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DEVELOPMENT OF MERCURY CONTROL TECHNOLOGIES

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Project Description

This project is intended to develop and test promising mercury control technologies such as sorbents that will provide rapid in-duct capture of mercury, additives that will oxidize elemental mercury (Hg^0) so it can be captured with solid sorbents or in a wet scrubber, further technology for regeneration and reuse of mercury sorbents, and the effect of rapidly quenching halogenated gas on mercury reactivity. A further goal is to determine the effects of flue gas constituents on mercury capture and oxidation by sorbents. This information has been used to develop and refine a model to explain the mechanisms for mercury capture, oxidation, and rerelease by sorbents in a flue gas.

Goal

The goal of the project is to develop improved mercury control technologies for both bituminous and lower-rank coals and to reduce the associated costs.

Specific Goals

Objectives for Task 1 are to:

- Continue to provide the infrastructure to support screening of sorbents developed by the EERC and other organizations.
- Quantify the effect of SO_3 on the ability of sorbents to capture both elemental and oxidized mercury
- Achieve 90% Hg control with sorbents for all applications including those with high Hg^0 and Hg^{2+} .

The objective for Task 2 is to:

- Provide a week of pilot-scale test operation for proof-of-concept testing on various measurement, oxidation, and control techniques developed under CATM and externally. This task provides for synergy between other pilot-scale evaluations by facilitating testing that would not be possible under the budgets for individual activities.

The overall objective for Task 3 is to achieve a greater understanding of the interactions between mercury and flue gas components on the activated carbon surface which is crucial to designing carbons with faster kinetics and greater capacities for mercury sorption in utility flue gas streams. The specific areas that are currently being explored include:

- Evaluation and optimization of mercury capture on a new generation of treated sorbents for gas-phase elemental mercury. The research is an extension of prior CATM research that provided exceptionally effective halogenated sorbents obtained by impregnating either HX (a reduced form of halogen [X]) or bimolecular halogen (X₂) reagents (highly oxidizing forms).
- Construct and investigate reactions of molecular structures representing the intermediate carbon species in the proposed model for mercury–flue gas interactions on the carbon surface. Further development of the mercury–flue gas carbon theory and establishing its validity will be pursued on a quantitative basis using the more complex structure/mechanism model we have recently developed by determining the stability and reactions of the carbene, benzyne, carbenium ions, and organomercury intermediates that represent those in the proposed model.
- Complete the development of a comprehensive reaction model for the interactions of flue gases and mercury on carbon sorbents. Results will provide important input to predictive models for quantifying mercury speciation transformations and capture being developed in other CATM-related projects.

Objectives for Task 4 are to:

- Further develop the sorbent regeneration process so it can be ready for demonstration and commercial deployment. The focus will be to show that the technology will reduce the cost and enhance the performance of sorbents typically used for mercury control.
- Demonstrate that a sorbent can be removed from ash using simple techniques, making multiple regeneration cycles possible by minimizing dilution.
- Address scale-up issues that will allow the system to be tested at larger scale.
- Refine the process design to coincide with the data received to date from testing at the bench- and pilot-scale levels.
- Prove that the regeneration process will reduce the cost of using sorbents for mercury removal.

The objective for Task 5 is to:

- Demonstrate that halogen species in the flue gas of a boiler can increase mercury oxidation and/or capture.
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Rationale

Task 1

The fixed-bed mercury sorbent tests continue to be the best experimental approach for screening EERC-developed and outside sorbents. In addition to our CATM research, this last year we had confidential projects with Praxair and another company to screen their sorbents. It is also the approach that has led to major discoveries concerning the effects of flue gas components on sorbent performance. For example, tests as part of a full-factorial design looking at the effects of NO, NO₂, SO₂, and HCl on the capture of HgCl₂ showed that under some conditions in the presence of SO₂, the HgCl₂ is reduced back to elemental mercury. This finding should lead to a better understanding of how SO₂ affects the capture of both elemental and oxidized mercury.

