

Potential groundwater contamination by fluoride from two South African phosphogypsums

MP Motalane* and CA Strydom

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Abstract

A study to investigate the fluoride content in two South African phosphogypsums, Kynoch and Omnia, and the potential threat to water sources was undertaken. Kynoch and Omnia phosphogypsums were found to consist of fluoride in the region of 0.12% and 0.03% by mass, respectively. The phosphogypsum samples were mixed with ZnO and anhydrous Na₂CO₃ and fluxes thereof prepared at 900°C. The cooled melt was dissolved in deionised water and the fluoride content of each sample determined using the ISE method. These unwashed samples were compared with purified phosphogypsum samples, prepared through a leaching process using deionised water, lime or diluted sulphuric acid solutions. The fluoride content for melts of the purified samples was also determined by the ISE method. The amount of fluoride leached from Kynoch and Omnia phosphogypsums when treated with water was 9% and 22% respectively. Lime pretreatment of Kynoch and Omnia phosphogypsums leached out 37% and 6% of fluoride respectively. On the other hand, the diluted sulphuric acid solution leached out in excess of 70% of the original fluoride from both Kynoch and Omnia phosphogypsums. The presence of fluoride, a species of environmental concern, in South African phosphogypsum as indicated in this study, indicates the need to have waste disposal facilities constructed in such a manner that safeguards the environment. The study also indicates that regular monitoring of fluoride in the environment in the vicinity of phosphogypsum waste disposal sites has to be undertaken.

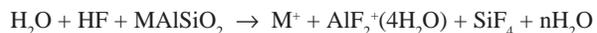
Keywords: fluoride, chemical gypsum, phosphogypsum, impurities

Introduction

Chemical gypsum encompasses all by-product and co-product gypsum produced from a variety of industries. These industries include, among others, electrical power plants, phosphoric acid plants and titanium oxide production plants. Phosphogypsum, a by-product chemical gypsum produced in the phosphate fertilizer industry, is produced in large quantities in South Africa. Only a small portion of the overall phosphogypsum produced is utilised by cement companies, such as LaFarge, as a set retarder in the place of natural gypsum. Another small portion is utilised in agriculture to combat alkalinity and salinity in soils that have a high sodium concentration. The bulk of the phosphogypsums produced is transported to repositories on land and stacked.

Phosphogypsum is acidic due to residual phosphoric acid, sulphuric acid and hydrofluoric acid within the porous structure. The acidic nature of fresh phosphogypsum may keep trace elements which have been dissolved from the phosphate rock in a potentially mobile state. Among the concomitant impurities are fluorides, sulphates, acids, organics, trace metals and naturally occurring radionuclides (U, Cd, etc.) (Rutherford et al., 1994).

Disposal of phosphogypsum on land may pose seepage problems beneath the repositories or the process water holding ponds. Fluoride contaminant present in phosphogypsum may attack silicate minerals and dissolve them, according to the equation:



where:

MAISiO₂ represents an aluminosilicate mineral

M represents Ca, Mg, Na, K, and Fe

AlF₂⁺(4H₂O) is a complex ion of Al (Rutherford et al., 1994).

* To whom all correspondence should be addressed.

☎+2712 429 8549; fax:+2712 429 8028;

e-mail: motalmp@unisa.ac.za

Received 19 April 2004; accepted in revised form 28 July 2004.

Some of the SiF₄ may hydrolyse to form H₂SiF₆ (fluorosilicic acid) within the phosphogypsum leachates. The presence of H₂SiF₆ may result in dissolution of clay soils at the bottom of phosphogypsum repositories, which may allow accelerated movement of contaminants into the groundwater over time.

Fluoride is a species of environmental concern and is regulated in the water supply. In domestic water supply as well as in the industrial supply used in the food and beverage industries, fluoride concentrations should not exceed the required levels. The South African drinking water standard is 1.5 mg/l (Coetzee et al., 2003). High levels of fluoride in drinking water may cause dental and skeletal fluorosis. In various African countries, such as Kenya and Tanzania, and certain parts of South African provinces (North West, Northern Cape and Limpopo) there are very high levels of fluoride in groundwater (as high as 30 mg/l) causing a preponderance of dental fluorosis in affected inhabitants who source drinking water from untreated groundwater (Coetzee et al., 2003).

