Distribution of Mercury in FGD Byproducts

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ABSTRACT

Recent reports on the partitioning of mercury (Hg) in flue gas desulfurization (FGD) sludge have differed on the distribution of Hg between the aqueous and solid phases. In one case, the Hg was accounted exclusively to the fine, rather than crystalline, portion of the solid gypsum.[1] In another, Hg was found to be about evenly distributed between the gypsum and the recycle water.[2] More effective Hg control strategies can be developed if the Hg is limited to, or more concentrated in, a particular fraction. For example, handling of the fines as a separate process stream might be beneficial if the Hg was present in that phase preferentially. To investigate the extent of partitioning of Hg among the different fractions of the sludge, a size separation based on sedimentation was applied to FGD product slurries. Those results showed that Hg reported preferentially to the top layer containing the more slowly settling solid. Further experiments resulted in the isolation of a mercury-binding phase present in at least some FGD gypsums.

INTRODUCTION

Recent studies and reports by the EPA make it clear that they view emissions of Hg from coal-fired utilities as a serious environmental problem.[3] Future regulation of the atmospheric emissions of Hg will shift the environmental burden from the flue gas to the solids formed as by-products of the combustion and flue-gas clean up processes, i.e. coal utilization by-products (CUB). The beneficial uses of CUB may then be in jeopardy.[4] This is particularly true for those uses that may allow for transport of the mercury into surface or ground water. For example, the use of CUB as a soil amendment puts the material in contact with irrigation and natural precipitation which could result in the leaching of any mobile metals. For this reason, it is important to understand the chemistry of the Hg-CUB interaction, to be able to predict the environmental fate of the CUB-bound Hg, and to be able to anticipate the effect of additional Hg loads in the CUB material.

The use of FGD-gypsum in wallboard manufacturing is a prime example of an economically favorable, beneficial use of a power plant by-product. It is estimated that more than 30 million tons of FGD materials were generated in 2003.[5] The largest reuse of this material was for the manufacturing of wallboard, which accounted for nearly 8 million tons. Wallboard plants have been built for the explicit purpose of using FGD

gypsum as their only gypsum source. Mercury balances across FGD units have shown that oxidized mercury can be captured and strongly retained in some FGD units, especially those employing forced oxidation.[6] This finding may be a two-edged sword. FGD units can be used for the co-capture of mercury thus limiting stack-gas emissions and their associated environmental concerns. However, the burden is transferred to the gypsum product which becomes suspect as a future environmental source of Hg. Experiments reported here to determine the mobility of FGD-captured Hg show that in some cases it is very limited. Further, the agent responsible for the immobilization appears to be not gypsum itself but an impurity that is probably introduced with the limestone used to form the SO_2-capture reagent.

EXPERIMENTAL

FGD drier material was collected from only one source. The material was obtained from the conveyor belt before and after the heated zone. FGD slurry samples were obtained from two different power plants. Each contained about 15% solids. Samples of gypsum, stucco, wallboard slurry, and/or finished wallboard were obtained from 4 wallboard plants using FGD gypsum. Reverse osmosis water was further purified using a Millipore® purification system to give Milli-Q® water with a specific conductivity of 18 MΩ•cm. All acids were trace-metal grade. The CSTX used to leach the FGD gypsum is described elsewhere in these proceedings.[7] Hg analyses in solids was performed using the Milestone DMA-80 analyzer. Solutions were analyzed for Hg by CVAA. Other metals analyses were performed via ICP-OES on microwave assisted digests of the solids.

RESULTS AND DISCUSSION

Samples were obtained from various unit-operations found in the FGD-product to finished wallboard production. Samples were obtained from at least 6 different power plants but all samples were not collected at any one plant. The purpose of the experiments reported here was to study the chemistry of the Hg-CUB interaction, not to do a mercury balance around any one plant or plants. Results from efforts by others to do such balances may be found on the NETL web site.[8]

Mercury stability during FGD-gypsum drying: In one case, samples were obtained before and after a drier that was used to reduce the moisture content of the FGD solids before they were moved to the wallboard manufacturing plant. The purpose of the drier was to improve the handling properties of the wet, clumpy FGD solids by reducing the moisture content. Two grab samples from both before and after the drier were analyzed in triplicate to give the Hg results shown in Table 1. The drier was effective in reducing the moisture content from about 30% to about 25%. The within-sample analytical replicates and the between grab-sample precision were all good, providing error estimates of less than 6% relative standard deviation. The values of 202 ± 8 µg/kg before and 205 ± 10 µg/kg after the drier indicate that, within analytical precision, no Hg is lost in this unit operation.

