

Selective extraction protocols and associated residual phases: a case study based on the recovery of base and critical metals from unconventional resources

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The historical mining sites in Central Europe, if not monitored properly, could be a pollutant source. However, mining waste can be an important non-traditional raw material source, especially for base (e.g., Zn-Pb-Cu) and critical metals (e.g., Ga-Ge-In), that are necessary for energy transition strategies through novel materials. In the present case study, we focused on the application of different selective extraction protocols – sodium acetate, sodium hydroxide, sodium dithionite, and oxalate buffer solutions – on mine tailing samples from the Wiesloch Mississippi Valley-type (MVT) Zn-Pb-Ba±Ag ore deposit in Germany. The selective extraction protocols generally target different minerals, which in our case, are the carbonate, the organic labile, the reducible Fe-oxide, and Mn-Fe-oxide bound fractions, respectively.

The sample material was characterized via XRD and SEM for mineralogy, grain morphology and mineral chemistry, both for the initial mining waste and for the residuals after the selective extraction process. Results show that the mineral composition of the tailings is mainly comprised of quartz, calcite, smithsonite, siderite, muscovite, kaolinite, and Fe-(oxyhydr-)oxides. Minor phases are cerussite, anglesite, adamite and other Al-silicates. This assemblage is a combination of gangue minerals and supergene alteration products on hydrothermal carbonate-hosted sulfide ore deposits.

After the extractions, the residual phases were composed of remaining minerals of quartz and phyllosilicates, like muscovite and kaolinite, as well as newly formed secondary phases. The developed secondary phases resulted from the supersaturation conditions generated by the specific chemistry of the extraction reagents and the inherently high concentrations of the Wiesloch mine waste in, e.g., Ca, Fe, Mn, Zn, and Pb. Examples of these are lead, zinc, or barium acetate hydrate oxides, wulfingite, zinc sulfite hydrate, iron arsenide, ammonium iron oxalate and whewellite. Residual phases exhibit low crystallinity and might be soluble in solutions utilized in hydrometallurgical applications.

Thus, we bring forward, for the first time, a second application to selective extraction schemes as potential environmentally friendly methods for element recovery from anthropogenic source material including a thorough identification of potentially harmful residual phases.

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