In the study reported here, the extent of fluoride impurity in two South African phosphogypsums, Omnia and Kynoch, was determined. The amount of soluble fluoride which can be removed by leaching the phosphogypsum with water was determined to investigate the potential threat to water sources. The effect of purifying the phosphogypsums with lime and a diluted sulphuric acid solution was also studied as potential methods to control fluoride leaching from phosphogypsum wastes.

Approach to the study

Phosphogypsum samples were sourced from two South African companies that produce phosphate fertilizers, namely Kynoch Fertilizers and Omnia Phosphates. Kynoch and Omnia companies are both situated in the North West province at Potchefstroom and Rustenburg respectively. The phosphogypsum samples were obtained as dried powdery substances.

The content of fluoride was determined from the solid samples in order to establish the quality of the phosphogypsum that would

remain in storage facilities (phosphogypsum stacks) after pretreatment at plant level. A separate batch of phosphogypsum samples was used for the sulphuric acid treatment. The results for sulphuric acid treated samples are provided separately from the water-washed and lime-washed samples.

In this study, phosphogypsum samples were prepared by means of a sintering technique using sodium carbonate-zinc oxide mixture as explained in the experimental section below. Previous studies used to bring fluoride into solution from cement and related materials were done to compare this sintering technique to fuse the sample using LiBO_2 (Javellana and Jawed 1981). The authors determined fluoride by the ion-selective electrode method and at the same time analysed various reference materials to validate the technique. The two sample preparation methods, namely, LiBO_2 fusion and zinc oxide-sodium carbonate sintering, produced identical results for most samples. The sintering method did, however, produce excellent results for samples that had high concentrations of Si, Al and Fe because these species were removed through the sintering process, and left behind as insoluble zinc silicates and aluminates. These species interfered in the LiBO_2 method, and the results were lower. Generally, the LiBO_2 method is rapid and gives excellent results for samples with relatively low SiO_2 , Al_2O_3 and Fe_2O_3 contents.

Experimental

Apparatus

A Metrohm 692 pH/Ion Meter with a Metrohm Fluoride ISE 6.0502.150 (ion selective electrode) indicator electrode coupled with Metrohm reference electrode 6.0733.100 was used for fluoride measurements.

Chemicals

All chemicals used to prepare reagents were of analytical reagent (AR) grade. Diluted reagents were prepared from concentrated reagents using MilliQ deionised water.

Sample preparation

The phosphogypsum samples were obtained from the Omnia and Kynoch plants at various stages. Due to the fact that samples tend to be non-homogeneous, the samples were categorised according to batches in order to keep track of each sample's identity.

Procedure for phosphogypsum sample preparation

A chemical gypsum sample was dried overnight at 45°C, as recommended in ASTM C-471-76 (cited by Gadalla et al., 1987). The sample was cooled in a desiccator and ground in a pestle and mortar to fine particles and then mixed thoroughly. This represented the unwashed sample.

For a water-washed sample, a slurry of phosphogypsum (Kynoch or Omnia) sample was prepared in water to produce a 12% (m/m) mixture. The mixture was stirred on a magnetic stirrer for 10 min and then filtered. The residue was dried overnight at 45°C. It was then cooled in a desiccator, ground in a pestle and mortar to fine particles and mixed thoroughly.

The lime-washed sample was prepared from the unwashed sample according to a similar method used for

the water washed sample, using a 0.1% (m/m) milk of lime solution instead of water. The 0.1% (m/m) milk of lime solution was prepared by weighing 0.1 g calcium hydroxide into a beaker and adding deionised water to give a 100 g solution. The mixture was thoroughly mixed and then the undissolved calcium hydroxide left to settle. The supernatant liquid was used to wash the chemical gypsum samples.

The acid-treated sample was prepared using a modified Jarosiński procedure (Jarosiński, 1994). The experimental conditions followed are summarised in Table 1.

TABLE 1
Adapted experimental conditions used to purify and recrystallise Omnia and Kynoch phosphogypsum

Parameters	Leaching	
	Kynoch	Omnia
Temperature	40°C	40°C
Sulphuric acid concentration (mass %)	12%	12%
Solid/liquid mass ratio	1 : 2	1 : 4
Time of stirring	45 min	45 min
Sample mass	15.0 g	15.0 g

The sample was filtered with a Whatman 41 filter paper and the residue dried overnight at 45°C. It was then cooled in a desiccator, ground in a pestle and mortar to fine particles and mixed thoroughly.

