

Karl Schroeder
U.S. Department of Energy
National Energy Technology Laboratory

Fixation and Mobilization of Mercury in FGD Gypsum

Wet FGD technologies used for the removal of SO_x can result in the co-removal of mercury (Hg). Subsequently, a large portion of this Hg can be incorporated into the slurry and its solid byproducts, including FGD gypsum. The amount of Hg in FGD products may increase in the future if these units are optimized for co-capture. Among the issues that arise are the potential for atmospheric and groundwater releases of Hg in their end-use environment or during manufacturing processes, releases from the manufactured products themselves, and post-disposal mobilization from wallboard or other products at the end of their service. The potential for release of Hg from FGD products and the potential for FGD products to retain Hg in insoluble forms are key issues relating to the utilization of coal byproducts as environmentally acceptable resources. These issues are being addressed in laboratory tests to determine the potential for Hg mobilization and parallel efforts to determine the natural mode of fixation of Hg in FGD products.

Laboratory tests have included leaching using both a semi-batch, continuously-stirred reactor and sequential batch methods. Leaching has been done at pH values ranging from the natural pH of the gypsum, usually around 8.5, to acidic values as low as 2. Volatilization of elemental Hg has been monitored using an environmental chamber under moist and dry conditions, with light and in the dark. More recently, volatilization of elemental Hg during continuous leaching experiments has also been measured. The nature of the phases responsible for immobilizing Hg in the solid phase has been investigated using a sequential extraction scheme in which material is subjected to a series of phase-targeted dissolution reagents.

Continuous and batch leaching of both FGD gypsums and wallboards made from them indicate that high levels of dissolved Hg are not often seen. Mercury in individual leachate samples is usually below 50ng/L (ppt), however, much higher values may occur early in the leaching experiment. None of the cumulative amounts of leached Hg have exceeded 5% of total Hg content of the material. The majority of the Hg often remains in the post-leaching residue.

Examination via mineral extraction of starting gypsums, leached gypsum residues, and FGD gypsum isolated from wallboard indicate that the Hg present in the solid is in neither an easily solubilized nor ion-exchangeable form. This is in agreement with the leaching studies and indicates that Hg is not present as a soluble salt and tends to rule out the importance of mercuric chloride or similarly soluble materials. Extraction with harsher reagents showed the presence of at least two Hg binding phases. The first, and major, release of Hg occurred upon the addition of 0.25M hydroxylamine hydrochloride in 0.25M HCl, a reagent specific for iron oxide/hydroxides. A second, but smaller, release occurred upon the application of hydrogen peroxide and heat, a combination that targets organically bound Hg as well as sulfides. However, the presence of Al, K, Mg, and Si in the first extract and the presence of iron in the second suggest that minerals other than those targeted may be responsible for binding the Hg.

Loss of Hg by volatilization of the elemental form appears to be as significant or, in some cases, more significant than loss via solubilization. The extent of volatilization did not correlate with the amount of leachable Hg. Dry samples, especially FGD gypsum from wallboard emit, at most, only low levels of elemental Hg. Moist samples, whether simply moistened in the environmental chamber or suspended in a slurry, almost always emit Hg although FGD gypsum removed from wallboard produces significantly lower emissions. Mercury emissions are more pronounced in the absence of oxygen, especially at elevated temperatures.

Mercury displays a rich chemistry in these systems despite the seeming simplicity of nearly pure calcium sulfate dihydrate. Part of the chemistry appears to involve a Hg fixation mechanism in which Hg, probably in an ionic form because of the weak bonding properties of the elemental form, is strongly sorbed on a mineral phase, such as an iron (hydr)oxide or iron-rich clay, and/or is present as a very insoluble material such as the sulfide, HgS. This Hg is released as a single large slug upon the destruction of these phases. Whether all of this Hg also serves as a large reserve pool for much slower reactions that lead to solubilization and/or volatilization or whether only a portion, which represents a separate, less fixated pool of Hg, is involved is not clear.