Mineralogical Associations of Mercury Retained in FGD Gypsum

William Lee Beatty, Karl Schroeder, Candace Kairies

U.S. Department of Energy, National Energy Technology Laboratory, 626 Cochrans Mill Road, P.O. Box 10940, Pittsburgh, PA 15236-0940

Abstract

The natural mode of retention of Hg in FGD products is a key issue in the utilization of coal byproducts as environmentally acceptable resources. This is being investigated with a sequential extraction scheme that subjects FGD material to a series of phase-targeted reagents. Mineral phases with the greatest affinity for Hg and the form in which Hg is naturally immobilized can be discovered by observing the amount of Hg mobilized by each successive extracting solution.

The extraction procedure consists of a prolonged water rinse in a continuously stirred tank extractor to dissolve $CaSO_4$ followed by a series of batch extractions. These extraction include: a water rinse of the resulting residue to remove any remaining water soluble and loosely sorbed ions, 0.11M acetic acid to target carbonate minerals and exchangeable ions, 0.1 M hydroxylamine hydrochloride to dissolve manganese oxides and hydroxides, 0.25 M hydroxylamine hydrochloride in 0.25 M HCl to dissolve iron oxides and hydroxides, and hydrogen peroxide and 0.1 M ammonium acetate to oxidize organic matter and dissolve sulfide minerals. Analysis of the supernatant after each extraction step includes ICP-OES or ICP-MS for major and trace elemental composition and CVAF for mercury.

Initial results indicate that Hg is released under specific conditions and is associated with two distinct fractions of FGD materials. Although most of the solubilized Hg is extracted by the iron oxide and hydroxide dissolution reagent, ICP analysis suggests a possible association with clay minerals present in this fraction. The organic matter and sulfide minerals fraction typically yields lower but still significant amounts of Hg.

Procedures

All extractants were made with Ultra-pure reagents and Milli-Q® water (MQW, 18 MΩ•cm). MQW was also used for the water rinse steps of the procedure. Extractions were carried out in 250 mL Teflon® centrifuge bottles. All Teflon® and glassware was cleaned using a Milestone TraceCLEAN Acid Reflux Cleaning System.

CSTX Leaching

Some samples subjected to the extraction procedure were concentrated residues obtained from Continuously Stirred Tank Extractor (CSTX) leaching experiments. This procedure delivers a small amount of solid residue enriched in metals. Unleached FGD gypsum samples were also subjected to the extraction procedure. These have much lower metals concentrations, but are more readily available in the amounts required for extraction.

Sequential Extraction

Single and sequential chemical extraction procedures have been developed to evaluate the mobility and availability of potentially toxic trace elements in sediments and soils. An extraction procedure based on Kairies (2003), itself a modification of a procedure developed by the Standards, Methods and Testing (SM&T) Programme of the European Commission (Ure et al., 1993), was used. MQW, rather than the extractant for each step, was used during each rinse phase.

The steps of the sequential extraction and their associated targeted phases are:

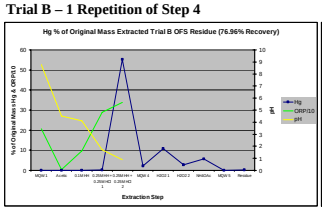
Extraction Step	Targeted Phase
MQW rinse	water soluble and loosely sorbed fraction
0.11M acetic acid	carbonate and exchangeable fraction
0.1 M hydroxylamine hydrochloride	manganese oxides and hydroxides
0.25 M hydroxylamine hydrochloride in 0.25 M HCl	iron oxides and hydroxides
hydrogen peroxide and 0.1 M ammonium acetate	organic matter and sulfide minerals

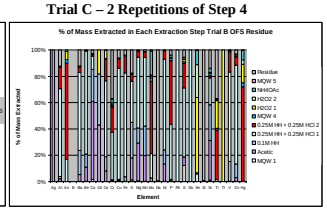
Results

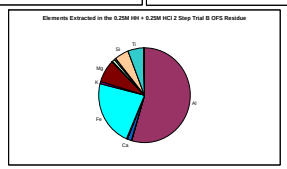
Four FGD materials have been subjected to the sequential extraction process over four trials. CSTX residues of OFS (orange fluffy stuff—a fine, Fe-rich slurry material collected in the FGD unit) and FGD gypsum materials were tested during trials A, B, and C to refine the experimental process, and two unleached FGD gypsum materials were tested in trial D to determine their suitability for extraction. Trial B was performed with one repetition of Step Four. Trials C and D were performed with two repetitions of Step Four.