During a PTC run using a Springfield bituminous coal, NORIT carbon was injected upstream of the *Advanced Hybrid*TM filter to capture mercury in the flue gas. Results indicated that the NORIT carbon did not capture any mercury when injected continuously. When the carbon was injected in a batch mode, there was some capture, but only for a short period of time. Other types of sorbents were also used during this run with similar results. Bench-scale tests using a simulated Springfield flue gas showed good capture similar to baseline tests with the NORIT carbon. The one component missing from the simulated flue gas was SO₃. It is suspected the high SO₃ concentration in the flue gas (estimated 30–40 ppm) was responsible for the poor mercury capture during the PTC run. The carbon/mercury model developed under CATM predicts that SO₂ and NO₂ interact on the carbon surface to form SO₃, which then binds strongly to the basic sites on the carbon and also displaces the captured mercury. In the presence of high SO₃, this reaction would not be necessary, and the SO₃ would quickly consume the basic sites and displace any captured mercury. Based on these experiences, it is clear there is a need for research to determine the effects of SO₃ on mercury sorption with carbon.

Task 2

Testing on real flue gas from a pilot-scale combustor will accelerate and facilitate development of new mercury measurement, oxidation, and control technologies and will generate data in support of model development. Rather than supporting a stand-alone hypothesis, Task 2 enables testing hypotheses from the other projects and Project 3 tasks.

Task 3

Injection of fine-powdered activated carbon into the hot flue gas stream of a utility power plant has been successful in removing a large portion of the mercury in the flue gas, even when the mercury is mainly elemental. But the amounts of carbon injected are still relatively large and, therefore, costly. High heterogeneous reaction rates of the gas-phase elemental mercury on the carbon sorbent surface may be needed to capture the mercury in the short contact time demanded when the sorbent is quickly removed from the gas stream, such as with electrostatic precipitation of ash and carbon particulates. Understanding the details of interactions between mercury and flue gas components on the activated carbon surface is crucial to design of carbons with faster kinetics and greater capacities.

Pioneering studies were conducted at the EERC that provided needed information on the flue gas mercury interactions. These studies included a large factorial series of tests using powdered activated carbons that were conducted using the EERC bench-scale system. Various simulated flue gas compositions consisting of acidic SO₂, NO₂, and HCl gases plus a base mixture of N₂, O₂, NO, CO₂, and H₂O (1, 2) were used. As a result of these experiments and two series of tests where carbon samples were

exposed to various flue gas compositions and analyzed by x-ray photoelectron spectroscopy (3, 4), a number of facts emerged that were important to understanding the activating and poisoning effects exhibited by flue gas. Conclusions based on these facts are summarized as follows (5):

1. The sorption of Hg^0 in flue gas is entirely chemisorption to form Hg(II) .
2. Hg(II) competes for the basic binding sites on the carbon with other acids in flue gas and the sulfuric acid formed from SO_2 oxidation on the carbon.
3. The main poisoning effect on the carbon basic sites results from accumulation of sulfur(VI).
4. NO_2 in the flue gas is the major oxidant for both Hg^0 and SO_2 on the catalytic carbon surface.
5. H_2O is also required for sulfur(VI) accumulation.
6. Most of the Hg emitted after breakthrough is (oxidized) Hg(II) .
7. Previously bound Hg(II) is emitted after breakthrough.

Based on these capacity data, an initial model was presented (5) that described the chemisorption of Hg^0 in flue gas. Conclusion 6 is very important for at least two reasons. Although the binding sites cannot effectively bind Hg(II) at breakthrough, the oxidation reaction is unaffected, since nearly 100% oxidation occurs even after complete breakthrough. This fact argues against any explanation for loss of capacity based on pore plugging by species resulting from acid gases, since this would inhibit both reactions. This fact also shows that the binding and oxidation steps can be decoupled. The Hg(II) species that forms or is released after breakthrough is volatilized as HgCl_2 or $\text{Hg(NO}_3)_2$ (6).

