

Testing Mechanisms of Mercury Retention in FGD Products

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Abstract

The natural mode of retention of Hg in flue gas desulfurization (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 procedure consists of a series of batch extractions, sometimes preceded by a prolonged water rinse in a continuously stirred tank extractor to dissolve CaSO₄. These extractions include: a water rinse 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 elementals and CVAF for mercury.

Initial results indicate that Hg 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 an 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 extracting agents 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.

Sample Preparation

Some samples subjected to the sequential extraction 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 and wallboard samples were also utilized. 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 extracting agent utilized in each step, was used during each rinse phase.

| 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 |

During the course of the experiments, the number of times an extraction step was performed was adjusted to provide more information regarding the specific timing of metals releases.

Samples

| Sample Name | Description |
|-------------|-------------------------------------------------------------------------------|
| OFS A | CSTX residue of OFS—a fine, Fe-rich slurry material collected in the FGD unit |
| G A | CSTX residue of Gypsum A |
| G B, G C | Unleached Gypsum B & C |
| G D, W D | Gypsum D and associated wallboard |
| G E, W E | Gypsum E and associated wallboard |

Results

CSTX Residues

Major Hg release occurred during two extraction steps in both CSTX residue materials tested: Step 4 (0.25 M hydroxylamine hydrochloride in 0.25 M HCl) and

Step 5 (30% hydrogen peroxide). The largest release occurred during Step 4, and this step was repeated in subsequent experiments. Concentrated residues released the majority of their Hg after two applications of 0.25 M hydroxylamine hydrochloride in 0.25 M HCl. Increasing the liquid to solid ratio caused the concentrated residue to release significant Hg after only one application.

Unleached Gypsum

Because the concentration of Hg-binding materials in unleached gypsum was much smaller than that in the CSTX residues, major Hg release occurred after the first application of Step 4. Materials released during this step include significant amounts of Fe, Al, Mg, K, and Sr. Significant Hg was again released during Step 5.

Unleached Gypsum/Wallboard Pairs

No significant difference in Hg release was observed between gypsums and associated wallboards subjected to the extraction process. The pattern of Hg release and the elements associated with Hg release were similar in all samples. Elevated levels of Hg in samples GD and GE were the result of fine solids present in the aliquot.

Acid Extraction of Unleached Gypsum

Because Hg release occurred under extremely acidic conditions ($\text{pH} < 1$) an experiment was conducted to determine if exposure to strong acid alone was sufficient to cause release. Samples GB and GC were subjected to three applications of 0.1M HCl. No significant release of Hg was observed in either material during any of the applications.

Conclusions

Two distinct phases present in the FGD materials tested appear to be responsible for Hg binding: an Fe oxide and hydroxide phase and an organic phase. The multiple applications of Step 4 required to release Hg from concentrated residues suggest that more than one fraction may have been present in the Fe oxide and hydroxide phase. In this scenario, the first, more easily soluble, non-Hg-binding fraction was dissolved completely before the Hg-binding fraction was attacked. Because the unleached gypsum and wallboard samples contained smaller amounts of the Fe oxide and hydroxide phase, both fractions would have been released with a single application of Step 4. It is also possible that Hg was liberated during early extraction stages and re-adsorbed

several times before finally being released. Additional concentrated residues are being investigated to determine the specific fraction responsible for Hg binding.

The pattern of Hg release and the elemental constituents of the material released with Hg were consistent throughout the samples investigated. No significant differences were observed between parent gypsum and wallboard products. The prominence of Al, K and Mg in the major Hg-binding fraction suggests that clay minerals may also be associated with this phase and could be at least partially responsible for Hg retention.

Hg release occurred in a narrow range of pH and reducing conditions. Extractions with acid demonstrated that low pH alone is not sufficient to release Hg in significant quantities. Figure 14 plots the relationship between Hg release, pH and Oxidation-Reduction Potential for 8 FGD materials (concentrated residues, unleached gypsums and wallboards) over 62 extraction steps. Hg release (represented by the blue box) is confined to the area $\text{pH} < 1$ and $250\text{mV} < \text{ORP} < 400\text{mV}$. No data has been collected for the region shaded in purple. It is possible that low pH and very low ORP ($< 250\text{mV}$) conditions may also promote Hg release.

References

Kairies, C.L., 2003. Characterization of Precipitates Associated with Bituminous 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.