OFS Residue

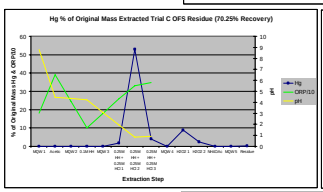
Trial B – 1 Repetition of Step 4

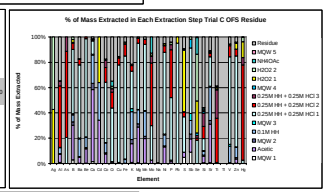


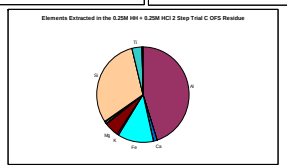




Trial C – 2 Repetitions of Step 4

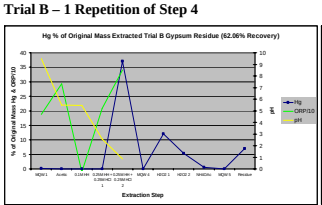


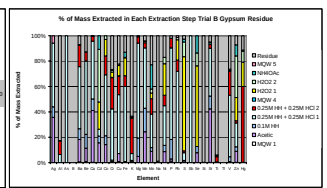


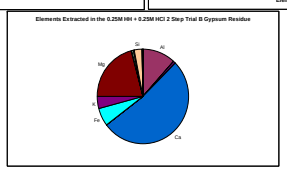


FGD Gypsum Residue

Trial B – 1 Repetition of Step 4

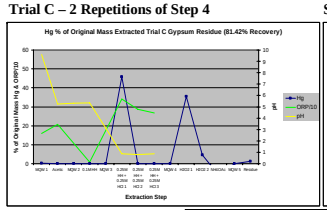


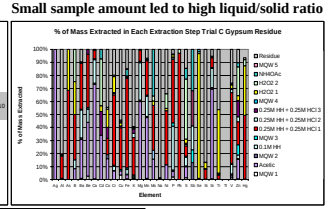


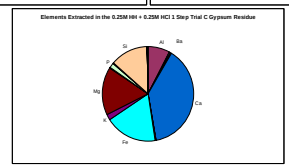


FGD Gypsum Residue

Trial C – 2 Repetitions of Step 4 — **Small sample amount led to high liquid/solid ratio**

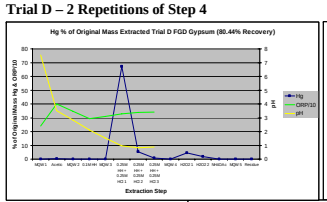


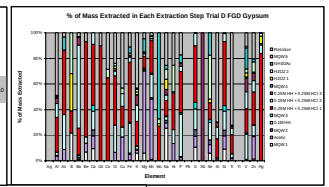


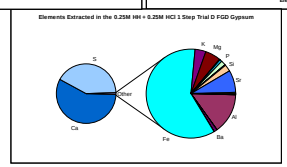


Unleached FGD Gypsum

Trial D – 2 Repetitions of Step 4







Discussion

After several slight modifications, the extraction scheme has shown suitable resolution to determine the specific conditions for mercury release. Significant amounts of Hg were not released in any sample until conditions of pH < 1 and ORP ~ 350mV were reached. A second release of Hg also typically occurred during the first H_2O_2 extraction. Although significant amounts of Fe were typically released in the first 0.25 M hydroxylamine hydrochloride in 0.25 M HCl step (Step 4), only the unleached gypsum sample and the residue sample with a high liquid/solid ratio showed Hg release during this step. All other samples showed Hg release during the first repetition of Step 4. This suggests the presence of a a non-Hg binding Fe phase that must be fully dissolved before the Hg-binding phase is released. The data also show Al, Mg, and Si are major components of the phase associated with maximum Hg release.

Future experiments will continue to evaluate new FGD materials as well as assess the possibility that Hg may be liberated during early extraction stages and re-adsorbed several times before finally being released. The extraction process will also be used to isolate concentrated Hg-containing phases for further investigation.

References

Kairies, C.L., 2003. Characterization of Precipitates Associated with Bitumonous Coal Mine Drainage, Northern Appalachian Region, USA, PhD Dissertation, The University of Pittsburgh, 88 p.

Ure, A.M., Quevauviller, P.H., Muntau, H. and Griepink, B., 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. Intern. J. Environ. Anal. Chem. 51, 135-151.