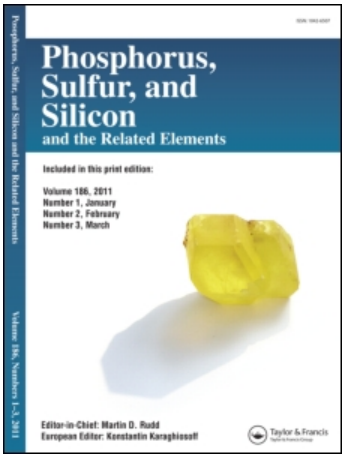

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Surface Investigation of the Reaction Products Between Apatite and Sulfuric Acid

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

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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[1]. This phenomenon is due to the formation of gel-like phases, which together with calcium sulfate, surround the surface of unreacted apatite. 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.

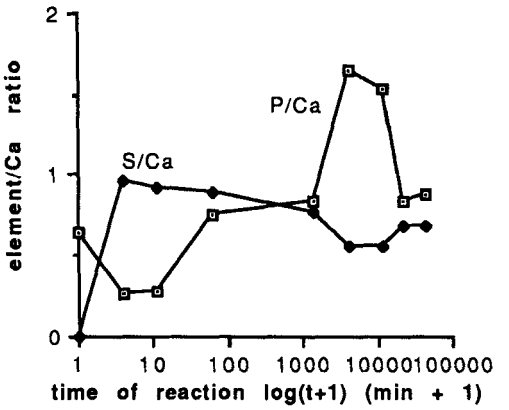

FIGURE 1 - Reaction between Araxa apatite and sulfuric acid (XPS analysis).

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 µl 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].

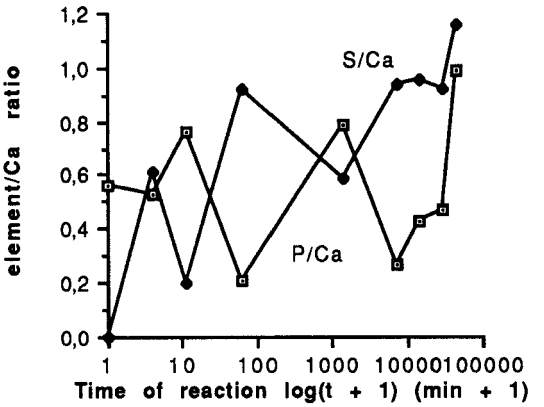

FIGURE 2 - Reaction between Durango apatite and sulfuric acid (XPS analysis).

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.

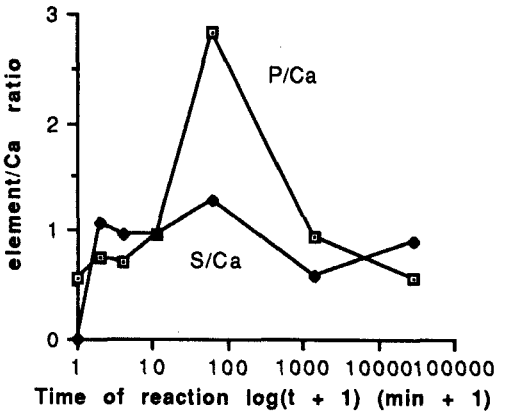

FIGURE 3 - Reaction between Durango apatite, sulfuric acid and Fe (XPS analysis).

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

	element/P ratio				
TIME	Ca	S	Si	Al	O
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.

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