

## **Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors**

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This presentation will summarize progress on Cooperative Agreement DE-FC26-04NT42314, "Kinetics Study of Mercury Reactions in FGD Liquors." The project is being co-funded by the U.S. DOE NETL and EPRI. URS Group is the prime contractor.

The objective of the project is to determine the mechanisms and kinetics of the aqueous reactions of mercury absorbed by wet flue gas desulfurization (FGD) systems, and develop a kinetics model to predict mercury reduction and re-emission reactions in wet FGD systems. The model will be used to determine optimum wet FGD design and operating conditions to maximize mercury capture in wet FGD systems and to ensure that mercury leaves the system in a form that is known and controllable.

An initial series of laboratory tests was done to identify the major variables for the rate of reduction of oxidized mercury by sulfite in solution. The reaction rates were initially determined by monitoring a mercuric-sulfite species concentration using UV/visible light spectroscopy. Other measurement methods were used to measure elemental mercury re-emissions from more complex chemical matrices where the UV spectra of several species overlap. This was done both by measuring the elemental mercury ( $\text{Hg}^0$ ) concentration in gas exiting the reactor and by periodically sampling the reactor liquor for total mercury. Results of this testing were presented at last year's meeting.

Previous researchers showed that sulfite-mercury complexes are important intermediates in the reduction of oxidized mercury by sulfite. In simple sulfite/mercury solutions, formation of the mercuric sulfite complex is the main pathway for reduction of oxidized mercury. As sulfite concentrations increase, a disulfite-mercury complex is formed which inhibits the overall reaction. In the presence of chloride (as in FGD systems on coal-fired plants), chloro-mercuric sulfite complexes are formed which also have a large effect on mercury reduction and re-emission rates.

Solution pH, sulfite concentration, and chloride concentration were all found to influence mercury re-emission rates under FGD conditions. The effects of temperature, ionic strength, initial reactant concentrations, thiosulfate, bromide, iodide, and other complexing agents or "inhibitors" on the rates of these reactions, and thus on the re-emission of Hg from FGD systems, have also been investigated. The strong inhibition of the reaction by sulfite means that species which react with sulfite, such as divalent cations found in FGD systems, can also affect the rates.

A chemical kinetics model has been developed to describe the aqueous mercury-sulfite-chloride-thiosulfate system and takes into account the simultaneous occurrence of a number of reaction steps. The model predicts the basic trends seen experimentally for pH, sulfite, and chloride effects, and is giving fairly good numerical agreement with experimental data. It has been used to design bench-scale experiments for testing as well as to predict kinetics in low pH regions, such as at the  $\text{SO}_2$  gas-aqueous interface, which are difficult to investigate experimentally.

An existing bench-scale (28 LPM) wet FGD system was modified to provide necessary controls and measurements for effective mercury re-emission testing. Modifications to the existing bench-scale wet FGD apparatus were necessary because of the complex relationship between pH, sulfite concentration and chloride concentration on mercury re-emissions. In particular, the need to set and closely control sulfite concentration is important. A method for controlling sulfite concentration was developed which uses real time measurement of sulfite concentration to vary the rate of hydrogen peroxide addition to the FGD liquor and consequent sulfite oxidation.

An extensive series of runs has been conducted using this apparatus. The general trends for pH-sulfite-chloride dependence predicted by the model have been observed in the data. Other results show a linear dependence of average Hg re-emissions on liquid phase Hg concentration. Additional testing has evaluated a number of other variables, including NO<sub>x</sub>, fly ash presence, organic acids, re-emission inhibitors such as TMT 15, calcium, and magnesium concentrations.

Bench-scale wet FGD results show that mercury re-emissions increase linearly with total concentration of mercuric salt added to the reaction tank. The effects of pH and sulfite concentration are complex and appreciable, particularly at low sulfite concentration such as would be encountered in gypsum-producing FGD systems. Thiosulfate (present in inhibited oxidation systems) appears to inhibit re-emission at low pH, but accelerate it at high pH. Effects of nitrogen compounds are also mixed, with more work needed on combination of sulfur-nitrogen species in the FGD liquor and NO<sub>x</sub> in the simulated flue gas. Carboxylic acid salts (such as FGD performance additives) can increase re-emissions, dramatically in some cases. Use of re-emission inhibitors is promising, but there is a need to characterize their effects closely, as some adverse effects (e.g., high re-emissions at some dosages) are also possible.