A refinement of the binding site model was proposed (7) that offers more detail on the nature of the carbon site and its interaction with flue gases and Hg (Figure 1). This model uses the concept of zigzag carbene structures recently proposed for states at the edges of the carbon graphene layers (8) rather than oxygen functional groups suggested by other authors. In the carbene model, the zigzag carbon atom positioned between aromatic rings is hypothesized to be the Lewis base site. The zigzag Lewis basic carbene reacts with the Hg(II) species, as shown in Figure 1, to form an organomercury carbenium ion and also with HCl , H_2SO_4 , and SO_2 to form carbenium ions with associated chloride and sulfate that can combine to form the observed organochlorine and, possibly, also ester moieties. In tests conducted at relatively high HCl concentrations (50 ppm), the capture of mercury at the start was always very high (greater than 90%), but in very low HCl concentrations such as those obtained when low-Cl coals are burned (1 ppm), initial mercury capture was only about 40%–50% (9), followed by an increase in capture efficiency to the 90%–95% level. The higher HCl concentration thus eliminated this induction period where poor capture is obtained. It is clear that HCl is not an oxidizing reagent, since it is already in the most reduced state. This is, therefore, a promotional effect of the HCl on the activity of the carbon in catalyzing the oxidation of mercury. A similar promotional effect of adding aqueous HCl to the sorbent was reported recently by Ghorishi et al. (10). As shown in Figure 1, the Hg^0 is oxidized at the carbenium site. Thus oxidation and binding occur at different forms of the same carbon site (11). A primary oxidant (for example NO_2) completes the cycle so that Hg(II) can be released from the site after breakthrough.

Task 4

Injection of activated carbon upstream of a particulate control device is proving to be a viable method to remove mercury from a flue gas stream generated by a utility boiler. The amount of carbon required by an individual plant can be significant. One way to reduce the amount of carbon is to capture it either with the fly ash or separate from it, and then regenerate the carbon for reuse. Therefore, sorbent requirements can be significantly reduced by the use of an economical regeneration process. In applications where the carbon is captured with the fly ash, separation technology is needed to provide a carbon-rich feed for regeneration and to purify the ash stream to maintain attractiveness for coal combustion by-product applications.

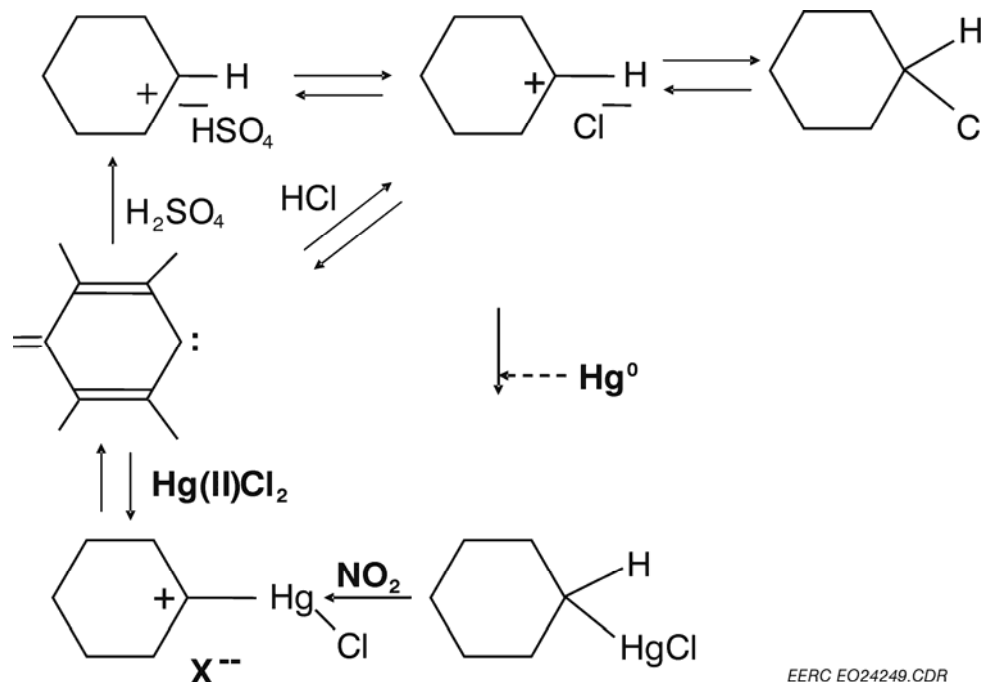


Figure 1. Oxidation mechanism – carbenium ion oxidant.

Task 5

Flue gas constituents that enhance mercury oxidation and adsorption, such as atomic halogen species, need to be tested further to increase understanding of the chemistry and variation in performance with coal properties.

