

Mineralogical Hosts of Germanium and Gallium in a Residue from Zinc Ore Processing

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The critical minerals germanium (Ge) and gallium (Ga) are crucial components in a wide variety of semiconductor and other technological applications. Residues from processing zinc (Zn) sulfide ores are a major source of the world's Ge, yet the mineralogy of these residues remains under-characterized. Understanding the mineralogical partitioning of Ge and Ga may help improve the metallurgical approaches used to extract them. In this study, we report X-ray diffraction (XRD) modal mineralogy, bulk chemistry, and electron microscopy results for a sample of Ge- and Ga-rich residue from the Nyrstar Clarksville smelter in Tennessee (USA).

The residue contains 3,450 ppm Ge and 7,820 ppm Ga and consists of aggregates of precipitated 0.5-3- μ m crystalline grains, an interstitial amorphous phase (~40 wt.% by XRD), and occasional large (10s of micrometers in diameter) partially roasted and dissolved residual ore minerals. The major crystalline phases are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), franklinite (ZnFe_2O_4), jarosite-group minerals ($\sim(\text{Pb,K})\text{Fe}_{0-3}\text{Zn}_{0-1}(\text{SO}_4)_2(\text{OH})_6$), sphalerite (ZnS), and anglesite (PbSO_4). The electron probe microanalyzer (EPMA) revealed distinct reservoirs of Ge and Ga: the minor mineral jacobsonite (MnFe_2O_4) and the abundant interstitial amorphous phase (which is heterogeneous, but rich in Fe, Zn, and Si). In both phases, Ge and Ga are present at ~0.5-3 wt.%. Discrete, ~200-500-nm Fe-Zn oxides with ~10 wt.% Ge and Ga are also interspersed in the fine groundmass of aggregated grains. Additionally, Ga is present at up to 2 wt.% in the jarosite-group minerals.

The small grain sizes and low concentrations of Ge and Ga in most minerals in the residue push the resolution limits of microanalytical technologies. Nonetheless, this improved understanding of Ge and Ga distribution among sulfates, oxides, and amorphous phases is important for optimizing recovery of these critical minerals. This work demonstrates the value of mineralogical characterization as a precursor to metallurgical evaluation.