<u>FGD mercury stability during wallboard production</u>: Mercury analyses obtained for samples from wallboard manufactures using FGD-produced gypsum are shown in Table 2. The Hg present in both the unprocessed FGD gypsum and the finished product ranged from about 100 to 1000 µg/kg or over one order of magnitude. Of the four sites providing samples, only one showed significant Hg losses during manufacturing. Three of the four wallboard samples showed high or complete retention of Hg in spite of the high temperatures and chemical processing endured by the FGD material. This is consistent with studies at EERC which have shown that little or no Hg is released below 170°C and that the extent of release above that temperature may be process dependent.[9] The reason for this stability is not known.

<u>Thermal stability of FGD-bound mercury in contact with an aqueous phase</u>: Figure 1 presents the results obtained when FGD gypsum containing about 200 µg/kg Hg was placed in contact with fresh, purified water and heated to various temperatures. Data for both desorption (increasing temperature) and adsorption (decreasing temperature) modes are included. No difference could be seen between the two approaches for equilibration times exceeding 6 hours. At shorter times greater scatter could be seen in the lower-temperature desorption data perhaps indicating that longer times are needed at the lower temperatures for effective desorption of Hg to its equilibrium limit. At temperatures higher than 70°C neither the mode of equilibration nor the time allowed for equilibration appeared to matter. Very little of the Hg was found in solution. Even at the highest temperature of 94°C, less than 0.5% of the Hg was released. This finding reinforces the previous finding that very little Hg remobilization is seen for some FGD products. Both thermal desorption into the gas phase, as might be expected during the calcining of the FGD-gypsum during wallboard manufacturing, and thermal desorption into the liquid phase as seen here were not found to be prominent remobilization pathways for most of the FGD gypsums studied here.

<u>The mercury-binding phase in FGD gypsum</u>: Settling and dissolution experiments were performed in an attempt to isolate the material responsible for the strong Hg-gypsum binding. Settling experiments have been partially successful in concentrating the Hg in the slower-precipitating fraction. Some of these results are presented in Table 3. In the 3 cases presented, the Hg was always more concentrated in the top-most, slower-settling layer of the gypsum. This layer also was more brownish in color whereas the majority of the gypsum was white. The top layers still contained mostly gypsum but where enriched in Si (8.3%), Al (2.4%), Fe (1.9%) and Mg (1.8%). The top layers were also enriched in the trace metals Ba, Mn, and Ti in addition to Hg. Thus, the strong adsorption seen for Hg may not be specific for this element but a more general phenomenon.

In a separate experiment using a continuous stirred-tank extractor, FGD gypsum was subjected to water and dilute acid leaching for a period of about 200 hours. The pH dropped from an initial value of over 8 to nearly 2.5 at the end of the experiment. Data obtained during the period of most-rapid pH change are shown in Figure 2. Samples were taken once an hour and analyzed for Hg in addition to a suite of other metals. No Hg was found in the leachate. The post-leaching residue accounted for less than 1% of

the original material but contained all of the Hg. A mercury balance of 102% was obtained. The residue contained only traces of remaining gypsum and was high in iron and aluminum. Thus, it appears that the phase responsible for the Hg retention is not fine, high-surface-area calcium sulfate but, more likely, an iron or mixed iron and aluminum phase. It may be an impurity in the limestone used to capture the SO_2 in the FGD scrubber. Efforts are underway to better characterize this naturally occurring, mercury-binding material.

CONCLUSIONS

The mercury captured in some FGD gypsums is bound tightly and is not easily removed by thermal or acid leaching processes. The phase responsible for this behavior appears to be an iron- or iron/aluminum-rich material. Recent reports on the partitioning of Hg in FGD sludge have differed on the distribution of Hg between the aqueous and solid phases. In one case, the Hg was accounted exclusively to the fine, rather than crystalline, portion of the solid gypsum.[1] In another, Hg was found to be about evenly distributed between the gypsum and the recycle water.[2] The presence of, what appears to be, a naturally occurring adsorptive phase in some FGD gypsums may explain the different results seen for different systems.