Approach

Task 1

The bench-scale mercury sorbent tests allow the continuation of development, screening, and evaluation of sorbents from both the EERC and external sources. These tests focus on sorbent capacity and applicability. Sorbent versatility has been evaluated in past measurements with the bench-scale system by varying the concentrations of several flue gas species. Interactions with SO_2 , NO_2 , and water vapor have previously been identified and quantified as well as interactions with HCl . The baseline flue gas mixture was utilized during these bench-scale screening tests and results were compared with those from a baseline activated carbon (NORIT FGD).

Fixed-bed tests will be performed using the EERC bench-scale system to obtain breakthrough curves for specified test conditions to evaluate the effects of SO_3 in the simulated flue gas matrix. In addition to SO_3 concentration, the temperature and concentration of the other gases will be varied.

Task 2

The particulate test combustor (PTC) will be operated for 1 week to provide a test platform for evaluation of various technologies from CATM-related projects such as from measurement, transformation, and control. Many of these projects will benefit from the opportunity to test with a larger system that is proven to produce “real” flue gas. Specific measurement and test activities related to each technology or measurement technique will be the responsibility of individual projects.

Task 2 includes all of the standard facility preparation, general test planning and scheduling, operation, data collection, and shutdown procedures. The testing is limited to 1 week because of budget constraints; therefore, communication with the researchers involved in the various CATM activities will be critical to coordinating the efforts and maximizing the value of these tests.

Task 3

A series of experiments was conducted to determine the effects of acid gas components on the kinetics of oxidation of Hg^0 . These experiments use the effect described above whereby the oxidation of Hg continues long after the capacity of the carbon has been exceeded. Thus the oxidation is uncoupled from binding and can be studied independently of binding by measuring the concentration of Hg^0 in the effluent from the carbon bed where the influent gas composition and temperature are varied.

The experimental procedure used a thin bed of the sorbent placed in a synthetic mixture of flue gas compositions, exactly as described previously (1, 2). Total and elemental mercury were continuously measured at the outlet of the fixed-bed reactor. The initial breakthrough as well as the oxidation experiments were conducted with high acid gas conditions, except when components (HCl, SO_2 , and NO_2) were turned off sequentially to determine effects on the oxidation. In Set A (single gas omitted), all the gases were turned off after breakthrough, and the spent carbon was stored overnight. All gases were turned on the next day to initiate the set of experiments. In Set B (one, two, and three gases omitted), the set of experiments was initiated immediately after breakthrough. Results revealed findings that are proving to be valuable in defining the fundamentals of mercury and sorbent chemistry.

Task 4

This task comprises two small efforts directed toward moving mercury sorbent regeneration technology closer to commercial viability. The first effort includes evaluation of the impact of various process parameters on the success of sorbent regeneration. The parameters selected will be among those that could impact the system design in order to improve commercial viability and economics. Regenerated sorbents will be tested in the thin-film fixed-bed bench-scale system to measure the success of the regeneration. The second effort is directed at evaluation of techniques for potential in separation of carbon sorbents from fly ash. The objective is to increase the applicability of carbon regeneration by identifying techniques to enrich carbon for regeneration and reuse. This step is needed for systems that capture all of the fly ash and sorbent in the same particulate control device. An added benefit for some plants could also be continued sale of fly ash for applications such as use in concrete which can be sensitive to even small amounts of activated carbon. A variety of in-house laboratory- and small pilot-scale systems were evaluated as methods to separate carbon (i.e., principally sorbent carbon) from fly ash samples with elevated LOI values. The methods evaluated were variations on techniques previously tested for the separation of mineral-containing fractions from coal. Techniques include float-sink testing, selective agglomeration, froth flotation, and Denver-cell flotation.

Task 5

This task was broken down into two subtasks: design and fabrication of a halogen delivery system and preliminary testing on the PTC. Task 5 will heavily rely on the opportunity created by Task 2 to allow testing at the pilot scale. Halogen gases will be introduced without sorbent to evaluate mercury oxidation and with carbon sorbents to determine the enhancement in sorbent-based mercury removal.

Progress

Bench-Scale Mercury Control Sorbent Development

Task 1

Sorbent Preparation and Bench-Scale Sorbent Screening. Tests were performed to evaluate two sorbent materials provided by an outside company that had shown good mercury capture in other applications. The fixed-bed tests showed results typical of activated carbons in terms of reactivity, capacity, and oxidation of elemental mercury.