Sample sintering and dissolution

An accurately weighed mass of the phosphogypsum was mixed with weighed Na_2CO_3 and ZnO in a platinum crucible. The actual masses weighed are tabulated in Table 2. The sample mixture was then sintered for 30 min at 900°C. The resulting melt was allowed to cool and then transferred to a 100 mL plastic beaker containing deionised water. A polythene coated magnetic stirrer bar was placed in the sample solution. While the solution was being stirred, concentrated nitric acid was added drop-wise to assist dissolution of the chemical gypsum and to lower the pH to approximately 5. This helps to avoid the formation of HF and HF_2^- at pH values below 5. High pH values were avoided because the electrode tends to be sluggish and higher fluoride concentrations are falsely indicated. The sample solution was then filtered using Whatman No 41 filter paper and the filtrate transferred into a volumetric flask and made up to volume with deionised water.

TABLE 2
Phosphogypsum sample preparation information

Phosphogypsum Sample	Mass sample (g)	Mass ZnO (g)	Mass Na_2CO_3 (g)	Volumetric flask (mL)	pH
Unwashed Kynoch	0.6250	0.5	2.5	250	5.1
Water-washed Kynoch	0.6285	0.5	2.5	250	5.1
Lime-washed Kynoch	0.6255	0.5	2.5	250	5.1
Unwashed Omnia	0.6273	0.5	2.5	250	5.1
Water-washed Omnia	0.6292	0.5	2.5	250	5.1
Lime-washed Omnia	0.6262	0.5	2.5	250	5.1

TISAB Buffer 1

A total ionic strength adjustment buffer (TISAB) was prepared to adjust the ionic strength, buffer the pH and break up metal-fluoride complexes during the ISE measurements. Sodium chloride (58.00g) was dissolved in deionised water and transferred into a 500 mL beaker. Sodium citrate (0.30g) was dissolved in deionised water and mixed with the sodium chloride solution. Glacial acetic acid (57 mL) was added to the mixture and the pH adjusted to 5.0 with 6M NaOH. The buffer solution was then transferred to a 1 L volumetric flask and brought up to the mark with deionised water.

Spiked samples for ISE measurements

Samples for ISE measurements were spiked with fluoride standards. Spiking the samples with the fluoride ion ensured that the Ion Meter measured at a higher fluoride concentration. This prevented working at fluoride ion concentrations that were too low and where calibration of the instrument might be irregular.

Spiked Omnia samples

An amount of 10.00 mL of a 10.00 mg/L fluoride standard was pipetted into a 100 mL plastic beaker. An amount of 10.00 mL of the Omnia phosphogypsum sample was added to the standard followed by 20.00 mL of TISAB Buffer 1 solution to bring the total volume of the spiked sample to 40.00 mL. This means that the concentration of added fluoride ion in the measuring vessel was 2.50 mg/L.

Spiked Kynoch samples

An amount of 10.00 mL of a 100.00 mg/L fluoride standard was pipetted into a 100 mL plastic beaker. An amount of 10.00 mL of the Kynoch phosphogypsum sample was added to the standard followed by 20.00 mL of TISAB Buffer 1 solution to bring the total volume of the spiked sample to 40.00 mL. This made the concentration of added fluoride in the measuring vessel 25.0 mg/L. Hence, the concentration of added fluoride in the Kynoch samples was ten times that of the Omnia samples. This decision was based on previous results which showed the percentage of fluoride in Kynoch phosphogypsum samples to be, on the average, in the region of ten times that of Omnia samples.

Fluoride standards and analysis

A series of four fluoride standards were prepared with fluoride ion concentrations of 5.00 mg/L, 10.00 mg/L, 50.00 mg/L and 100.00 mg/L respectively. Each of the prepared fluoride standard solutions was mixed with the same volume of the TISAB Buffer 1 solution for use during the calibration of the Ion Meter. Hence, on taking account of dilution effects, the concentrations of added fluoride ion in each of the fluoride standards were halved. This range of fluoride ion concentrations ensured that the Ion Meter was properly calibrated for the quantitative determination of fluoride in Omnia samples, as well as in the Kynoch samples. The Metrohm Ion Meter was calibrated using the four standards in the direct mode.

Calculations and analysis of results for Kynoch and Omnia phosphogypsum samples

The amount of fluoride in each fused and digested chemical gypsum sample was determined and tabulated in Table 3.

