

Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

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This paper 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 are being used to measure elemental mercury re-emissions from more complex chemical matrices where the UV spectra of several species overlap. This has been done both by measuring the elemental mercury (Hg^0) concentration in gas exiting the reactor and by periodically sampling the reactor liquor for total mercury.

Previous workers showed that sulfite-mercury complexes were important intermediates in the reduction of oxidized mercury by sulfite. Formation of the mercuric sulfite complex is the main pathway for reduction of oxidized mercury, but as sulfite concentration increases to FGD levels, an inert disulfite-mercury complex is formed which inhibits the overall reaction. We have found that in the presence of chloride (as in actual FGD systems), chloro-mercuric sulfite complexes are formed which also have a large effect on mercury reduction and re-emission rates. Our initial kinetics model was built and checked out on the literature data along with experimental data from this project that show pH and sulfite concentration effects. Data for the reactions involving the chloro-mercuric sulfite complexes were added to the model along with the effects of other chemical species. The model is theoretically based and solves the rate equations for a set of about 30 chemical reactions, given the rate constants and activation energies of the reactions, the initial concentrations of key species, and the temperature.

For model verification, kinetic results were also obtained by measuring the gas phase evolution (re-emission) of mercury from sparged solutions, and/or periodic analysis of the reaction solution for liquid phase mercury. These measurements of the rate of re-emission of elemental mercury from solution as a function of time have been used to verify and extend the spectrophotometric results to high chloride and long reaction time conditions. In the absence of chloride, the Hg^0 stripping rate measurements confirmed the first order disappearance of oxidized mercury (Hg^{+2}) and equivalent rate constants are obtained for this case as well as at low chloride concentrations. At elevated chloride levels the Hg^0 stripping rate measurements show a sharp initial release of Hg^0 , but then very low rates of release are observed for extended times. The Hg^0 stripping

apparatus results verified the importance of pH in the pH 4 to 6 region and the effect of sulfite on this dependence. In general, the rate decreases with increasing sulfite concentration, though the dependence seems to be more pronounced in the transition region between high and low pH.

These results suggest that mercury re-emissions in full-scale wet FGD systems could be greatly influenced by factors such as slurry droplet pH drop, sulfite pick up, and sulfite oxidation within the absorber rather than reaction tank 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, are also under investigation. 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.

The 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 is predicting the basic trends seen experimentally for pH, sulfite, and chloride effects, and is giving fairly good numerical agreement with experimental data. It is being used to design bench-scale experiments for testing as well as to predict kinetics in low pH regions, such as at the SO₂ gas-aqueous interface, which are difficult to investigate experimentally.

An existing bench-scale 28 LPM 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.

A series of runs using this apparatus is underway. 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. Testing of a number of other variables, including NO_x, fly ash presence, organic acids, precipitants such as TMT 15, and re-emission inhibitors is underway.