

Potential groundwater contamination by fluoride from two South African phosphogypsums

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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.

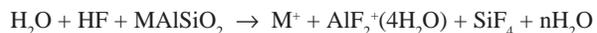
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Introduction

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).

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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