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DEVELOPMENT OF MERCURY CONTROL TECHNOLOGIES

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Project Description

This project is intended to develop and test promising sorbents and catalysts that have high reactivities to provide rapid in-duct mercury capture or oxidation when injected upstream of a particulate control device. In-duct capture sorbents would provide a useful method for both electrostatic precipitators (ESPs) and baghouses, while the ability to oxidize mercury would make scrubbers more effective in removing mercury. Several sorbents have been tested, with varying levels of success, with respect to mercury capture. Several flue gas components such as SO₂, NO₂, HCl, and fly ash have been shown to improve sorbent effectiveness. Understanding these interactions will lead to cost-effective mercury control options that could be applied to most coal-fired applications.

Goal

The overall goal is to develop cost-effective mercury control in an approach consistent with the research needs itemized in the U.S. Environmental Protection Agency *Mercury Study Report to Congress*.

Specific goals are to:

- Further develop protocols to test the required sorbent reactivity and capacity necessary for effective mercury capture.
- Test new sorbents (based on previous successes at the EERC and elsewhere) that are likely candidates for rapid in-duct sorption of mercury and can overcome the SO₂-NO₂-induced breakthrough problem.
- Further refine the understanding of flue gas concentrations on sorbent reactivity, capacity, and desorption.
- Investigate the effect of carbon basicity on the activated carbon (AC) sorption mechanism.
- Evaluate catalysts or additives that can be utilized with flue gas desulfurization (FGD) systems to consistently achieve 90% Hg capture.

Rationale

Mercury emissions from combustion systems have become recognized as a significant source of anthropogenic mercury. Several approaches are suggested for mercury control from coal-fired boilers, including enhancing the ability of wet scrubbers to capture mercury. However, many coal-fired boilers are

not equipped with wet scrubbers. Since almost all coal-fired boilers are equipped with either an ESP or a baghouse, sorbent injection upstream of either an ESP or a baghouse appears attractive, because it has the potential to control both elemental and oxidized mercury species, would appear to be easy to retrofit, and would be applicable to both industrial and utility boilers.

Since mercury in the gas stream from coal combustion is present in only trace quantities, usually in the range of 5 to 10 : g/m^3 (about 1 ppbv), only very small amounts of sorbent may be necessary. Assuming a mercury concentration of 10 : g/m^3 and a sorbent-to-mercury mass ratio of 1000:1, the required sorbent loading is 10 mg/m^3 , which is only 0.1% to 0.2% of a typical dust loading of 5–10 g/m^3 (2.2–4.4 grains/scf). At these levels, the amount of sorbent material in the ash would not be expected to have an impact on control device performance or ash disposal, but may have an impact on utilization. One example where ash utilization was negatively impacted by the use of small amounts of AC was seen during testing at the Pleasant Prairie Power Plant where the resulting ash failed foaming index tests preventing use in concrete manufacture [1]. Stability of the mercury captured in ashes with carbon-based sorbents has been demonstrated in recent tests where leachabilities and volatilities have generally been shown to be negligible [2, 3].

The rate of sorption depends on a number of factors including diffusion from the bulk gas to sorbent particles, diffusion within the particle, the rate of any heterogeneous reactions that may occur, and the ultimate capacity of the sorbent. Assuming the sorbent has the capacity and reactivity to trap the mercury that reaches the sorbent particles, the final critical step is the long-term stability of the sorbed mercury.

Previous bench-scale testing established that ACs, such as fine powdered Norit FGD AC, are effective for mercury capture in simulated flue gas mixtures containing all components found in coal combustion gases, but mercury breaks through most sorbents in about 1 hour, mainly due to a NO_2 – SO_2 –water interaction that limits the capacity and results in release of oxidized mercury species [4]. The current model for explaining the capture of Hg(II) formed in the initial oxidation step describes the sorption of the Hg(II) at a basic site on the carbon to form a nonvolatile salt [5, 6]. This occurs until the basic sites are exhausted (by reaction with SO_2 , sulfate, or HCl). At this time, the Hg(II), which continues to form, reacts with nitrate (from NO_2) or with HCl to form volatile salts such as the nitrate hydrate or chloride, and breakthrough appears. In addition, the release of oxidized mercury from the basic binding sites on the sorbent occurs, resulting from the conversion of these nonvolatile basic salts, in which the Hg(II) is initially captured, into volatile Hg(II) salts.

