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Indium in metalliferous mine wastes of the Iberian Pyrite Belt

Maria Wierzbicka-Wieczorek and Bernd G. Lottermoser
RWTH Aachen, Mineral Resources Engineering, Aachen, Germany (wierzbicka-wieczorek@mre.rwth-aachen.de)

Indium is a rare, post-transition metal that is widely used in modern technological applications such as liquid crystal displays and photovoltaic solar panels. It is one of a number of so-called "e-Tech" elements whose supply is considered to be insecure and critical. By contrast, the geology and geochemistry of indium is poorly understood. Moreover, there are currently no environmental guidelines with respect to indium; the element is rarely monitored and its behavior in the environment is poorly known. This is despite the fact that there is considerable evidence suggesting that indium compounds have significant, if not extreme toxicity. Thus, there is a need to understand geochemical processes of indium and to identify indium pathways and sinks in the mining environment, also in the context of improved processing technologies and environmental protection.

This study reports on the sources and sinks of indium in acid rock drainage (ARD) environments at six selected metal mine sites of the Iberian Pyrite Belt (IPB). Past mining of sulfide ore (pyrite-chalcopyrite-sphalerite) at the abandoned mines has resulted in numerous mine workings, waste dumps, degradation of local soil and vegetation as well as local streams and pits highly contaminated by ARD waters. Sulfide-rich materials comprising the ore and waste at the selected mine sites were sampled in detail. At these sites, the sulfidic waste rocks are invariably enriched in indium (mean of 43 samples: 6 ppm In), with concentrations well above average crustal abundances (50 ppb In). Indium-bearing sulfide minerals include kësterite (max. 0.5 wt% In), sphalerite (max. 0.27 wt% In) and chalcopyrite (max. 0.05 wt% In). Moderate to strong correlations of indium with tin ($r = -0.39$), iron ($r = -0.43$) and zinc plus iron ($r = -0.64$) also point to cation substitutions in the crystal structure of sulfide minerals. The sulfidic wastes have undergone extensive oxidation prior to and after mining, with partially oxidized sulfidic waste rocks invariably enriched in indium (mean of 70 samples: 2 ppm In). Weathering has led to the development of an abundant and varied secondary mineral assemblage throughout the waste material. Post-mining minerals are dominantly metal and/or alkali (hydrous) sulfates (e.g. anglesite, copiapite, coquimbite, hematite, jarosite, kroehnkite, rhomboclase, szomolnokite, voltatite). Sulfide oxidation and subsequent ARD development lead to mobilization of indium into acid waters (max. 6.7 mg/l In, pH 2.6). Subsequent oxygenation of ARD waters, hydrolysis of iron and evaporation lead to the formation of iron-rich precipitates and salts (e.g. Fe-copiapite, halotrichite, jarosite, hematite, szomolnokite and amorphous hydrous ferric oxides). These precipitates incorporate only to some degree indium through adsorption and coprecipitation (mean of 12 samples: 2 ppm In). Thus, indium displays significant mobility in ARD environments, with its mobility only somewhat constrained by iron precipitation. Finally, while mine sites of the Iberian Pyrite Belt (IPB) are well known contaminant sources, the abandoned waste repositories may be considered as low-grade resources for metals, including high-technology and critical metals such as indium.