

REE desorption from basaluminite and schwertmannite at pH between 4 and 7.5

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Palabras Clave: Schwertmannita, Basaluminita, Desorción, Tierras Raras, Drenaje Ácido de Mina. **Key Words:** Schwertmannite, Basaluminite, Desorption, Rare Earth Elements, Acid Mine Drainage.

INTRODUCTION

Rare Earth elements (REE), Y and Sc are strategic raw materials due to their increasing demand in current society and shortage of supply (Hatch, 2012). REE concentrations are several orders of magnitude higher in acid mine drainage (AMD) than in natural river waters (Noack et al., 2014), making them a potential complementary source of REE.

Previous studies have shown that basaluminite ($\text{Al}_4\text{SO}_4(\text{OH})_{10}\cdot 5\text{H}_2\text{O}$) and schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) can retain REE through adsorption mechanisms (Lozano et al., 2019, 2020). These minerals tend to precipitate in estuaries (e.g., Huelva), where the water pH increases due to the interaction between AMD and seawater. As a result, adsorption of REE onto basaluminite and schwertmannite is expected to occur.

Therefore, it is critical to know whether the adsorbed REE remain on the surface of these minerals or they are released back into solution. Consequently, the main objective of the present work is to study the capacity of basaluminite and schwertmannite to retain the adsorbed REE, Y and Sc over time, at the pH range of the AMD-seawater mixture.

METHODOLOGY AND RESULTS

Solid Synthesis

Basaluminite and schwertmannite were synthesized in accordance with the methods described by Adams and Rawajfih (1997) and Bigham et al. (1990).

Following the procedure described by Lozano et al. (2018), XRD analyses of the synthetic solids showed the absence of impurities on the minerals. The calculated sorption site density of basaluminite and schwertmannite were 787 and 750 $\mu\text{mol/g}$ respectively.

Adsorption and Desorption Batch Experiments

The method described in Lozano et al. (2019, 2020) was followed to enrich basaluminite and schwertmannite with REE. A solution with pH of 6, 1 ppm of REE and 20 mM of SO_4^{2-} reacted with the synthetic minerals for 6 h. The equilibrated solution was analyzed using ICP-MS to quantify the adsorbed amount of REE, Y and Sc.

After the adsorption experiments, the REE-enriched basaluminite and schwertmannite reacted with several solutions (20 mM SO_4^{2-} and variable pH, ranging from 4 to 7.5) for 48 h. Liquid samples were taken at different times to determine the desorption kinetics. Distribution coefficients, K_D (L/kg), were calculated (Fig. 1) from the REE desorbed onto the solution and the concentration of REE remained in the minerals and normalized by the volume of solution and mass of solid (solid to liquid ratio):

$$\text{Distribution coefficient} = \frac{[\text{REE}]_f(\text{mineral})}{[\text{REE}]_{\text{solution}}} \times \frac{V_{\text{solution}}}{M_{\text{solid}}}$$

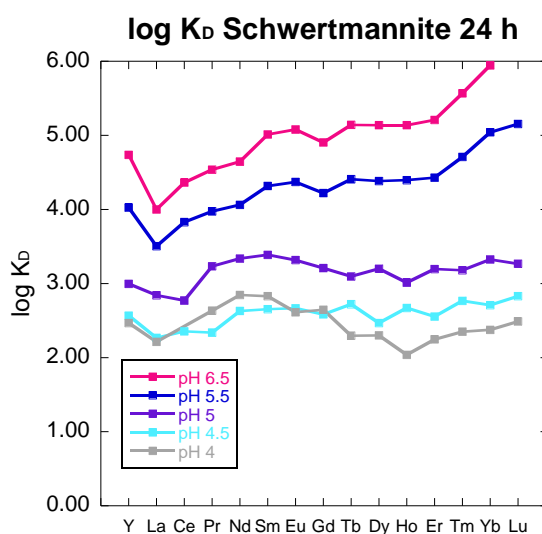
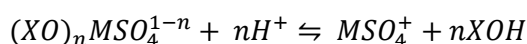


Fig 1. Log K_D patterns of schwertmannite at different pH values: lanthanide M-type tetrad effect. The higher log K_D values at higher pH indicate dependence between the capacity of retaining REE and pH.

Geochemical Modeling

The desorption reaction consists of the exchange of an aqueous protons with the adsorbed REE complex (MSO_4^+ , M is equivalent to each REE), which is expressed as



In this reaction, the equilibrium constant (K) associated with each REE are obtained from the desorption data. To validate the K values, a geochemical model will be performed using the PHREEQC software.

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