Approach

Fixed-bed tests were performed to determine the capacity of promising sorbents and to evaluate the conversion of elemental mercury (Hg^0) with time that reflect the effects of pretreatment and cohort gases.

Previous work has shown that very high sorbent reactivity and capacity can be achieved under some conditions (e.g., HCl present without SO_2 and NO_x). Therefore, there is evidence that a sorbent can be designed to provide effective mercury capture when injected into a duct upstream of an ESP. To further elucidate sorption mechanisms, the work included selected tests to better understand the relative effects of SO_2 , NO, NO_2 , HCl, CO, Cl_2 , and H_2O on sorbent performance.

Earlier work in this and other mercury control projects established that the oxidation of Hg^0 and the capture of the oxidized mercury operate independently, since mercury that is emitted from the sorbent after breakthrough is essentially completely oxidized. Thus the oxidation site on the carbon surface continues to work even after the capture site is inhibited or poisoned by the accumulation of acids such as sulfuric acid derived from the SO_2 in the flue gas. The capture site for the oxidized mercury, presumably Hg(II) species, must be a basic site in order to form a stable bond to the Hg(II). Understanding the nature of the capturing site focused first on determining whether the basic binding site for Hg(II) is on the carbon structure or on the inorganic material, which for a commercial sorbent like Norit FGD is about 35%. The inorganic material in this sorbent contains a large amount of CaO or possibly CaCO_3 when exposed to air. A series of experiments

was performed to sequentially remove the mineral content, through ion exchange, acid washing and, finally, decomposition of remaining silicates with HF [6]. None of these treatments produced a carbon sorbent with a significantly different capacity for mercury. Therefore, it is likely that the basic binding site for the Hg(II) is actually on the carbon surface, most likely an edge structure. The presence of CaO in the FGD sorbent and Na₂O in a North Dakota lignite-derived carbon likely binds some of the SO₂ and H₂SO₄, but there is always ample guarantees of acid gases to react at the basic site to cause the breakthrough phenomenon.

To improve the capacity for capture of the Hg(II) on the sorbent, the attachment of additional bases to the sorbent was investigated. The hypothesis was that these could react either directly with Hg(II) to effect capture or with the acid gases to lower their concentration and thereby attenuate the poisoning effect at the basic carbon binding site. In the 2001 CATM annual report, a series of sorbents were described that consisted of soft-base complexing agents impregnated on a reactive carbon support. The sulfur- and phosphorus-containing ligands offer the potential to increase sorbent capacity owing to their high affinity for mercury(II) ions formed at the oxidation sites on the carbon surface. However, the bench-scale thin-bed test results showed that breakthrough times were not longer with these impregnated sorbents. Thus either the reagents were not effective in capturing Hg(II), owing to their not residing in a proximate site to the oxidation site, or they were being destroyed by the flue gas components.

Further research in 2002 investigated this issue further with experiments using sorbents impregnated with hard bases intended to capture mainly SO₂ and H₂SO₄, so that their lower concentrations would result in longer breakthrough times. The sorbents tested included carbon sorbents with highly dispersed MgO and NaOH on the surface.

As an alternative to altering the capacity via addition of reagents to the carbon surface, the intrinsic basicity of carbon sorbents has been increased in work reported in the literature. This alteration of the carbon structure was effected by activation in a hydrogen atmosphere [7]. Sorbents were prepared and tested with this structural alteration.

Efforts to determine the nature of the mercury binding in loaded or spent sorbents by x-ray photoelectron spectroscopy (XPS) were thwarted in past work by the silicon interference from the mineral content of the carbons. To avoid this interference, aerogel carbons that contain no silicates were loaded with mercury under flue gas conditions and submitted for XPS analysis.

