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Formation of tenorite and brochantite from Cu-enriched electroplating wastewater

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Metal finishing through the production of coated surfaces is based on baths with various metal salts and other chemicals. Consequently, electroplating produces a large volume of wastewater containing heavy metals. Commonly, hydroxide precipitation of metals is applied for wastewater treatment. The principle is based on the pH adjustment of the wastewater to a range in which metal hydroxides (M-OH) show minimal solubility. However, this process produces large quantities of sludge with low metal contents. Generally, their high water content makes the recovery of the metals obsolete, and accordingly, these sludges are land-filled, meaning that the metals are lost to the circular economy. Recently, the increasing demand for raw materials has caused the reconsideration of the recycling of heavy metals from waste and novel recycling techniques that meet the criteria of the circular economy.

We work in the field of chemical precipitation on the recovery of metals as oxides or zero-valent metals. In this context, we investigate the effect of parameters, such as Eh/pH conditions, molar ratios, reaction temperatures and ageing, among others, on the speciation of metal phases in liquid solutions. One of our topics is the study of the optimal conditions for the formation of tenorite (CuO) from Cu-enriched electroplating wastewater and the delineation of reaction conditions for the formation of brochantite, a copper sulfate ($Cu_4(OH)_6SO_4$). We observed that the stirring speed during precipitation impacts the mineral assemblage. At a low stirring rate and low redox potential, tenorite is formed with a minor amount of spertiniite ($Cu(OH)_2$), which alters to tenorite during ageing. With increasing stirring speed, the redox potential shifts towards oxidising conditions and brochantite, a copper sulfate ($Cu_4(OH)_6SO_4$), is formed. Comparable experiments with low Fe concentrations in the aqueous solution showed that the formation of brochantite is suppressed in favour of cuprospinel ($CuFe_2O_4$) in phase assemblage with cuprite (Cu_2O) and tenorite.

Our results indicate that brochantite can only be formed under particular conditions in natural environments. Accordingly, the presence of Fe in the soil solution would preclude the direct formation of brochantite in oxidised zones of natural mineral deposits.