Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.18871

A controlled bioprocess of mineral alteration to recover W, Cu, Zn, Mn, and Mg from a mine shaly hardrock waste: coupling experiments and geochemical modeling.

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The improvement of mining techniques as well as the societal push towards circular economy concepts lead today to consider mining dumps not as a waste but as a resource that can be re-exploited. The waste from the Panasqueira mine (Portugal), whose main metal is tungsten, was studied to assess the extractability of the critical metals W, Cu, Zn, Mn, and Mg. Extractions were performed in oxygenated batch reactors with a starting pH shifted from 3.7 to 2 by addition of sulfuric acid. Experiments were performed under sterile and non-sterile conditions with/without the addition of elemental (S°/Fe(II), Fe(III)) and/or mineral nutrients (biostimulation), and/or bacterial inoculum (bioaugmentation) inputs. The best results after 60 days were obtained in the biostimulation trials with nutrient addition only, with ~100% zinc, manganese and magnesium, 30% copper and 13% tungsten recovered compared to hydrofluoric acid digestion trials. Addition of native sulfur without nutrient addition lowers pH to 1.0 while producing up to 550 mmol/L sulfate, but with slightly decreased extraction yields, similar to the bacterial inoculum. In comparison, experiments under sterile conditions are greatly reduced in terms of metal extractions and acid production, regardless of the condition tested. The presence of Ferberite $FeWO_4$ and its solid solution parent, Wolframite (Fe, Mn, Mg, Zn... - WO_4) is evidenced by both macroscopic and microscopic observations. Presumably, oxygen decomposed the Fe(II) crystal lattice of this highly acid-resistant mineral, while releasing the metals into the acid solution, which could have resulted in the highest yields (Zn, Mn, Mg). Hypothetically, tungsten could have been extracted quantitatively and then re-adsorbed under acidic conditions due to its oxyanion nature. Copper behaved differently, suggesting its dominant presence in chalcopyrite or other sulfide phases. Its extraction would then depend on the availability of sulfur oxidizing Fe(III) electron acceptors, produced by biologically controlled Fe(II) => Fe(III) re-oxidation, this process seems to work in our experimental conditions. Overall, the effectiveness of biostimulation is encouraging in view of its in situ applicability, especially considering the the difficulty of injecting exogenous bacteria into the thin and poorly permeable matrix of the Panasqueira mine waste