

Mercury speciation in bulk and colloidal mine wastes: origins, influences, and implications

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The speciation of mercury is one of the main factors dictating its potential bioavailability in the environment. Determining Hg speciation in Hg-bearing mine wastes is critical to understanding its release from such point sources and its distribution in surface aqueous systems. In this study the initial species of Hg present in contaminated mine wastes and the variables that may control or influence speciation in natural environments were investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy. Additional techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), inductively coupled plasma (ICP) spectroscopy, and BET surface area measurements, were utilized to further characterize the samples in terms of matrix mineralogy, particle size/morphology, and bulk chemistry.

EXAFS speciation analysis of roasted Hg ore (calcines), waste rock, Hg condenser soot, gold mine tailings, distributed downstream sediments, and colloidal particles released from column experiments shows a variety of Hg-bearing phases present among the samples studied, with highly insoluble mercuric sulfides (cinnabar, metacinnabar) most common. Soluble Hg-chlorides, oxides, and sulfates were also identified in several samples and may represent more significant contributors of Hg to the environment.

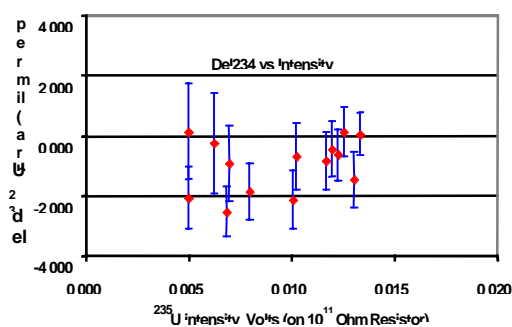
Hg concentration and speciation in mine wastes were found to correlate closely with factors such as the initial conditions of Hg ore deposition, the roasting and weathering processes to which the samples were subjected, and particle size. Most notably, Hg in all samples, even those far downstream from their sources, appears predominantly in the crystalline phase and not as Hg sorbed to sediment particle surfaces. This discovery extends to the colloidal phase, where discrete particles of cinnabar (HgS, hex) as small as 20 nm in diameter were identified by TEM. This type of information is important to regulating agencies in assessing Hg-contaminated mining regions and devising remediation strategies.

Isotopic composition of uranium standards and sea-water determined using Finnigan Neptune multi-collector sector ICP- MS

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We have developed methods for U isotope measurements using a newly acquired Finnigan Neptune multi-collector ICP-MS. The instrument is equipped with a multi-cup Faraday (F) array and a single secondary electron multiplier (SEM) with a retardation lens system (RPQ) to eliminate tailing from intense near-mass beams. Uranium isotopes were measured in a two-step process. Firstly ²³⁴U (SEM), ²³⁵U (F) and ²³⁸U (F) were measured. Then, ²³⁵U (SEM) and ²³⁸U (F) were measured. The second step is intended to calibrate the SEM-Faraday-cup gain and the intensity of the ²³⁵U beam was sufficiently low (typically <700,000 cps) to avoid overloading the SEM. In principle, this step should account for all non-linearities between the two detectors other than count-rate dependent effects. There is significant tailing from ²³⁸U in the region of the ²³⁴U peak. The RPQ is able to reduce the scattered beam to negligible amounts with minimal loss of intensity. The RPQ lens parameters were adjusted to match the quality of the SEM peak shape to that obtained from Faraday cups. Initially the transmission through the RPQ was ~98%. However, this has subsequently deteriorated to about 75% for reasons that are not clear. However, the method for calibrating the SEM-FAR yield remains robust. NIST Uranium standard U-500 with sub-equal ²³⁵-²³⁸U was used to minimize the influence of tailing from ²³⁸U without having to use the RPQ. The results with and without the RPQ are identical within errors. Count-rate dependence of the results were tested and showed no significant effects within errors. All of the data are shown in the figure. For ²³⁵U intensities between 12 to 15 mV (10¹¹ Ohm resistor), the precision is better than ±1%.



There is a discrepancy in the ²³⁴U/²³⁸U ratio in sea-water as determined from modern corals and directly from sea-water. Corals are close to 149 whereas mean sea water value is 143%. Our results give values close to those measured in modern corals.

References

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