REFERENCES

[1] Babcock & Wilcox Co. And McDermott Technology, Inc. (2003) "Full-Scale Testing Of Enhanced Mercury Control Technologies For Wet FGD Systems" Final Report, DE-FC26-00NT41006, Babcock & Wilcox Co. And McDermott Technology, Inc. May 7, 2003.

[2] Hein, K.R.G. (2004) "Status and Prospects of Air Toxic Emissions Reduction Technologies for Coal-Fired Power Plants in Europe" Dipl.-Ing. Sven Unterberger, Prof. Dr.-Ing. Klaus R.G. Hein, Presented in Glasgow, Scotland, 2004.

[3] EPA (2005) "Mercury - Controlling Power Plant Emissions: Overview " Available at: http://www.epa.gov/mercury/control_emissions/index.htm

[4] Aljoe, W.W., Feeley III, T.J., Murphy, J.T., Brickett, L.A. (2004) "The Fate of Mercury in Coal Utilization By-Products - DOE/NETL's Research Program", Presented at the Combined Power Plant Air Pollutant Control Mega Symposium, September 1, 2004. Available at: http://www.netl.doe.gov/coal/E&WR/cub/ index.html

[5] American Coal Ash Association (2003) "2003 Coal Combustion Product (CCP) Production and Use Survey Results" Available at: http://www.acaa-usa.org/PDF/ 2003_CCP_SURVEY(10-1-04).pdf

[6] Pavlish,J.H., Sondreal,E.A., Mann,M.D., Olson,E.S., Galbreath,K.C., Laudal,D.L., and Benson,S.A. (2003) "Status Review of Mercury Control Options for Coal-fired Power Plants." *Fuel Process. Technol.* **82** (2-3), 89-165.

[7] Kairies, C., Cardone, C. and Schroeder, K. (2005) "Leaching of CUB Using a CSTX" Presented at the World of Coal Ash (WOCA) Symposium, April 15, 2005.

[8] DOE-NETL (2005) http://www.netl.doe.gov/coal/E&WR/mercury/index.html

[9] Heebink, L.V. and Hassett, D.J. (2003) "Mercury Release from FGD in the Wallboard Manufactring Process" Presented at Air Quality IV, Sept. 22-24, 2003.

Mercury and Moisture Analysis	Before Drier		After Drier	
	Sample 1	Sample 2	Sample 1	Sample 2
As-Received Mercury (μg/kg)	140 ± 6	142 ± 6	151 ± 2	158 ± 9
As-Received Moisture (%)	29.9	30.3	24.6	24.9
Mercury, Dry Basis (μg/kg)	200 ± 8	204 ± 8	200 ± 3	211 ± 11
Hg, 2-Sample Average (μg/kg)	**202 ± 8**		**205 ± 10**	

Table 1. Mercury and moisture analyses for samples taken before and after a FGD gypsum drier.

Mercury in FGD Products (μg/kg = ppb)				
	Site A	**Site B**	**Site C**	**Site D**
Feed FGD-Derived Gypsum	143 ± 4	210 ± 10	1017 ± 45	1167 ± 40
Product FGD-Derived Wallboard	147 ± 2	87 ± 5	1035 ± 52	1107 ± 75
% Hg Retained during Processing	**103 %**	**42 %**	**102 %**	**95 %**

Table 2. Mercury retention during the manufacturing of wallboard from synthetic gypsum.

Mercury in FGD Sludge Layers (μg/kg = ppb)	Top Layer	Bottom Layer	Ratio of Hg in Top to Bottom Layer
Sludge 1, Aliquot 1	3,560 ± 170	72 ± 6	49
Sludge 1, Aliquot 2	2,900 ± 80	180 ± 10	16
Sludge 2	13,000 ± 800	700 ± 27	16