Progress

Sorbent Development

Inorganic base-augmented sorbents were prepared by a proprietary method. Thin-bed test results with the sorbent impregnated with NaOH showed breakthrough times in full flue gas composition that were somewhat shorter than that of the unimpregnated FGD carbon in similar flue gas concentrations. The MgO-impregnated carbon was an exceptionally poor sorbent, showing immediate breakthrough and very low capacity (Figure 1). The negative effect in adding the inorganic base must be explained by either pore plugging or deactivation of the oxidation site. In other sorbent studies where MgO was added in this manner, the capacity was not reduced, and pores were, therefore, not blocked. It remains to explain how the bases are able to cause the decrease in capacity.

In contrast to these base effects, an increased concentration of HCl in the flue gas (50 ppm) usually results in a substantially higher mercury capture, especially at the start of the experiment where an induction period for activity is seen when HCl concentration is low (1 ppm). The added bases in these augmented sorbents may be simply reacting with the HCl in the gas and eliminating the promotion effect of the HCl at the oxidation site. This is an important insight into determining the role of HCl in the flue gas as well as sodium in the sorbents, such as those obtained from Fort Union lignites.

Test results from the hydrogen-activated carbons showed inferior capacities. In augmenting the intrinsic basic character of the carbon by hydrogen activation, the effect may have been to also make the carbon less oxidizing to the Hg^0 , as happened when extrinsic bases were added.

A dual functionality model for mercury–flue gas interactions with carbon sorbents has been constructed (Figure 2) [8]. This model shows the independent oxidation and capture chemistries that are consistent with hypothesis that SO_2 poisons the binding site for $Hg(II)$ capture on the sorbent surface, as well as the fact that mercury that is emitted from the sorbent after breakthrough is entirely an oxidized mercury species, as described in previous annual reports [9, 10]. Furthermore, in reactions conducted with NO_2 and SO_2 and no HCl , this emitted volatile oxidized mercury product was actually trapped and identified as mercuric nitrate [11, 12]. The model is also consistent with the flue gas interaction chemistry identified in other projects [13].

Entrained-Flow Reactor

In the previous year, an entrained-flow reactor was fabricated to evaluate sorbents for in-flight mercury capture and to study mercury transformations as a function of residence time and temperature. Figure 3 provides a schematic of the original concept for the reactor. The reactor was fabricated from stainless steel and is 5 feet in height, including the concentric reducer at the outlet. Ten ports allow sampling at multiple residence times up to 10 seconds for a given gas flow rate. During the past year, the design was modified to include a single-wire ESP (Figure 4). The ESP allows rapid separation of the entrained material from the gas stream, while minimizing gas–sorbent contact. The goal of this testing approach is to provide a way to test sorbent reactivity and effectiveness by controlling the in-duct contact time, while minimizing sampling effects. One of the advantages of this system is that it is portable enough to be used either in the laboratory with simulated flue gas or sampling real flue gas slipstreams from pilot- or full-scale combustion systems.

