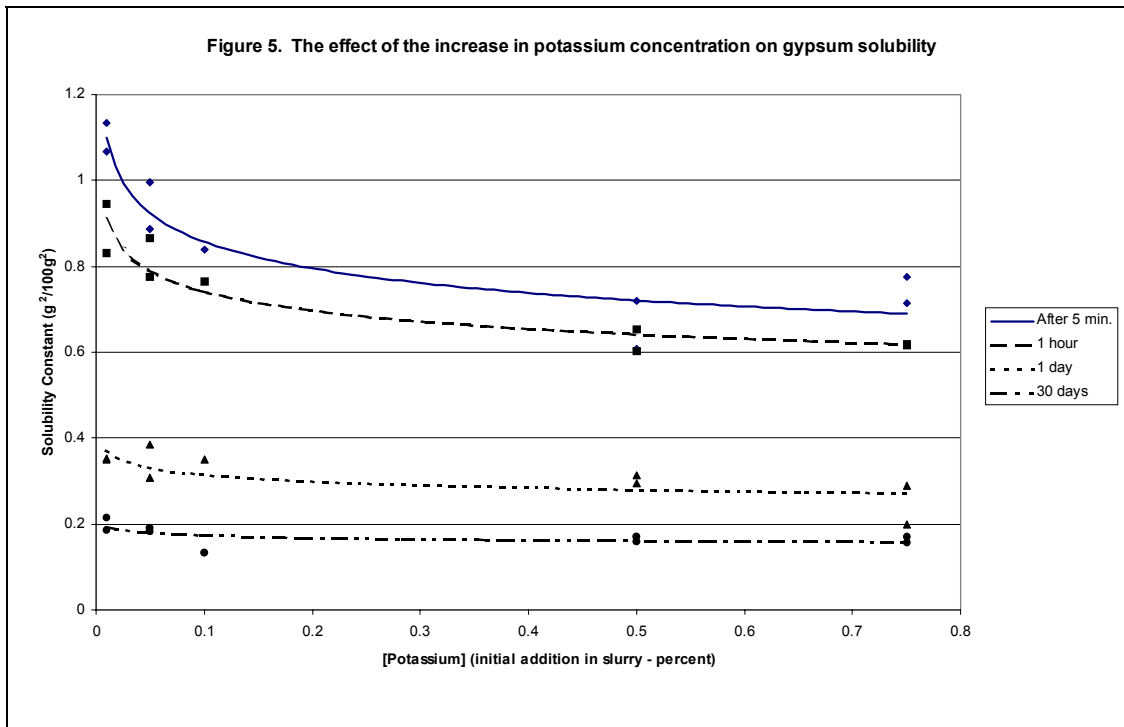
An increase in sodium concentration will enhance the precipitation of sodium hexafluorosilicate. This is evident in the analyses of gypsum produced.

Table 1 - Analysis of gypsum produced in the presence of high sodium levels

	Initial sodium concentration added (percent)				
	0.05	0.25	0.5	2.5	3.75
P ₂ O ₅	5.14	3.66	6.64	8.88	11.56
F	0.55	0.85	1.50	1.90	1.80
SiO ₂	0.11	0.13	0.07	0.08	0.12
Na ₂ O	0.09	0.58	1.07	3.30	4.91

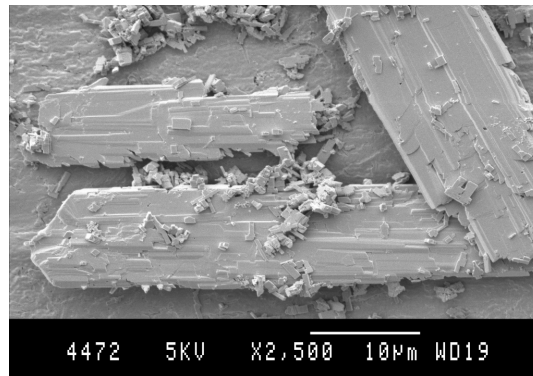
3.1 The effect of potassium

The effect of potassium impurity was very similar to sodium in that the solubility of gypsum was depressed (Figure 5), that is, the crystallisation rate increased, giving rise to the potential of poor filtration rates on a phosphoric acid plant.