SO₃ Tests. The tests to evaluate the effects of SO₃ on mercury capture by activated carbons have been scheduled for the beginning of 2005. The SO₃ generator is first being used to evaluate the effects of SCR on mercury speciation.

Task 2

A 1-week pilot-scale test has been completed at the EERC, and the goal was to provide real coal combustion flue gas for mercury-related research activities. Two coals, subbituminous Belle Ayr coal and Texas lignite, were selected and combusted in a 580-MJ/hr pulverized coal (pc)-fired unit, known as the PTC to generate flue gases. The generated flue gas was treated in an ESP followed by a fabric filter. Temperature across the ESP and fabric filters was maintained at approximately 300°F. The ESP was operated at 3–4-mA corona current to provide an over 98% fly ash removal, while the downstream fabric filters were operated at a 6-ft/min filtration velocity with an overall 99.9% particle collection efficiency across the entire system. Five different projects benefited from the 1-week pilot-scale:

1. An EERC-developed large-size sorbent has been tested in Belle Ayr flue gas under TOXECON™ (ESP/activated carbon injection/fabric filter) configuration for mercury removal. The ash-sorbent mixture was collected for next-step recycle and regeneration processes.
 2. Three EERC-treated activated carbons have been tested in Belle Ayr and/or Texas lignite flue gases to evaluate their effectiveness on mercury removal under ESP or TOXECON configurations.
 3. A series of slipstream entrained-flow reactor (EFR) tests have been completed to continue our understanding on mercury kinetics in Belle Ayr and Texas lignite flue gases. Also, furnace additives of CaCl₂ and SEA2 were used during the test to evaluate their impacts on mercury transformation in flue gas.
 4. Two treated activated carbon-based sorbents provided by SaskPower have been tested in Texas lignite flue gas in an ESP configuration to evaluate their mercury removals.
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5. Preliminary study has been performed to understand the integrated impact of quenched halogen species and activated carbon on mercury oxidation and removal in coal flue gases.

Task 3

A new test protocol was developed to evaluate the Hg capture capacity of highly active sorbents. The method used a thin bed consisting of 150 mg of a sand-carbon mixture that contained 37 mg of carbon (compared to 150 mg in the old test procedure). The flow velocity was also reduced from 30 to 15 scfh. Using this protocol, breakthrough occurs very fast (3 min) for the baseline unmodified FGD carbon, but can be extended for up to an hour for a treated activated carbon. Using this protocol, a series of halogen-treated sorbents were evaluated. The test matrix variables included using five different halogen forms, two treatment methods, and three concentrations of reagent. A bituminous carbon, baseline NORIT FGD, carbon black, and a calcium-impregnated lignite-derived carbon were all treated with one of the reagents. The results showed a decrease in reactivity of the carbons in the order listed with the bituminous the most reactive and the calcium-impregnated the least.

Two sets of tests were completed using the EERC bench-scale system to investigate the interactions between mercury and flue gas components on the activated carbon surface which affect oxidation. The first set of tests were completed using the same carbon sample, and the second set used a fresh carbon sample. The following is a description of each test and the results. All tests were run after the complete breakthrough had been achieved. Every time a gas component was turned off, the nitrogen flow was increased to maintain the same total flow rate and mercury concentration through the fixed-bed reactor.

Set A (single gas omitted)

Experiment 1. All of the flue gas components remained on. There was no increase of Hg^0 with time, indicating that SO_2 was not poisoning the oxidation sites. All Hg was emitted as oxidized mercury, consistent with earlier observations.

Experiment 2. The HCl was turned off. The Hg^0 concentration increased slightly (to 2% of inlet), indicating that the HCl is not a requirement for oxidation and has only a small promotion effect on the oxidation rate when all the sites are already acid-promoted. The total Hg concentration decreased significantly over a 45-minute period to 55% of the inlet concentration. This indicates that there is less conversion of bound Hg(II) to volatile products when HCl is absent.