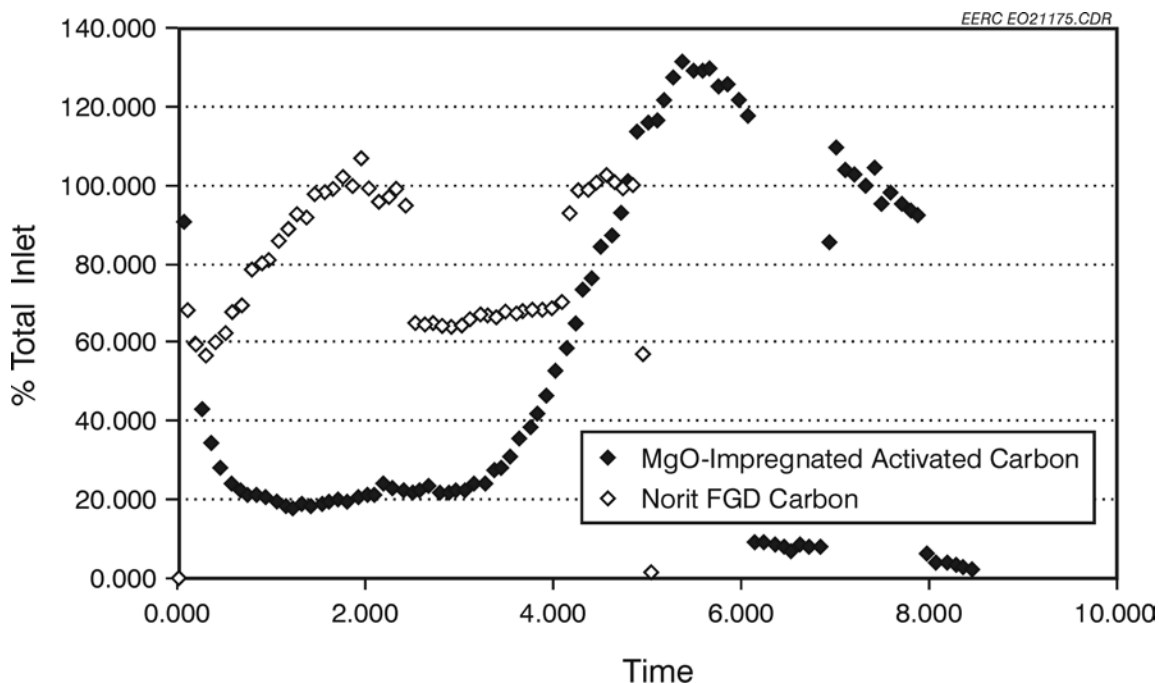


Figure 1. Comparison of Breakthrough Curves for FGD vs. MgO-Impregnated Carbon

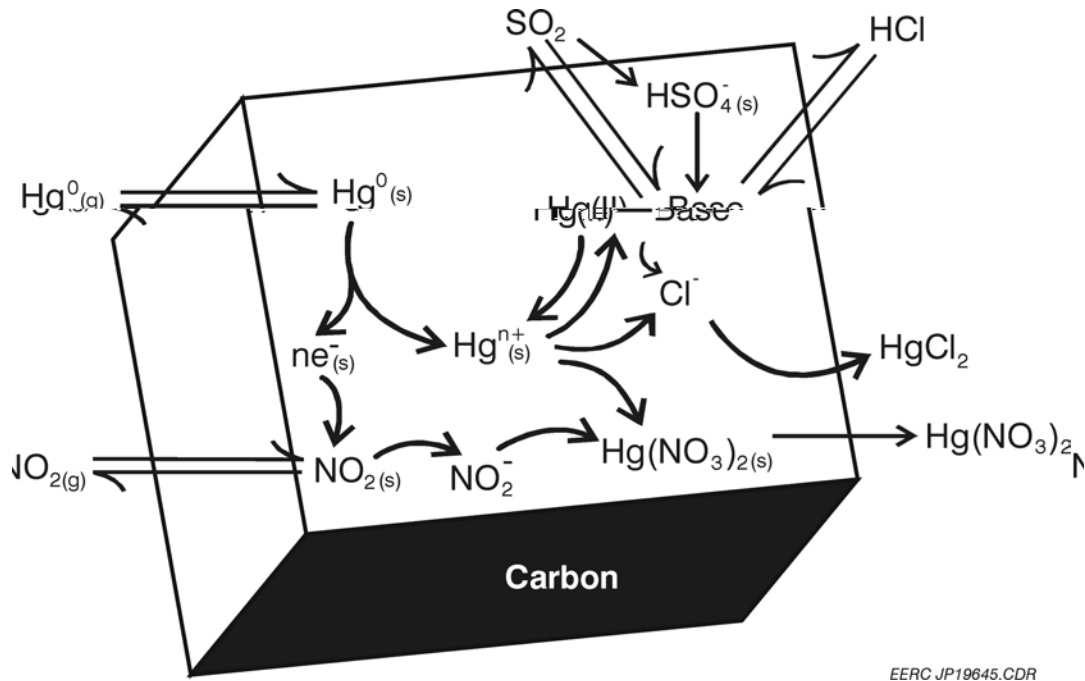


Figure 2. Mechanism for Mercury Capture on FGD Sorbent

Shakedown tests were completed with the entrained-flow reactor to evaluate the effect of residence time on the level of mercury oxidation when coal is burned in the EERC pilot-scale combustion test facility (Figure 5). Results in Figure 6 show that both lower temperature and longer residence time lead to a higher fraction of oxidized mercury. These effects are in addition to the known influence of gaseous flue gas components on mercury speciation.

