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Rare-earth-elements retention by oxyhydroxysulfates in an estuary impacted by Acid Mine Drainage

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In the Tinto and Odiel basins (South of Spain), the waters of numerous streams and rivers affected by acid-mine-drainage (AMD) are enriched in rare-earth elements (REEs), which are critical raw materials in increasing demand for modern technology as well as harmful aqueous contaminants [1]. Under AMD conditions, forming Fe- and Al-oxyhydroxysulfates (schwertmannite ($Fe_8O_8(OH)_6SO_4$) and basaluminite ($Al_4(SO_4)(OH)_{10}\cdot 5H_2O$), respectively) retain REE via chemisorption.

Earlier studies have focused on REE retention by Fe- and Al-oxyhydroxysulfates under AMD conditions [2] but not under AMD-seawater mixing conditions. At the Estuary of Huelva the acidic Odiel and Tinto rivers mix with seawater, strongly affecting the marsh ecosystem. High ionic strength and pH may affect the stability of REE retention on Fe-Al-oxyhydroxysulfates. This study focuses on the effects of ionic strength on REE sorption/desorption on basaluminite and schwertmannite.

Series of batch experiments were conducted at different pH (4.5-7) and ionic strength (0.01-0.6 M) under atmospheric pressure to obtain equilibrium constants for the REE-oxyhydroxysulfate sorption/desorption reactions. Additionally, Extended X-ray Adsorption Fine-Structure (EXAFS), High Energy X-Ray Scattering (HEXS) and density functional theory (DFT) simulations were performed to elucidate binding characteristics at the surfaces of the REE-enriched oxyhydroxysulfates.

The results indicate that (1) the ionic-strength effect on the obtained equilibrium constants is negligible, (2) La- and Ce-chloride compounds adsorb onto basaluminite at high ionic strength, (3) the presence of chloride changes the basaluminite structure due to chloride-sulfate exchange and (4) REE-sulfate surface complexes show a coordination number of 8, sharing an oxygen with the sulfate tetrahedra on the mineral surfaces.

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