Task 2.8 - Mercury Speciation and Capture in Scrubber Solutions

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TASK 2.8 - MERCURY SPECIATION AND CAPTURE IN SCRUBBER SOLUTIONS

1.0 INTRODUCTION

U.S. Environmental Protection Agency (EPA) investigation into health risks associated with mercury emissions from utility steam generators, municipal waste combustion units, and other sources was mandated by the Clean Air Act Amendments (CAAA) of 1990. In anticipation of mercury emission regulation, attention has been focused on quantification of mercury emissions, which require verifiable sampling and analytical techniques. Several sampling and analytical methods are currently under the final stages of development as well as a variety of emission control methods. In particular, wet scrubber systems designed for SO₂ control in coal-fired utilities have been targeted for mercury control. Conventional wet-scrubbers remove mercury in a variety of soluble oxidized forms. Oxidized mercury is highly water-soluble and can be removed by scrubber slurry, theoretically limited only by gas-film mass transfer. However, since some oxidized mercury forms such as HgCl₂ are both soluble and volatile, the final fate of mercury trapped in scrubber solutions is unclear. Elemental mercury is not water-soluble, remaining in the vapor state at temperatures through pollution control devices and exiting the stack into the environment. However, notable exceptions to this rule exist. Depending on the type of mercury-sampling method used, an increase of $\leq 10\%$ in elemental mercury concentrations across wet scrubbers has been measured but is yet unconfirmed. Also, significant amounts of elemental mercury (metallic form) have been removed during wet scrubber maintenance. In addition, questions concerning 1) the initial speciation between oxidized and elemental forms of mercury in flue gas from coal-fired boilers and 2) the effects of scrubber slurry composition and pH on the mercury species have been raised.

2.0 OBJECTIVES

The objectives of this project are to determine under controlled bench-scale conditions if:

- Capture of elemental and/or oxidized mercury in wet scrubber slurry is dependent upon pH.
- Laboratory-prepared slurries show the same results as commercial slurries which contain antibacterial agents and other oxidizers.
- Mercuric chloride is converted to elemental mercury in a wet scrubber solution in a detectable, repeatable amount.

It is anticipated that data obtained from the bench-scale operation will limit sampling variability and achieve good mass balance information by utilizing the entire gas flow for gas-phase mercury samples and the entire slurry sample rather than slip- or split-stream samples from full-scale sampling results which are often difficult to interpret because of large variability in operating conditions.

3.0 SCOPE OF WORK

The initial scope of work intended to use two laboratory-prepared slurries: one lime and one limestone. Commercial scrubber slurry includes many oxidizing and chlorine-containing additives for disinfection, etc., which have the potential to impact mercury chemistry in the scrubber slurry. The scope of work was revised to include only the laboratory-prepared limestone-distilled water slurry when a commercial slurry from a wet-scrubber on a lignite-fired boiler became available. The commercial slurry additives were sulfuric acid, polymaleic acid, polyacrylate, chlorine, chlorine dioxide, and zinc chloride.

A test matrix for the pure limestone-distilled water solution was developed and is shown below. Previous EERC research has determined that wet chemistry mercury measurement methods are affected by the presence of HCl and NO_x, but the effect is not concentration-dependent for the range of concentrations typically found in combustion flue gas. The utility slurry from the lignite-fired boiler was run without the addition of HCl/NO to better simulate the actual conditions at the utility site. Therefore, Runs 1-8 from the test matrix were completed for the laboratory-prepared slurry, while Runs 1-4 were completed for the utility slurry. After steady-state operation was achieved, an outlet sample was performed followed by an inlet sample. A second outlet sample was then performed. Slurry samples were filtered and analyzed as solid and liquid. The limestone-distilled water slurry did not require digestion before analysis. The utility slurry was digested to remove interferences from organic components. In summary, duplicate runs (data) are available for all of the outlet flue gas mercury concentrations; however, only some duplicate data exist for mercury concentrations in the liquid and solid fractions of the slurry. One inlet mercury concentration data point was measured in between two outlet tests. Major variables were:

pH: - = low pH and + = high pH
HCl/NO - = no acid gases, + = 50 ppm HCl and 500 ppm NO
Hg Species: - = Hg⁰ and + = Hg⁺²