Preliminary entrained-flow reactor tests were also completed sampling real flue gas from another EERC facility, the particulate test combustor. Results shown in Figure 7 demonstrate the effect of residence time and carbon injection rate on in-flight capture of mercury when AC is injected into the flue gas stream.

Fixed Thin-Bed Test Protocol

The EERC fixed thin-bed reactor has been used for many years as an approach to evaluate the effects of temperature and flue gas components on the capacity for a variety of sorbents to capture mercury. The approach has proven to be highly repeatable with simulated flue gases and has demonstrated the significant impact that acid gases have on the mercury capture ability of various sorbents. However, very little testing of this system with real flue gas had previously been completed. This past year, with support from a U.S. Department of Energy (EPA)-funded project, direct comparison tests were completed sampling real flue gas and simulated flue gas tests where the flue gas concentrations were matched to the measured gas levels from the coal combustion tests. Results presented in Figure 8 show that the simulated flue gas results are within the range of three repeat tests sampling real flue gas produced during firing of a subbituminous coal. These results provide confidence that the fixed thin-bed test protocol is a valid approach to screen and compare sorbents.

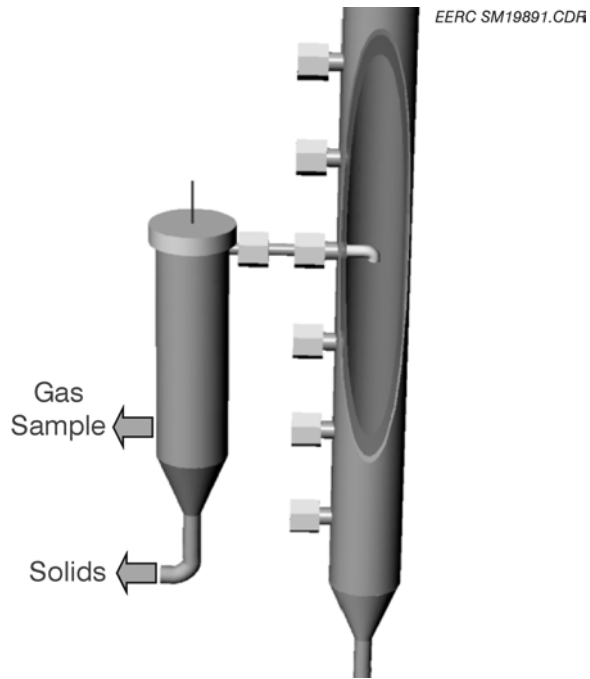


Figure 3. Entrained-Flow Reactor Concept

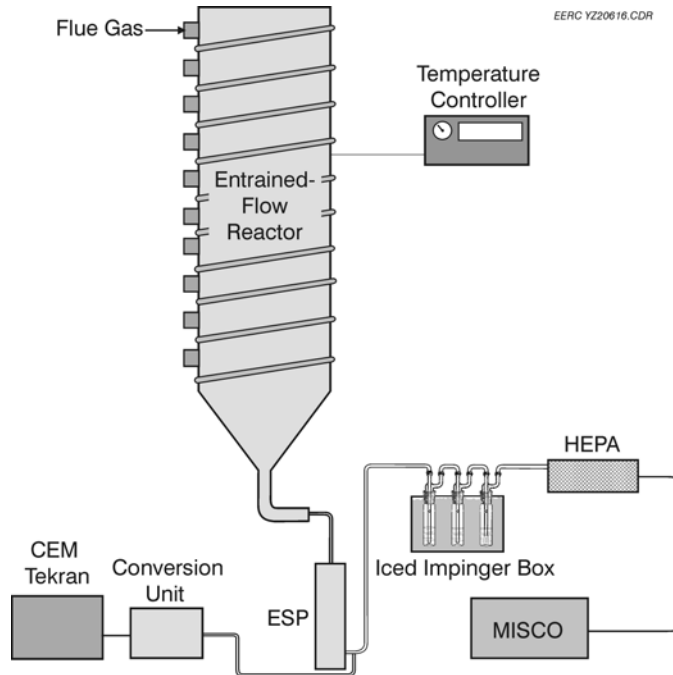


Figure 4. Modified Entrained-Flow Reactor



Figure 5. Entrained-Flow Reactor Sampling Real Flue Gas on the EERC Combustion Test Facility

