

## **Sulfate mineral salts associated to dehydration of mine waters: effects of humidity and temperature conditions**

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### **Abstract**

Sulfate salt efflorescences such as halotrichite ( $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ) and melanterite ( $\text{Fe}_2+(\text{H}_2\text{O})_6\text{SO}_4 \cdot \text{H}_2\text{O}$ ) are typical minerals associated to acid mine waters. Rhomboclase ( $\text{H}_5\text{O}_2\text{Fe}_3+(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ) and voltaite ( $\text{K}_2\text{Fe}_2+5\text{Fe}_3+3\text{Al}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$ ), although more rare, may also form from the precipitation of dissolved ions in AMD, with a relevant role in mining environments since they are highly soluble and can contain potentially toxic metals. The evaporation-dissolution cycle, associated with dry and raining seasons, controls the crystallization process of these salts that are readily mobile in the air, or their dissolution might lead to the increase of metallic contamination and acidity in the ecosystem. Information about stability and thermodynamics of these mineral phases is essential to comprehend the possible behavior in dehydration reactions of mine waters.

The present work aims to characterize the transitions phases related to dehydration processes. For that, experiments with mine water were performed in laboratory conditions. Collected in the Riotinto mine (Iberian Pyrite Belt, Spain), this water is highly acidic (96250 mg L<sup>-1</sup> of CaCO<sub>3</sub> and pH of 1.13) and sulfated (2569 gL<sup>-1</sup>). Air dehydration experiment was conducted in the laboratory, where the temperature and relative humidity (RH) were obtained using HANNA digital Thermo-hygrometer HI9564, with RH probe HI 70602. Temporal evolution of the mineral crystallization during the laboratory test was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM-EDX). Each sub-sample was observed with a binocular lens for morphological characterization and sorted for XRD and SEM analyses. For quantification of the amount of voltaite, during the lab test, digital image analysis of the temporal photographic record was used, more precisely the pixel counting method.

The results indicate that the sequence of sulfate precipitation is mainly influenced by RH variation. The paragenesis sequence of the neoformed minerals was: first melanterite-halotrichite; in a second phase occurs formation of voltaite due to the decrease of humidity, and with its continuous decrease the amount of voltaite incremented and rozenite starts to appear; and finally there is the mineral assemblage rhomboclase-halotrichite-voltaite-rozenite/szomolnokite.

Monitorization of the RH and temperature during the experiment revealed: (1) the voltaite formation occurs when the RH is below 65%, (2) transformation of melanterite into rozenite is observed when the RH is between 40 to 30%, (3) low humidity promotes the increase of voltaite, and (4) the temperature (around 15-20°C) had no relevant impact in this process.

**Key words:** sulfate salt efflorescences; mine waters; temperature; relative humidity.

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