

Microprobe Techniques for Speciation Analysis and Geochemical Characterization of Mine Environments: The Mercury District of Almadén in Spain

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Metallurgic calcines with very high mercury and methylmercury content from the Almadén mining district were analyzed by synchrotron-based microprobe techniques. Information about mercury speciation was obtained by μ -EXAFS (microscopic extended X-ray absorption fine structure) spectroscopy, whereas elemental associations were evaluated by μ -XRF (microscopic X-ray fluorescence analysis) mapping. Complementary characterization methodologies, including X-ray diffraction (XRD), inductively coupled plasma-optical spectroscopy (ICP-OES), as well as a sequential extraction scheme (SES), were used to predict the potential availability of mercury. Analysis of total metal content revealed extremely high concentrations of mercury and iron (between 7 and 35 and 65–70 g kg⁻¹, respectively) and high zinc concentrations (2.2–2.5 g kg⁻¹), whereas other metals such as copper, nickel, and lead were found at low concentration levels (30–300 mg kg⁻¹). μ -EXAFS results indicate that cinnabar (HgS_{red}) is one of the main species within the studied mercury-rich particles (5–89% of total mercury content), together with more soluble mercury compounds such as Hg₃(SO₄)O₂ (schuetteite) and HgO (5–55% of total mercury content). Additionally, element-specific μ -XRF maps of selected mercury-rich particles in the studied samples revealed an evident correlation among Hg–Pb–Ni (and S), indicating a possible geochemical linkage of these elements. Correlations were also found among Fe–Mn and Hg, which have been attributed to sorption of mercury onto oxyhydroxides of Fe and Mn. This finding was supported by results from a sequential extraction scheme, where a significant

amount of Hg was extracted with the fraction soluble in 6 M HCl.

Introduction

Natural mercury deposits are globally distributed in three types of mineral belts: silica–carbonate, hot-spring, and Almadén type, which are cogenetic and reflect similar tectonic and volcanic processes that contribute to the concentration of mercury (1). The most important of these is the Almadén mercury mineral belt in central Spain, where over one-third of the world's mercury has been produced. The mining activity dates from the Roman age, while the Hg extracted from the mine amounts to about 8.3 million Hg flasks (approximately 285 000 metric tons of Hg) (2). The deposit is primarily composed of cinnabar (HgS_{red}, hexagonal) and appreciable amounts of native Hg (3).

During metallurgical beneficiation, mercury was extracted from the mineral by volatilization, involving the crushing and roasting of the ores in large furnaces at temperatures higher than 600 °C. The process decomposes most of the Hg minerals producing Hg vapor, which is subsequently passed through condenser columns and collected as metallic (liquid) Hg in flasks. The roasted mine wastes (calcines) were typically transported short distances from the furnace and dumped in loose, unconsolidated piles, containing high Hg concentrations, typically ranging from 160 to 34 000 g kg⁻¹ (4).

Although Hg mining activity in the Almadén district ceased in May 2002, abandoned and untreated mine wastes continue releasing Hg to the nearby streams (5) and the atmosphere (6, 7) given the associated weathering, transport, and biological processes controlling the Hg cycle in these mine-impacted environments (8). Only a few studies have been conducted to evaluate the environmental impact of mercury contamination in this area (9–13). These studies show an important gap concerning the identification and quantification of inorganic mercury compounds, which are known to be the dominant components of mercury chemistry. This gap has a significant importance, because molecular-level speciation is one of the main parameters governing mercury mobility, toxicity, and bioavailability (14).

Recent studies have shown the applicability of synchrotron-based X-ray absorption spectroscopy (XAS) techniques to the characterization of both crystalline and noncrystalline Hg compounds in mine environments (15–17). This technique is becoming widely used for the study of molecular-level environments, showing species-specific detection capacities, while needing almost no sample pretreatment (and consequently with a minimum species modification) (18).

During the past decade, synchrotron-based microprobe techniques, with X-ray beams of 1–20 μ m in diameter, have become increasingly utilized to map elemental distributions in environmental samples. The mapping process allows one to establish correlations among elements, while also identifying particles enriched in the target element (Hg in this study case). Both XANES (X-ray absorption near-edge structure) and EXAFS spectroscopy measurements can be performed at each spot of the incident microbeam.

The present study takes advantage of μ -XRF and μ -EXAFS microprobe techniques for the determination of mercury species in old furnace calcine samples. Complementary techniques, such as XRD, total digestion and elemental analysis by ICP-OES, or SES schemes, have been also applied to obtain an adequate knowledge of the bulk mineralogy of the sample matrixes, as well as to identify and understand

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