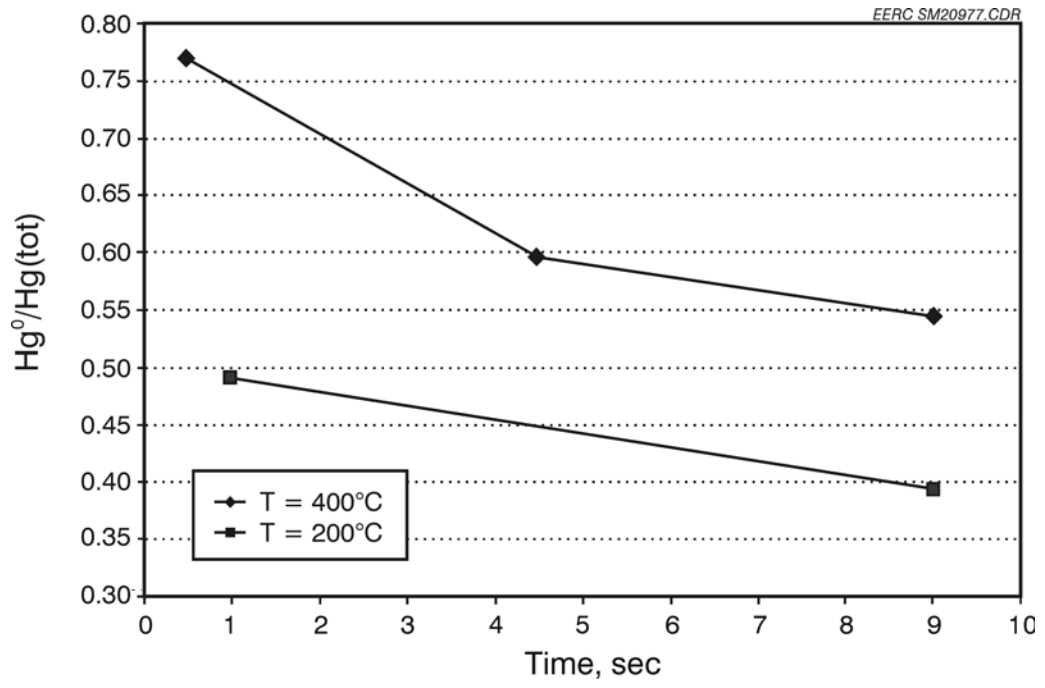


Figure 6. Normalized Mercury Species Distribution under Two Temperatures (Colbert coal)