Experiment 2A. The HCl was turned back on (original condition). The Hg^0 concentration decreased to 1% of the inlet concentration. Since it did not return to 0%, it suggests that the oxidation became slightly poisoned. The total Hg mercury concentration jumped up to 150% of the inlet concentration before leveling at 100%. This indicates that HCl is available for conversion to volatile products, giving an initial spike of HgCl_2 from Hg(II) that had been accumulating.

Experiment 3. The NO_2 was turned off. The Hg^0 concentration increased significantly up to 10% and leveled out. This indicates that oxidation of Hg is less effective without NO_2 , but still occurs. The total Hg concentration spiked and then lined out at 90% of the inlet concentration. An explanation is that less H_2SO_4 formed, so more HCl binds and frees Hg(II) as HgCl_2 . Then the loss of H_2SO_4 by evaporation results in the capacity being not entirely filled.

Experiment 3A. Turned the NO₂ back on (original condition). The Hg⁰ concentration dropped back down to 2%, indicating effective oxidation returned. The total Hg concentration lined out at about 100% of the inlet concentration.

Experiment 4. The SO₂ was turned off. The Hg⁰ concentration increased very slightly from 2.0% to 2.4% of the inlet concentration over a 2.3-hour time period. This indicates that SO₂ has little effect on oxidation of Hg⁰. The total Hg concentration increased significantly, then lined out at 90%, for the same reason as explained in Experiment 3 above.

A fresh carbon sample was loaded into a fixed-bed reactor and exposed to elemental mercury in a simulated flue gas until complete breakthrough was achieved. At that point, the following experiments were begun.

Set B (one, two, and three gases omitted)

Experiment 1. All flue gas components were on. The Hg⁰ concentration increased from 0% to 5% over a 2-hour time period, then leveled out at 5% of the inlet concentration.

Experiment 2. The NO₂ was turned off. The Hg⁰ concentration increased from 5% to 12.5% where it lined out, consistent with the NO₂ oxidation effect (Set A).

Experiment 3. The HCl and NO₂ were both turned off. The Hg⁰ concentration increased from 12.5% to 14.5% and lined out. The effect of turning off these gases is exactly additive. The total Hg concentration decreased to 50%, consistent with the decrease in mercury emission observed in Set A when the HCl was turned off.

Experiment 4. The HCl, NO₂, and SO₂ were all turned off. The Hg⁰ concentration decreased to 11%, indicating the SO₂ had a small negative effect on oxidation, but only when the HCl was off. The total Hg concentration decreased further to 30%, indicating additional restoration of binding sites.

Experiment 5. The HCl was turned on while the NO₂ and SO₂ remained off. The Hg⁰ concentration stayed at 11%, consistent with the small HCl oxidation effect when carbon is acid-promoted. The total Hg concentration increased to 80%, consistent with HCl liberation of bound Hg(II).

Experiment 6. The NO₂ was turned on, the HCl remained on, and the SO₂ remained off. The Hg⁰ concentration dropped to 5%, which is consistent with the positive NO₂ effect on oxidation and negligible SO₂ effect on oxidation observed during the Set A experiments.

Experiment 7. The NO₂ remained on, the HCl was turned off, and the SO₂ remained off. The Hg⁰ concentration increased slightly to 5.5%, consistent with small rate increase for HCl. The total Hg concentration decreased to 70%, consistent with the HCl effect on volatilization of bound Hg(II).

Further experiments demonstrated that the oxidation rates were faster at higher temperatures, in contrast to the negative effects of temperature on capacity. The negative effect on capacity is, however, due to the increase in sulfur oxidation at higher temperature, which poisons the carbon more quickly. Further experiments with other gas components showed that oxygen and NO are also able to oxidize Hg⁰ on the carbon surface, but require much higher concentrations.

By decoupling the oxidation of Hg⁰ from the binding of Hg(II) by using beds of spent sorbent that emit mostly Hg(II), the effects of acid gases were demonstrated on the oxidation rate and are in agreement

with the oxidation-binding model. That oxidation was not responsive to changes in SO₂ showed that SO₂ exerts very little poisoning effect on oxidation. NO₂ at 6 ppm is highly beneficial for the oxidation kinetics and, therefore, plays a major role in oxidation. HCl exhibits a much smaller effect. These experiments allow us to calculate space velocities for mercury oxidation.