Table 3. Mercury in samples taken from the top and bottom of a sludge column after settling.
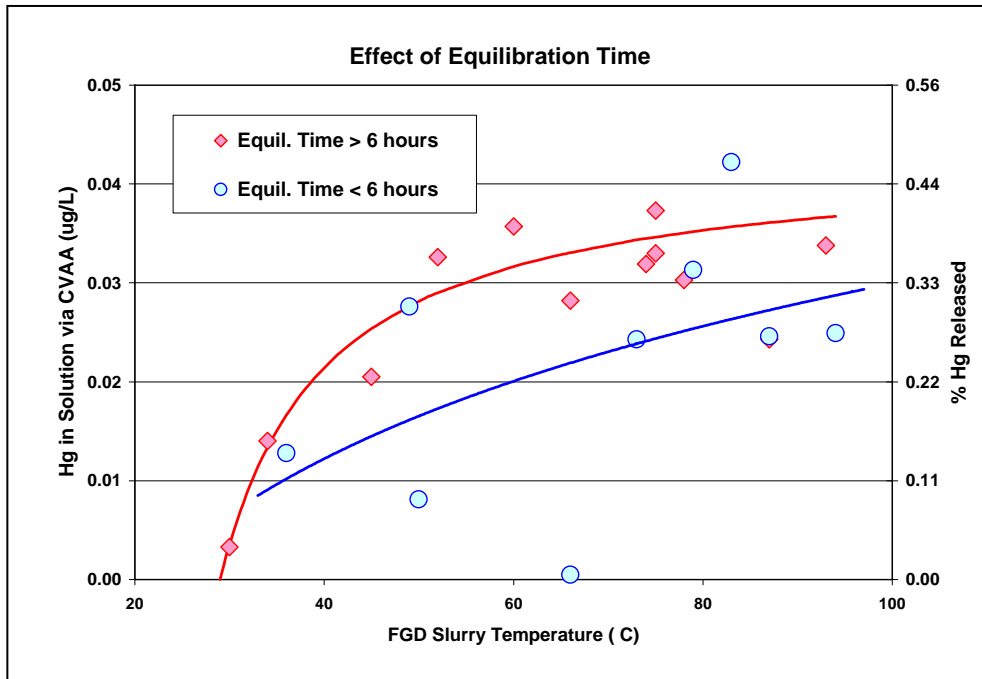
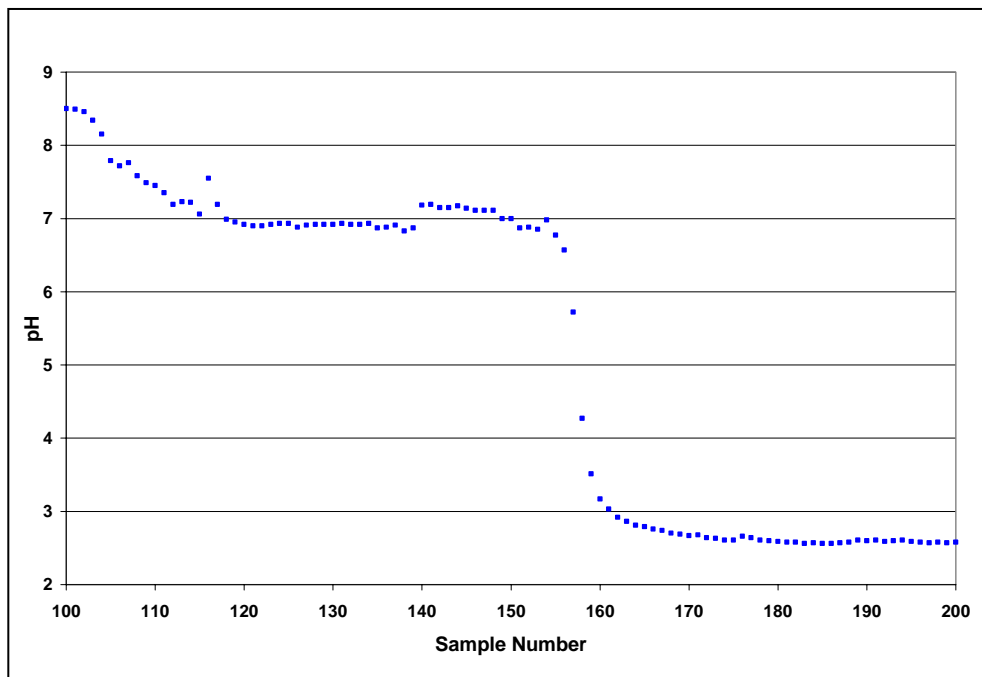Figure 1. Thermal stability of FGD-bound mercury in contact with an aqueous phase.

Figure 2. pH change during the continuous leaching of an FGD gypsum.