TABLE 1

Revised Test Matrix			
Run	Hg	pH	HCl/NO
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1

The mercury bench-scale test unit in the EERC Particulate Research Laboratory (PRL) shown in Figure 1 was used in conjunction with a wet scrubber simulator consisting of two heated-glass impingers and reservoir and pump. Liquid-to-gas ratios ranged from 83 to 92, and sulfur removal was 85% at pH = 5 and 100% at pH = 7. Major variables were high and low pH (5 and 7, respectively) and slurry type (pure limestone-distilled H₂O and a scrubber solution from a utility wet scrubber firing lignite coal). Simulated flue gas (SO₂ ≈ 750 ppm, NO_x ≈ 500 ppm, CO₂ ≈ 15%, H₂O ≈ 10%, O₂ ≈ 4%-6%, HCl ≈ 50 ppm, balance N₂) was spiked with either elemental or oxidized mercury from utility-manufactured calibration tubes. Budget constraints precluded tests spiked with both elemental and oxidized mercury. The scrubber simulator was operated with an inlet flue gas temperature of 325°-340°F, a scrubber solution temperature of 70°-90°F, and an outlet temperature ranging from 105°-116°F. Repeatability for inlet elemental and oxidized mercury concentrations was less than 1% and for outlet concentrations was 1%-2%. Tests were conducted after inlet gas conditions and temperatures had reached a steady state. SO₂ concentrations were held between 725-763 ppm, and NO concentrations were held between 496-536 ppm. Concentrations were monitored periodically with an ElectroChem IR (infrared) analyzer. The pH was continuously monitored in the reservoir solution. For runs conducted using the limestone-distilled water slurry, the increase in pH due to collection of SO₂ was controlled by adding known quantities of lime or NaOH. The initial pH of the utility slurry was 7, and known quantities of the slurry were added to the system to maintain the pH as needed. Sulfuric acid was used to achieve pH = 5 for both slurries. The entire amount of inlet and outlet flue gas was sampled, and all of the slurry was collected. A well-mixed aliquot was taken for filtration and digestion for analyses.

Inlet and outlet elemental mercury concentrations were measured using 1-hour EPA Method 29, rather than using the on-line continuous emissions monitor, SEMTECH 2000. Problems with the conversion system (used to convert oxidized mercury into elemental state) associated with the SEMTECH 2000 precluded measurement of oxidized mercury. (The SEMTECH analyzer only measures elemental mercury and uses a conversion system to convert oxidized forms of mercury to elemental mercury. The oxidized fraction is measured by difference between the total mercury in converted samples less the mercury in unconverted samples. At this time, the SEMTECH analyzer is working, but the conversion system is still under characterization.) Therefore, wet methods were preferable.

4.0 DISCUSSION

4.1 Limestone-Distilled H₂O Slurry

Elemental mercury removal across the laboratory-prepared limestone-distilled water slurry ranged from 0.0 to 1.7% for pH = 5. The presence of HCl and NO at the concentrations used did not affect the removal. As expected, the flue gas water concentration increased across the scrubber for tests conducted at pH = 5. However, repeated tests conducted at pH = 7 showed that the impinger solutions were actually dried during testing even though the simulated flue gas water inlet concentration was verified at 10%. Although various types of corrections were applied to these data to compensate for the loss of water and other factors, the data showed a 5%-7% increase in elemental mercury across the slurry. It must be emphasized that this noted increase is very insignificant and is, potentially, not real. Elemental mercury concentration of the limestone-distilled water slurry was not performed.

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Figure 1. Mercury bench-scale test unit.