Phosphogypsum samples	[F⁻] (mg/L) for each replicate
Unwashed Kynoch	52.87 ± 0.06
Water-washed Kynoch	52.63 ± 0.06
Lime-washed Kynoch	51.83 ± 0.06
Unwashed Omnia	5.81 ± 0.01
Water-washed Omnia	5.64 ± 0.01
Lime-washed Omnia	5.75 ± 0.01

Kynoch phosphogypsum samples were spiked with 10.00 mL of the 100.00 mg/L standard, i.e. the added fluoride ion concentration was 25.00 mg/L as described previously. However, the Ion Meter had a dilution correction of 2 programmed in the method of analysis. This implied that the fluoride ion concentration, after spiking, could be computed from the simplified equation:

$$[F^-]_{total} = 2([F^-]_{spiking} + [F^-]_{present})$$

where:

[F⁻]_{total} represented the observed concentration of fluoride from the Ion Meter reading

[F⁻]_{spiking} was the calculated concentration of fluoride introduced by spiking

factor 2 was the dilution factor due to TISAB dilution effects

[F⁻]_{present} represented the fluoride concentration of Kynoch phosphogypsum in the measuring vessel.

For example, an observed concentration of fluoride in the unwashed Kynoch phosphogypsum sample of 52.80 mg/L for the first replicate, and added fluoride for spiking the samples of 25.00 mg/L, the amount of fluoride ion present in the measuring vessel is calculated as:

$$52.80 = 2(25.00 + [F^-]_{present})$$

$$\Rightarrow [F^-]_{present} = 1.40 \text{ mg/l}$$

However, this calculation assumes a dilution factor of 2 for the sample (due to TISAB). The sample was, however, actually diluted four times i.e., 10.00 mL diluted to a final volume of 40.00 mL in the measuring vessel. Thus the result has to be multiplied by a factor of 2 to give the final answer of 2.80 mg/L F⁻ in the original Kynoch phosphogypsum sample. The amount of fluoride present in all analysed phosphogypsum samples was obtained in the same way. The results were statistically analysed for both Omnia and Kynoch phosphogypsums and summarised in Table 4.

The amount of fluoride for each of the Kynoch and Omnia phosphogypsums was determined as a percentage in each sample. The results are tabulated in Table 5 (for Kynoch and Omnia phosphogypsum samples).

Sulphuric acid treated samples

The results for a separate batch of samples used to investigate the effect of sulphuric acid treatment were computed in the same manner as for the water-washed and lime-washed samples. The results for unwashed Kynoch phosphogypsum were a percentage fluoride of 0.116 ± 0.002 (RSD = 2%). The sulphuric acid treated Kynoch

TABLE 4 Fluoride ion concentration for both Kynoch and Omnia samples in the original sample solutions	
Phosphogypsum samples	[F] (mg/l) for each replicate
Unwashed Kynoch	2.87 ± 0.06
Water-washed Kynoch	2.63 ± 0.06
Lime-washed Kynoch	1.83 ± 0.06
Unwashed Omnia	0.81 ± 0.01
Water-washed Omnia	0.64 ± 0.01
Lime-washed Omnia	0.75 ± 0.01

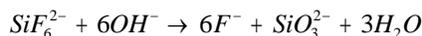
phosphogypsum contained per cent fluoride of 0.010 ± 0.000 (RSD = 1%). On the other hand, unwashed Omnia phosphogypsum contained a per cent fluoride of 0.045 ± 0.000 (RSD = 1%). The sulphuric acid treated Omnia phosphogypsum contained per cent fluoride of 0.012 ± 0.000 (RSD = 1%)

Discussion and conclusion

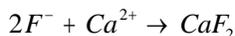
Comparing the results for the unwashed and washed samples in Table 5, the study has shown that when Kynoch phosphogypsum is washed with water, 9% of the total fluoride is soluble and is removed. Kynoch phosphogypsum thus seems to contain more than 90% water-insoluble fluoride that was taken up in the structure when the gypsum formed. On the other hand, the amount of water-soluble fluoride removed from Omnia phosphogypsum was 22%. Omnia phosphogypsum seems to contain 78% water-insoluble fluoride. Water-soluble fluoride exists on the surface of gypsum crystals and in the interstices of agglomerated crystals (Singh et al., 2000). It is this water-soluble fluoride which poses a potential threat to underground aquifers when it is mobilised due to seepage during rainy seasons.

