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Halotrichite-Group Minerals as Indicators of Critical Metals in Mine Waste

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Mine wastes derived from sulfide ore exploitation constitute major environmental liabilities due to acid drainage generation and metal dispersion. However, these deposits may also represent secondary sources of critical metals under a circular-economy framework. In semi-arid climates, evaporation of acid mine drainage promotes the formation of efflorescent sulfate salts, among which the halotrichite group (Fe–Al, Mg–Al and Mn–Al double sulfates) plays a key role as transient metal reservoirs. Understanding their formation, stability and metal uptake capacity is essential both for predicting contaminant release and for evaluating their potential in sustainable resource recovery strategies.

This study assesses the incorporation of Cu, Co and As into three representative halotrichite-group phases—halotrichite (Fe–Al), pickeringite (Mg–Al) and apjohnite (Mn–Al)—and evaluates their discrimination using VNIR–SWIR spectroscopy as a non-invasive exploration and monitoring tool. Eighteen synthetic samples were crystallized under controlled temperature (≤40 °C) and relative humidity conditions simulating semi-arid environments. Precursor solutions were enriched with Cu, Co and As (20–1000 ppm). Mineralogical and chemical characterization was conducted by XRD, ICP–OES, SEM–EDS and LIBS, and results were compared with natural efflorescent salts from abandoned Cu tailings in northern Chile.

Trace-metal incorporation strongly depends on the dominant structural cation. Halotrichite (Fe–Al) exhibits the highest retention capacity for Cu, Co and particularly As, with incorporation efficiencies up to 670%, acting as a significant temporary sink. Pickeringite shows intermediate behavior, preferentially incorporating Cu, whereas apjohnite displays limited affinity for the evaluated elements. SEM–EDS and LIBS analyses reveal both structural incorporation and late-stage coprecipitation processes, reflecting evolving geochemical conditions during evaporation.

VNIR–SWIR spectroscopy enables reliable discrimination among halotrichite-group phases despite their structural similarity, supporting remote mapping of metal-bearing sulfate crusts in mine wastes.

These results highlight the dual environmental and economic relevance of halotrichite-group minerals: they regulate seasonal metal storage and release during wetting events, and they may serve as mineralogical guides for targeted reprocessing of metal-enriched zones within mining environmental liabilities.