Oxidized mercury removal across the laboratory-prepared limestone-distilled water slurry was 98.7% to 99.4% at pH = 5 both with and without acid gases. At pH = 7, removal was 96.0%–98.0%. These data indicate that oxidized mercury removal is nearly 100% as expected, and there is no significant effect of pH or acid gases on removal. Mercury concentrations in the liquid and solids of the limestone-distilled water slurry were only analyzed for the tests conducted at pH = 7. Unlike the tests conducted with elemental mercury, the impinger solutions were not dried at pH = 7. However, the amount of water stripped by the flue gas was only half that stripped at pH = 5. It was expected that if mercury were completely recovered in the slurry, the total quantity would be slightly greater than the total amount calculated from the inlet concentration, flow rate, and run time because of mercury capture in the slurry before run conditions reached steady state. However, only a disappointing 35% of the mercury was recovered as measured by analyses of the liquid and solids. The ratio of mercury in the liquid/solid was about 5:1. These data indicate that the captured oxidized mercury is concentrated in the liquid phase of the slurry rather than in the solid-sludge phase, which may affect final waste disposal considerations.

4.2 Utility Scrubber Slurry

Elemental mercury removal across the utility solution did not yield the same results as the laboratory-prepared limestone solution. In one set of tests (including duplicate outlet samples), at both pH = 5 and pH = 7, 20% of the elemental mercury was captured in the scrubber solution. In a third set of tests, intended to repeat the first set, only 10%–11% of the elemental mercury was captured. The filtered utility slurry also yielded a much different result from the laboratory-prepared limestone-distilled water solution. The liquid fraction of the utility slurry showed a non-detectable amount of mercury equal to that of the unused slurry. The solids fraction showed a slight increase from unused to spent slurry. However, recovery of the mercury found in the solids was only around 20%. It appears, then, that some elemental mercury (10%–20%) may be removed in utility scrubber solution. The difference between the outlet water concentration between tests conducted at pH = 5 and pH = 7 was also 5%.

Oxidized mercury removal across the utility scrubber slurry was repeatable at both pH levels at 98.3%–98.4%. However, recovery of the mercury from the liquid and solid fractions of the slurry was not nearly complete. Runs conducted at pH = 5 showed a slight increase in mercury in the liquid fraction, from nondetect to 1.3 $\mu\text{g/L}$, accounting for less than 1% of the inlet quantity. The mercury concentration in the solids was slightly less than in the unused slurry. Runs conducted at pH = 7, showed almost no change in the mercury concentration of the liquid (from nondetect <0.1 $\mu\text{g/L}$ to 0.2 and 0.3 $\mu\text{g/L}$). However, there was an increase in the amount of mercury in the solids fraction that was equal to approximately 60% of the inlet mercury. These data indicated that in real scrubber systems, oxidized mercury is captured in the solid-sludge phase rather than in the liquid phase of the slurry.

It is clear that recovery of both oxidized and elemental mercury in the scrubber solution is nonideal. The greatest factor in this problem is probably the temperature of the scrubber solution (between 70°–90°F). In addition, the reservoir solution which existed as a loop in the system was also heated and open to the atmosphere. The validity of future mercury bench-scale test mass balances for scrubber solution testing may be dependent on the temperature of the solution.

5.0 CONCLUSIONS

- There is no measurable effect of $\text{pH} = 5$ to $\text{pH} = 7$ on either elemental or oxidized mercury removal across limestone-water slurry or one utility lime slurry.
- One utility scrubber solution showed 10%-20% capture of elemental mercury from simulated flue gas.
- Laboratory-prepared slurries may not be appropriate for mercury capture studies because they do not show elemental mercury capture as did the utility slurry and because they retained the majority of the oxidized mercury in the liquid phase rather than in the sludge phase of the slurry.
- Mercury mass balance information is still difficult to obtain even at the laboratory-scale. Loss of mercury in the bench-scale system must be explained and mitigated before thorough experiments can be conducted.