Again the higher levels (0.5 percent initial addition) of potassium result in the co-deposition of K₂SiF₆, as can be seen in micrograph EM2 (Figure 6).

Figure 6 - Micrograph (EM2) of gypsum crystals showing the presence of co-deposited K_2SiF_6



Elevated levels of potassium can also result in increased amounts of post-precipitation and scaling, as is the case with sodium. The presence of potassium together with ferric ion can however, result in the formation of the so-called X-compound $[(Fe,Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O]$. This has the potential of resulting in substantial losses of phosphate [3].

3.3 The effect of magnesium

Despite the reports that magnesium affects both gypsum crystal morphology and solubility, it has been found that in the ranges of magnesium concentrations investigated (0.01 – 0.75 percent) a relatively low effect on gypsum supersaturation and solubility was observed. A comparison of Figure 7 (solubility constant versus magnesium initial concentration) with Figures 3 and 5 shows that the supersaturation and saturation curves of gypsum have a constant, linear tendency, that is, high magnesium has virtually the same result as lower values on the gypsum solubility product. Generally the morphology was unaffected by changes in magnesium levels.

Figure 7. The effect of an increase in Magnesium concentration on gypsum solubility

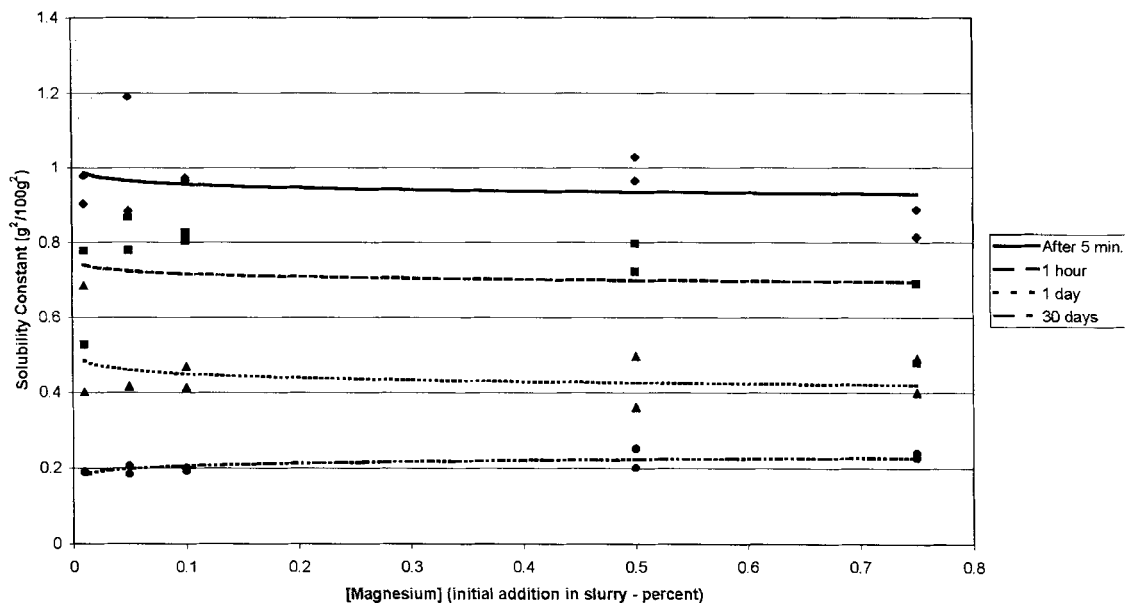
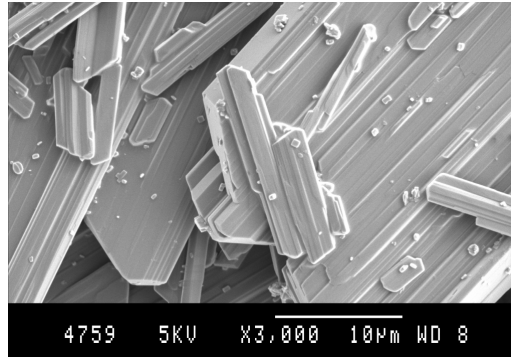


Figure 8 (micrograph EM3) is a typical example indicating this.

