This article was downloaded by:

On: 29 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: <a href="http://www.informaworld.com/smpp/title~content=t713618290">http://www.informaworld.com/smpp/title~content=t713618290</a>

# Surface Investigation of the Reaction Products Between Apatite and Sulfuric Acid

Efraim Cekinski<sup>a</sup>; Jean-Hugues Thomassin<sup>a</sup>; Patrick Baillif<sup>b</sup>

<sup>a</sup> Laboratoire Matériaux et Géologie Environnementale ESIP, Poitiers, France <sup>b</sup> Laboratoire d'Etude des Matériaux Minéraux, Orléans, France

To cite this Article Cekinski, Efraim , Thomassin, Jean-Hugues and Baillif, Patrick(1993) 'Surface Investigation of the Reaction Products Between Apatite and Sulfuric Acid', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 235-238

To link to this Article: DOI: 10.1080/10426509308032402 URL: http://dx.doi.org/10.1080/10426509308032402

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1993, Vol. 76, pp. 235-238 © 1993 Gordon and Breach Science Publishers S.A. Reprints available directly from the publisher Photocopying permitted by license only

SURFACE INVESTIGATION OF THE REACTION PRODUCTS BETWEEN APATITE AND SULFURIC ACID.

EFRAIM CEKINSKI\*, JEAN-HUGUES THOMASSIN\* and PATRICK BAILLIF\*\*

- \* Laboratoire Matériaux et Géologie Environnementale ESIP, URA CNRS 721, Université de Poitiers, Poitiers, France.
- \*\* Laboratoire d'Etude des Matériaux Minéraux, URA CNRS 1366, ESEM Université d'Orléans, Orléans, France.

Abstract In order to understand the mechanism of reactions in SSP system, a series of tests with industrially treated apatite (Araxa, Brazil) and reference apatite (Durango, Mexico) were performed. Results were acquired by chemical analysis of the liquid phase and X-ray diffraction, XPS, photonic microscopy and SEM on the solids. The main results concern the growth of gel-like layers around the grains and their influence on the industrial process.

#### INTRODUCTION

In the manufacture of single superphosphate (SSP) one can observe a number of problems which are related to the mineralogy of the apatite and associated minerals like goethite, magnetite, gorceixite, etc. For example, iron and aluminium can influence the rate and amount of conversion of apatite into SSP and in addition tie up phosphate in a non-water soluble form. These kinds of difficulties lead to several technical and economical problems for fertilizer industries.

#### Test with Araxa apatite

Brazilian phosphate was added to sulfuric acid at 60 °C, stirred for 30 sec. and transferred into an oven maintained at 80°C. At predetermined time, the reaction was stopped by the immersion of the products into a mixture of acetone and dioxane.

The results of chemical analysis show that even after 30 days the reactions were not entirely completed<sup>1</sup>. This phenomenon is due to the formation of gel-like phases, which together with calcium sulfate, surround the surface of unreacted apartite. These facts are well observed by photonic microscopy and SEM.

Figure 1 shows the P/Ca and S/Ca ratio analyzed by XPS on the surface of the grains. First a drastic decrease in P/Ca ratio occurs, secondly this ratio increases up to values near those of monocalcium phosphate compounds and finally it decreases to values closed to dicalcium phosphate compounds.

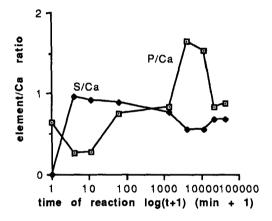


FIGURE 1 - Reaction between Araxa apatite and sulfuric acid (XPS analysis).

For the S/Ca ratio, we notice the formation of calcium sulfate which covered the apatite grains and after that, a regular decrease in this ratio due to the precipitation of calcium phosphate.

#### Test with Durango apatite

The experiments on this reference apatite were performed by reaction between 10  $\mu$ l of either sulfuric acid (a), or sulfuric acid mixed with iron (b), or sulfuric acid mixed with iron and aluminium (c) and an apatite crystal of approximately 5 mm in

height. The ratio (volume of solution/apatite surface) corresponds to that used in the experiments with Araxa apatite.

Figures 2 and 3 present the results obtained by XPS analysis on the samples of the experiments "a" and "b".

In figure 2, in the reaction without  $R_2O_3$ , the precipitation of calcium sulfate is followed by a precipitation of monocalcium phosphate which occurs in two stages, 0-10 min and 10-1440 min. The last sample presents a unexpected values which were analysed by SEM as a material containing P and S  $^2$ .

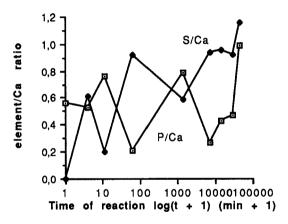


FIGURE 2 - Reaction between Durango apatite and sulfuric acid (XPS analysis).

In figure 3, after precipitation of calcium sulfate, the precipitation of monocalcium phosphate and other phosphate compounds occurs. SEM analysis showed that products presenting P and Fe were formed. XRD confirmed  $Fe_3(H_3O)H_8(PO_4)_6.6H_2O$  as crystalline phase.

Concerning "c" experiment, XPS data are presented in Table 1. It is seen that the products coating apatite were composed by present P, S, Si, and Al. SEM analysis showed that this product is a gel-like phase which avoids any contact between acid and apatite.

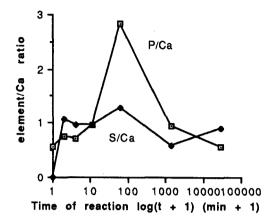


FIGURE 3 - Reaction between Durango apatite, sulfuric acid and Fe (XPS analysis).

TABLE I - Reaction between Durango apatite and sulfuric acid "c" experiments (XPS analysis).

				<u> </u>			
element/P ratio							
	TIME	Ca	S	Si	Al	0	
	0 min	1.79	0.00	0.00	0.00	5.80	
	3 min	1.25	0.29	1.38	0.00	6.54	
	10 min	0.44	0.43	0.48	0.60	5.77	
	1 hour	0.00	0.49	4.30	0.87	14.54	
	1 day	0.00	0.60	0.85	0.87	8.11	
	5 days	0.18	0.76	0.29	0.64	6.43	
	20 days	0.00	0.37	0.32	0.71	5.19	

# CONCLUSION

The results confirm the role of impurities as Fe, and Al on the SSP manufacturing. These elements indeed favour the growth of gel-like layers which decrease the reaction kinetics.

### REFERENCES

- 1. E. Cekinski and J. H. Thomassin,  $\underline{\text{Fertilizer Research}}$  in press (1992).
- 2. M. S. White, N. Z. J. of Science, 14(2):364-391 (1971).