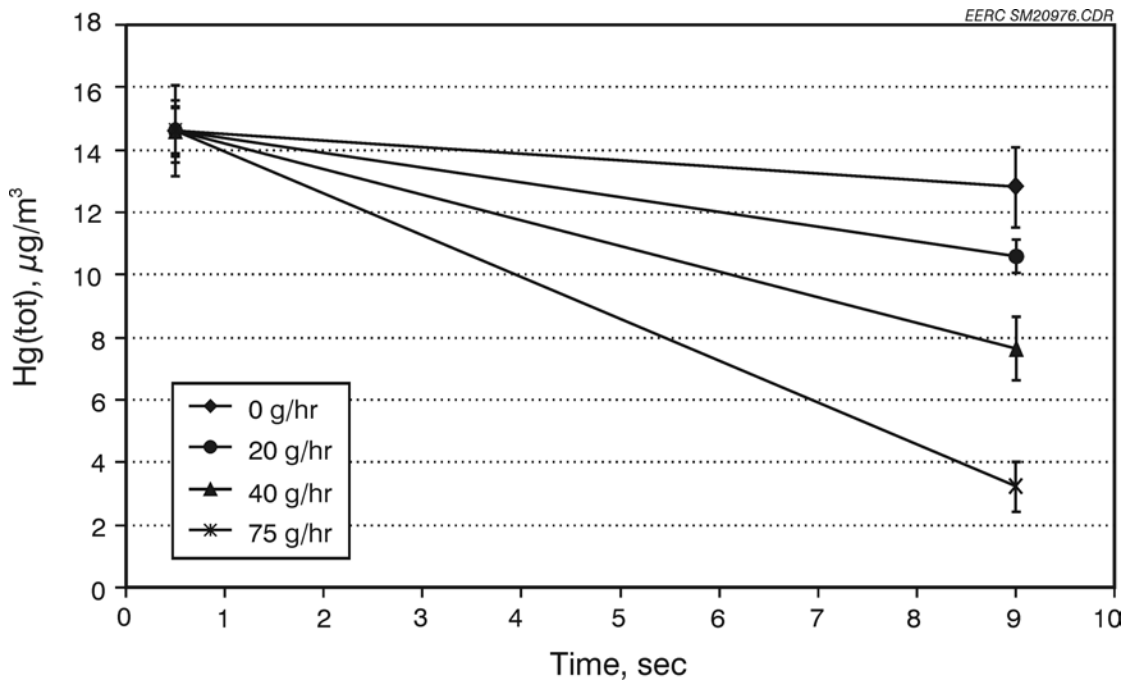


Figure 7. Total Mercury Vapor at Different Sorbent Injection Rates

Status

Research is currently focused on understanding the mercury species bound on the surface of the carbon by using XPS to determine the C–Hg or other bonding mechanism. Flue gas–mercury interactions on sorbents other than carbon are also being examined. Additional improvements in the proposed model for the oxidation and bonding mechanisms on the carbon sorbents are in progress as further details of the participation of carbon edge structures in the reactions are revealed.

Both the thin fixed-bed and the entrained-flow test systems will be used to screen and compare sorbents. As opportunity permits with combustion tests funded by other projects, testing with both systems sampling real flue gas will also be completed with the most promising sorbents.

Potential Users/Technology Transfer

The work is focused on potential applications in the utility industry. Information generated will assist EPA in determining appropriate regulations and assist utilities in developing mercury control strategies. Additionally, the successful identification of an inexpensive reactive sorbent for Hg control would be of potential benefit to other industries requiring a mercury control technology.

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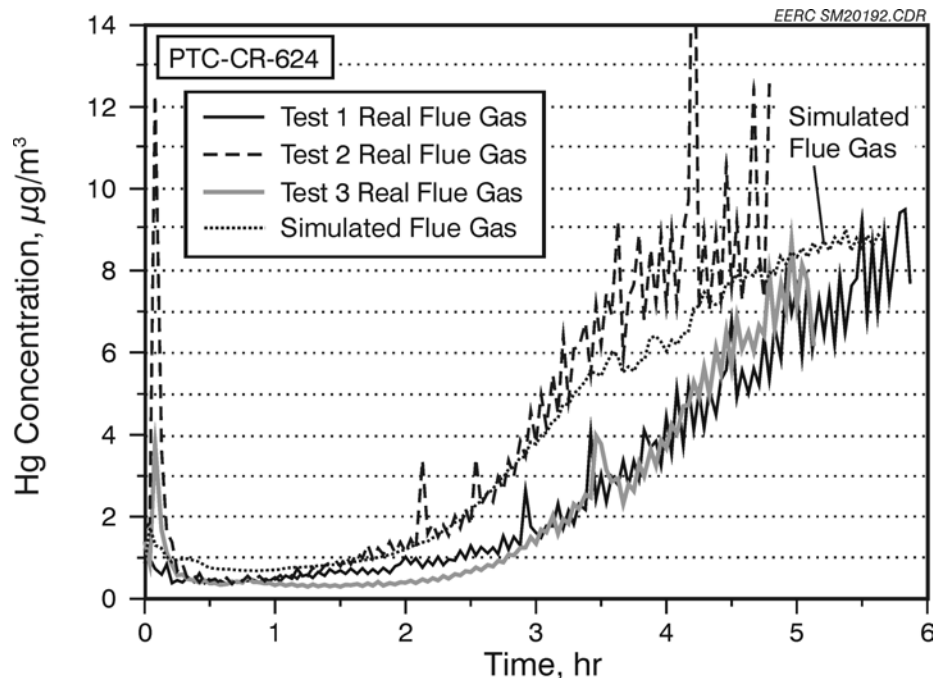


Figure 8. Bench-Scale Breakthrough Tests, Comparison of Results Using Simulated Gas with Results Using Real Flue Gas

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