Figure 8 - Micrograph (EM3) of gypsum crystals produced from slurry with a 0.75 percent initial magnesium concentration



This rather unusual finding can perhaps be explained by the fact that magnesium is mostly soluble in phosphoric acid and very little deposits to the gypsum. Slack [4] has pointed out that magnesium has a major influence on the viscosity of the acid by the fact that magnesium polarises the water molecules surrounding the phosphate ions and strengthens the hydrogen bonding with and stabilises the lattice structure of phosphate.

It should therefore be concluded that although the presence of magnesium has a lesser effect on crystal morphology, high levels might indeed cause poor filtration simply due to an increase in acid viscosity.

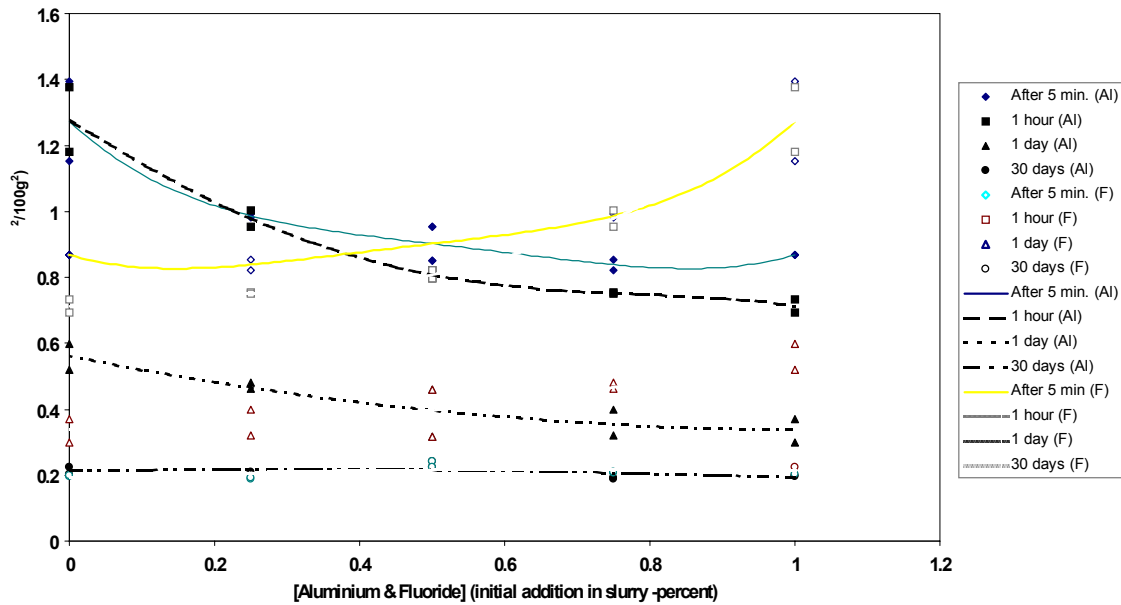
4 The effect of aluminium and fluoride

In order to study the role of aluminium and fluorine, calcium fluoride and aluminium hydroxide were added in varying amounts with the sulphuric acid. A plot of the solubility constants versus the initial aluminium and fluorine concentrations is presented in Figure 9.

Elevated levels of aluminium increases the solubility of gypsum, and enhances three-dimensional growth, which would have the result of promoting filtration. With progress of time, however, the solubility of gypsum is reduced, that is, the levels of calcium and sulphate in solution are lowered resulting in smaller crystals that will reduce filterability.

Although higher concentrations of aluminium initially promote crystal growth and thus filtration rates, it also brings disadvantages. It increases the acid viscosity and density and lowers the acid strength, resulting in poorer filtration rates[3].