Task 4

Task 4 focuses on testing the impacts of different process variations on performance of the carbon regeneration process and on evaluation of several techniques to separate activated carbon from ash. Most of the effort to date has focused on the carbon–ash separation. The goal of these tests is to determine if the applicability of sorbent regeneration technologies can be expanded by segregating the carbon from the bulk ash stream in applications that employ a single particulate control device. Currently, regeneration is most applicable to systems such as TOXECON where mercury is removed by carbon injected downstream of an ESP and then captured in a fabric filter, or for any other applications where most of the ash is captured separately from the carbon.

Brief investigations have been performed on several separation techniques. The methods evaluated were variations on techniques previously tested for the separation of mineral containing fractions from coal. Techniques include float–sink testing, selective agglomeration, froth flotation, and Denver-cell flotation. Results show varied degrees of potential. A few brief float–sink tests were conducted and were generally not very promising. Additional specific gravity solutions are available commercially and would need to be tested to fully evaluate this technique. Selective agglomeration is a process that utilizes a surface-compatible liquid that preferentially wets the carbon surface over the mineral (in this case, fly ash) surface. Results of testing with both xylene and toluene as solvents indicated significant potential for separation of the activated carbon and ash. Two froth flotation tests showed some potential as well. The carbon fraction was well concentrated, but the recovery rates were down at 15% to 20%. Results from three Denver-cell flotation tests show more promise, but optimization of carbon recovery and product purity is needed. In summary, several of the technologies show potential, and more thorough evaluations are required to evaluate economics and other issues associated with determining commercial viability.

Task 5

The delivery system design and fabrication began along with the initial testing on a preliminary version of the system. Initial testing appears promising, and fabrication of the delivery system is under way. Final testing, analysis, and reporting will occur in the 2005 reporting period.

Status

Task 1

For Project Area 3, several bench-scale tests have been performed in support of sorbent development research being conducted under Task 3. Additional tests are planned in support of sorbent regeneration (Task 4). Under Task 1.2, the bench-scale system is being set up to inject SO₃ along with the other flue gas constituents. Tests with SO₃ will begin in early March and include a full-factorial matrix looking at the effects of SO₃ on the ability of carbon sorbents to capture mercury in a simulated flue gas. Under Task 1.1, two tests have been completed to evaluate monolithic carbon samples. The results from these tests have shown that mercury capture with monolith structures made of activated carbon is possible.

Task 2

Five activities were evaluated during the pilot-scale combustion test with the PTC. All have been successfully completed, data reduction is in progress, and the results will be reported in the near future.

Task 3

A catalytic carbon was also treated with halogen reagents, but has not yet been tested. It was discovered in other research that some of the chlorine-treated samples were unstable with respect to time. Thus the chlorine-treated samples prepared for this program were not evaluated since they could not be run immediately after they were made. Two or three more samples will be made at a time when they can be evaluated immediately in the bench-scale system and then again after 2–3 weeks have passed.

Task 4

Limited testing of a variety of techniques for separation of the carbon and ash fractions was completed, and several of the technologies show potential. More thorough evaluations are required to fully evaluate economics and other issues associated with determining commercial viability. Several process parameters will be evaluated to determine their effects on the carbon regeneration process in order to further define the requirements for commercial application of the technology. The regenerated products will be tested in the thin-film fixed-bed system for determination of the impacts on mercury removal performance.

Task 5

The initial pilot-scale results appear promising for oxidation and mercury removal. Final testing, analysis, and reporting will occur in the 2005 reporting period.

The feed system also needs to be upgraded to provide a feed rate up to 100 g/hr. The feed materials can be in a liquid, aerosol, or gas form. Depending on the form of the feed halogens, a pump, spray nozzle, or a dry power dispersing system will be needed.

Quality objectives are defined for each task before research begins. As part of the QA/QC effort, project results and deliverables are compared to the quality objectives throughout the project to ensure those objectives are met.

Quality Objectives

The EERC is committed to delivering consistent and high-quality research that meets our clients needs and expectations. In order to ensure that the goals of this project were realized, specific quality objectives were established and defined as follows:

1. Successful preparation and measurement of mercury capacity for a range of sorbents.
 2. Measurement and evaluation of the impact of additives on the behavior and performance of a number of sorbents.
 3. Preparation, performance measurement, and evaluation of the mercury capture potential for the sorbents under development.
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4. Evaluation of ash–sorbent separation techniques to enable ash resale.
5. Demonstration of sorbent regeneration (measurement) techniques and evaluation of associated costs.
6. Design and demonstration of flue gas-quenching techniques to provide reactive halogen and carbon species for mercury removal.

