

TITLE: THE HOMOGENEOUS FORCING OF MERCURY
OXIDATION TO PROVIDE LOW-COST CAPTURE

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1. ABSTRACT

Objectives

Mercury that exits the furnace in the oxidized form (HgCl_2), as opposed to elemental mercury, is known to be much more easily captured in existing pollution control equipment (*e.g.*, wet scrubbers for SO_2). This is principally due to the high solubility of the oxidized form in water. Work over the last several years in our lab and elsewhere has identified the general outlines of how this oxidation occurs.

The scenario is as follows. In the flame the mercury is quantitatively vaporized as elemental mercury. Also, the chlorine in the fuel is released as HCl. In the high temperature flame, a small fraction of the HCl decomposes to give atomic chlorine. As the gases cool, the recombination of the atomic chlorine to Cl_2 is kinetically inhibited, leading to a superequilibrium excess in the post-flame region. Once the gases drop below about 550°C , the mercury equilibrium shifts to favor HgCl_2 over Hg, and this superequilibrium chlorine atom promotes oxidation via the fast reactions $\text{Hg} + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M}$ and $\text{HgCl} + \text{Cl}_2 \rightarrow \text{HgCl}_2 + \text{Cl}$. Thus, the high temperature region provides the Cl needed for the reaction, while the quench region allows the Cl to persist and oxidize the mercury in the absence of decomposition reactions that would destroy the HgCl_2 . The next question is how to make use of the knowledge to *promote* oxidation. The hypothesis is that introduction of fuel species (specifically H_2 or CO) in the post flame gases will lead to an enhancement in atomic chlorine concentrations, leading to increased fractional mercury oxidation. Chemical kinetic modeling suggests that this occurs due to the free radicals generated by the decomposition of the fuel. This leads to reactions such as: $\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$. The present grant focuses on exploring and optimizing this hypothesis.

Accomplishments to Date

The experiments are conducted in a quartz plug flow reactor system. The reactants are preheated separately and mixed in a system that allows an approximately 0.5 second residence time at a selected constant temperature. The gases are then quenched to room temperature in a well

characterized quench zone before the mercury oxidation state is measured by cold vapor atomic absorption. Previously we have systematically examined the influence of temperature, HCl, and water vapor on mercury oxidation. Figure 1 below summarizes the results of several tests in which H₂ was injected into the system (approximately 400 ppm). The results indicate that H₂ does indeed significantly promote oxidation. The following observations are consistent with the data. First, the H₂ leads to oxidation at low temperatures where none is seen otherwise. Second, the oxidation shows a maximum around 700°C. Further increases in temperature lead to less oxidation with H₂, but more for the base case. Thus, at the highest temperature studied, the H₂ actually inhibits oxidation. Testing with CO has shown no influence on oxidation, both in the presence and absence of CO.

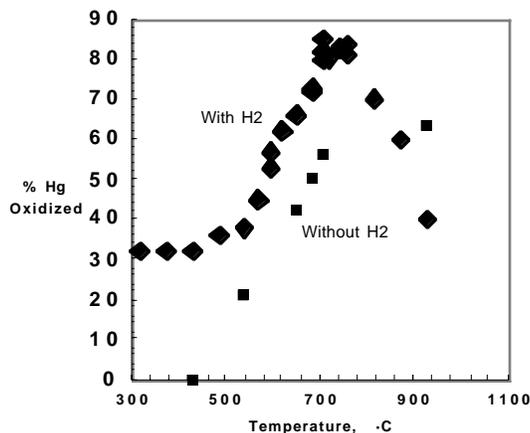


Figure 1. Influence of H₂ on mercury oxidation.

Future Work

We plan to finish filling in our experimental matrix and complete a full temperature evaluation of CO. We also will work briefly with gas mixtures containing SO₂ and/or NO as these have been noted by others has modifying Hg oxidation behavior. We will use a detailed chemical kinetic model, cast in plug flow form, to attempt a complete chemical interpretation of our data and to extrapolate our results to utility boiler time-temperature profiles.

2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS, AND STUDENTS RECEIVING SUPPORT FROM THE GRANT

Conference Presentations

- Study of the forced oxidation of mercury in post-combustion gases. L. Castiglone and J. Kramlich. Pacific Northwest Regional Environmental Symposium, 2004.

Students Supported Under this Grant

- Linda Castiglone, Ph.D. student in the Department of Mechanical Engineering, University of Washington