Figure 9. Increase in Aluminium and Fluoride concentrations versus gypsum solubility



The presence of fluorine can reverse the effect of aluminium. According to Glazyrina *et al*, the maximum solubility of calcium sulphate was obtained in phosphoric acid solutions containing aluminium and fluoride ions in an ionic ratio corresponding to the maximum formation of AlF_3 [6]. At elevated fluorine levels the “free” fluorine ions interact with calcium sulphate to form relatively insoluble calcium fluoride and sulphuric acid [7]. Analyses of the gypsum obtained at varying levels of aluminium and fluoride are presented in Table 2.

Table 2 - Analysis of gypsum produced in the presence of different aluminium and fluorine levels

	Initial aluminium and fluorine concentration added (percent)				
	1.0F 0.0Al	0.75F 0.25Al	0.5F 0.5Al	0.25F 0.75Al	0.0F 1.0Al
P ₂ O ₅	4.4	7.1	8.0	9.8	11.3
F	1.6	1.4	1.2	0.8	0.4
SiO ₂	0.33	0.45	0.27	0.15	0.11
CaO	32.0	30.0	30.0	27.0	24.7
SO ₄	40.7	38.8	40.0	38.0	38.3
Al ₂ O ₃	0.06	0.31	0.50	0.70	1.20

Although most of the aluminium departs to the phosphoric acid, the amount in the gypsum product increases with an increase in initial (added) aluminium concentration.

A comparison of electron micrographs EM5 and 6, as presented in Figures 10 and 11, shows the agglomeration and three-dimensional growth under high aluminium concentrations.

Figure 10 - Micrograph (EM5) of gypsum crystals produced from slurry without any additional aluminium

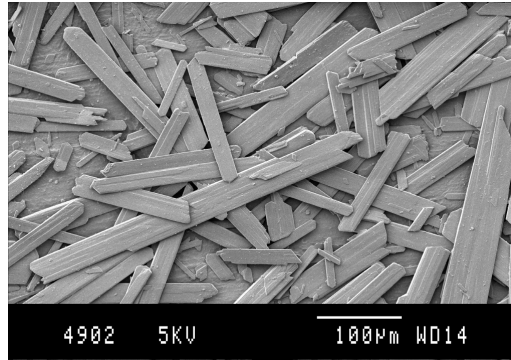
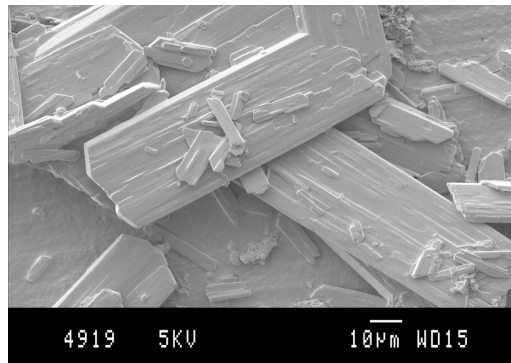


Figure 11 - Micrograph (EM6) of gypsum crystals produced from slurry with a 0.75 percent added aluminium concentration



4. CONCLUSIONS

The effect of elevated concentrations of dissolved ions on gypsum solubility and morphology was studied in a plant-simulated WPA environment. This study was conducted on phosphoric acid produced from concentrate of pyroxenitic (igneous) origin.

- i) The saturation and supersaturation curves were determined for 88BPL rock phosphate. The curves and thus saturation of calcium sulphate in phosphoric acid are time dependent, and true equilibrium saturation is only attained after an approximately 30-day period.
- ii) Sodium and potassium have a similar influence on the solubility of gypsum. The solubility is markedly suppressed and crystals are smaller and finer which would affect plant filtration rates negatively. "Twinning" (a visual phenomenon in which crystal growths occur at right angles to the original growth plane) is characteristic at high levels of sodium.
- iii) Magnesium has little effect on the morphology and solubility of gypsum. Filtration however, would be affected by the increased viscosity of the phosphoric acid produced.
- iv) The presence of aluminium promotes three-dimensional growth on gypsum crystals and would therefore enhance filtration on a WPA plant. The presence of fluorine decreased the positive role of aluminium (presumably through complexation as AlF_3 and AlF_6^{3-}). The viscosity of the acid, as with magnesium, is increased by appreciable levels of aluminium.

5. ACKNOWLEDGEMENTS

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