In this study, lime washing had the effect of removing more fluoride from the Kynoch phosphogypsum (37%), compared to 6% from Omnia phosphogypsum. It is proposed that the Omnia phosphogypsum has different intrinsic properties compared to the Kynoch phosphogypsum that make the two phosphogypsums behave differently for the water wash and the lime.

Omnia phosphogypsum appears to have a higher rate of dissolution in the water, which in turn exposes more of the water-soluble impurities to be removed during the water wash, compared to the Kynoch phosphogypsum. However, during the lime wash, it seems that the water-soluble impurities such as hexafluorosilicates break down to fluorides as:



but more of the soluble fluoride released tends to reform as insoluble compounds as:



in Omnia phosphogypsum than Kynoch phosphogypsum, thereby resulting in low removal of fluoride in Omnia compared to Kynoch phosphogypsum.

In this study, the sulphuric acid treatment of the chemical gypsum has been highly effective for the removal of fluoride

TABLE 5 Fluoride content (% F) of Kynoch and Omnia chemical gypsum samples	
Sample	% Fluoride
Unwashed Kynoch	[F] = 0.115 ± 0.002 ; RSD = 2%
Water-washed Kynoch	[F] = 0.105 ± 0.002 ; RSD = 2%
Lime-washed Kynoch	[F] = 0.073 ± 0.002 ; RSD = 3%
Unwashed Omnia	[F] = 0.032 ± 0.000 ; RSD = 1%
Water-washed Omnia	[F] = 0.025 ± 0.001 ; RSD = 4%
Lime-washed Omnia	[F] = 0.030 ± 0.000 ; RSD = 0.8%

impurities. The amount of fluoride leached during the sulphuric acid treatment of Kynoch phosphogypsum was 91%. In the case of Omnia phosphogypsum, the amount of fluoride removed by the sulphuric acid treatment was 74% of the original amount in the untreated phosphogypsum.

Judging collectively from the research work carried out by Jarosiński (1994), in which fluoride and phosphate impurities were removed from the hemihydrate phosphogypsum by the sulphuric acid treatment, as well as from the work of Strydom and Potgieter (1999), who found that a great proportion of the Omnia phosphogypsum they studied was predominantly in the hemihydrate form, it is proposed that the proportion of the soluble hemihydrate phase of the chemical gypsum utilised in this study, was dissolved under the sulphuric acid treatment conditions to produce a liquid phase saturated in calcium ions and sulphate ions. Since gypsum is less soluble than the hemihydrate, it precipitates immediately, removing calcium and sulphate ions from solution. Hence, the impurities are freed leaving purer, recrystallised chemical gypsum.

In order to minimise the potential for groundwater contamination by fluoride impurities contained in phosphogypsums, it is proposed that an effective purification regime such as the sulphuric acid pretreatment be effected prior to disposal of this waste product from the plant. This would go a long way to protecting groundwater quality in the vicinity of the plant or disposal site.

References

- COETZEE PP, COETZEE LL, PUKA R and MUBENGA S (2003) Characterisation of selected South African clays for defluoridation of natural waters. *Water SA* **29** (3) 331-338.
- GADALLA A, ROZGONYI T and SAYLAK D (1987) Beneficiation of by-product phosphogypsum. In: Ariman T and Verizoglu TN (eds.) *Particulate and Multiphase Processes (Vol. 2)* Hemisphere, Washington. 161-172.
- JAROSIŃSKI A (1994) Properties of anhydrite cement obtained from apatite phosphogypsum. *Cement and Concrete Res.* **24** 99-108.
- JAVELLANA MP and JAWED I (1981) Determination of fluoride in cement and related materials. *Cement and Concrete Res.* **11** 205-210.
- SINGH M, GARG M and REHSI SS (1993) Purifying phosphogypsum for cement manufacture. *Construction and Building Materials* **7** (1) 3-7.
- STRYDOM CA and POTGIETER JH (1999) Dehydration behaviour of a natural gypsum and a phosphogypsum during milling. *Thermochim. Acta* **332** (1) 89-96.
- RUTHERFORD PM, DUDAS MJ and SAMEK RA (1994) Environmental impact of phosphogypsum. *Sci. Total Environ.* **149** 1-38.