The first three quality objectives were met by evaluating a number of sorbent materials using the EERC bench-scale mercury system under Tasks 1 and 3 of this program. Breakthrough curves were developed for each sorbent tested, and the results were compared with those from established baseline sorbent materials. Tests were also completed to evaluate the effects of including SO₃ in the simulated flue gas mixture.

For Task 2, a week of pilot-scale operation was provided for proof-of-concept testing on various measurement, oxidation, and control techniques developed under CATM and externally. There were no specific quality objectives for this task, but established equipment operation and instrument calibration procedures were followed to ensure real flue gas from a pilot-scale combustor was available for the various tests.

To meet the fourth quality objective, modified coal-upgrading techniques were evaluated for removing carbon from fly ash. The primary focus was carbon recovery, and the secondary focus was to produce salable fly ash. No conclusions were drawn regarding the suitability of any process to produce a fly ash with low enough loss on ignition (LOI) to allow sale. No fly ash testing (e.g., foaming tests or others) was done to confirm this. LOI tests on residual fly ash seemed to show that separation solvents or chemicals may be present. More testing would have to be done to show good separation and recovery of carbon from fly ash before confirmation tests on fly ash would be done.

The fifth quality objective was met by evaluating several acid wash treatments used for the regeneration of activated carbon sorbents. The sorbents were tested following the regeneration treatments using conventional bench-scale tests and comparing the initial capture activities as well as capacities to the original and HCl-treated FGD sorbents. Several higher pH methods were successful in providing highly active regenerated sorbents, and several gave lower-activity sorbents. A major cost factor in the regeneration is the equipment needed to process the strong acid solutions involved in the regeneration. Several schemes were investigated for lowering the acidity of the regeneration solutions and thus minimizing the corrosion factor.

The quality objective in Task 6 was met by designing and fabricating a high-temperature halogen dissociation chamber where the feed halogen compounds were decomposed into atomic or molecular halogens under the high-temperature environment. The high-temperature halogen dissociation unit was tested in a coal combustion flue gas to evaluate the impact of the dissociated halogens on mercury species in flue gas. Carbon-based sorbent was treated in situ by the quenched dissociated halogens and injected into coal combustion flue gas to capture gaseous mercury. Preliminary testing data showed the quenched halogen species were able to oxidize mercury and improve carbon reactivity with mercury in flue gas.

Measurement/Data Acquisition

The Mercury Laboratory at the EERC was responsible for performing the mercury measurements for all of the tasks. Daily calibration checks are performed on the mercury analyzers. The mass flow

controllers for the simulated flue gas delivery system are periodically calibrated, and the permeation rate of the mercury sources is periodically measured using wet-chemistry techniques. Laboratory analyses for Ontario Hydro samples were performed by the Analytical Research Laboratory (ARL) at the EERC.

Assessment and Validation

The compiled data were evaluated for accuracy, validity, and completeness. Method validation and evaluation of measurement accuracies were included as part of the Mercury Laboratory and ARL procedures.

Repeated independent experiments and mass balance analysis were completed in order to obtain reliable data with defined confidence limits. Results of independent measurements obtained using different analytical methods were compared to ensure that valid conclusions are drawn. This means that mercury gas analysis is based on a combination of data from CMMs and batch methods such as the Ontario Hydro method. Where tests involved the collection of mercury across a control device, the removal is based on inlet–outlet gas analyses as well as the amount of mercury in the spent sorbent. Only when mass balances are within $\pm 30\%$ will results be considered valid. To date, all mass balances have been within $\pm 20\%$.

Potential Users/Technology Transfer

The research is focused on technology development and 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 inexpensive reactive sorbents for Hg control will be of benefit to other industries requiring a mercury control technology.

Assuming success, there should be many potential users, including coal-fired utilities across the world. Commercial offering of the technology will likely involve equipment suppliers (e.g., B&W, Alstom, and ADA-ES to name a few), and/or sorbent vendors.

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