

Advanced Emissions Control Development Program

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Executive Summary

The objective of the Advanced Emissions Control Development Program (AECDP) has been to develop practical, cost-effective strategies for reducing the emissions of hazardous air pollutants (HAPs), commonly called air toxics, from coal-fired utility boilers. Development work initially concentrated on the capture of trace metals, hydrogen chloride, and hydrogen fluoride. Later work focused exclusively on the control of mercury emissions. The appropriateness of this focus was recently confirmed when, in December, 2000, the U.S. Environmental Protection Agency (EPA) announced its intention to regulate mercury emissions from electric power plants.

Work reported, herein, was performed by McDermott Technology, Inc., (MTI) and the Babcock & Wilcox Company (B&W) as an extension, or amendment, to the AECDP. The original AECDP scope of work, completed in July, 1999, was conducted in three phases over a five-year period, and was jointly funded by the United States Department of Energy's National Energy Technology Laboratory (DOE), the Ohio Coal Development Office within the Ohio Department of Development (OCDO), and B&W. The additional work conducted under the amendment was funded by the DOE, and comprised a more thorough evaluation of mercury control concepts developed earlier in the project

Results of Earlier AECDP Work

Development testing was conducted in B&W's Clean Environment Development Facility (CEDF). The CEDF is a one-of-a-kind boiler simulator with a rated capacity of 100 MBtu/hr (about the equivalent of a 10 MW_e power plant). It simulates a large commercial generating station from the coal pile to the stack, and includes a full complement of back-end pollution control equipment (electrostatic precipitator, fabric filter, spray dryer, and wet scrubber). Extensive benchmarking tests performed at the start of the project verified that CEDF HAP emissions are representative of those of commercial coal-fired plants.

Trace metal emissions – with the exception of mercury – were found to be well controlled by both the electrostatic precipitator (ESP) and fabric filter. *Particulate-phase* mercury was also efficiently captured in both the ESP and fabric filter. However, due to the high volatility of most

mercury species, particulate-phase mercury accounted for only a small fraction of the total mercury for the coals tested. Vapor-phase mercury was not captured by either the ESP or the fabric filter. HCl and HF emissions were captured with high efficiency in the wet scrubber (wet flue gas desulfurization or wet FGD).

Enhanced control of mercury with the ESP by way of upstream sorbent injection was demonstrated using a sorbent of low cost relative to activated carbon. Carbon injection is a commercially-proven technology for the control of mercury emissions from municipal solid waste incinerators. However, application of carbon injection technology to coal-fired utility boilers is projected to be expensive due to the low utilization of carbon expected for such systems. Injection of low-cost limestone into the upper furnace of the CEDF provided 45-56 % removal of total mercury compared to an 18% baseline removal. This mercury removal performance is similar to that obtained during carbon injection testing in the CEDF.

Initial testing with wet FGD consistently yielded significantly less mercury removal for an ESP/wet FGD system as compared to a fabric filter/wet FGD system – *even though there was no significant difference in mercury removal or speciation across the particulate collectors*. Also, elemental mercury concentration *increased* across the scrubber when the ESP was used upstream. This phenomenon was not observed with the scrubber when operating downstream of a fabric filter. Based on hypothesized mechanisms for these surprising results, three enhancement approaches were identified to improve mercury capture in a wet FGD system operating downstream of an ESP. Each of the three approaches significantly improved mercury capture across the wet scrubber, and also prevented the increase in elemental mercury.

Results of Current Work

The B&W enhanced wet FGD and sorbent injection processes have been further evaluated under the AECDP amendment. Preliminary designs based on the application of the processes to representative commercial boilers were developed and used to identify design uncertainties, as well to quantify the sensitivity of performance and cost on design specifications. For each process this activity included the preparation of a process flow diagram, material balance, major

equipment list and budgetary equipment cost estimate. Based on the preliminary designs, budgetary capital and operating costs were also developed.

Enhanced Wet FGD. Based on testing conducted in the CEDF under the AECDP and other projects, the B&W enhanced wet FGD process, alone, provides the means for controlling up to 90% of the vapor-phase mercury emitted during the combustion of Ohio coals. There are three primary factors that contribute to this success:

- Ohio coals – as well as many other eastern U.S. bituminous coals – exhibit the property whereby approximately 70 to 85% of the vapor-phase mercury is emitted in the oxidized form (presumably HgCl_2).
- A conventional lime/limestone scrubber provides the ability to effectively capture the oxidized form of mercury.
- The B&W process prevents the conversion of the captured oxidized mercury in the scrubber back to the elemental form, thereby precluding its reemission.

As impressive as these results are, it is unlikely that this approach, alone, will consistently yield mercury removal efficiencies in excess of 90% – especially with coals that produce a larger percentage of elemental mercury. One way to address this limitation is to oxidize the elemental mercury in the flue gas upstream of the wet FGD system. A selective catalytic reduction (SCR) system – commonly used for the control of NO_x emissions – was identified as one potential means for accomplishing this.

It has long been known that conventional SCR catalysts have a tendency to oxidize SO_2 to SO_3 . Testing was performed under a separate program to determine the extent to which SCR catalysts also promote the oxidation of elemental mercury. During three tests conducted in B&W's Small Boiler Simulator using an Ohio bituminous coal, the average percentage of oxidized mercury in the flue gas increased from 50.9% to 93.4% in the presence of the SCR catalyst. This significant result suggests that B&W's enhanced wet FGD process operating downstream of an SCR system should yield high (on the order of 90%) mercury removal efficiencies for a wide variety of coals. It should be noted that while every effort was made to ensure that the test conditions closely simulated commercial SCR operation, these results must be verified at full scale.

The levelized cost for the B&W enhanced wet FGD mercury removal process added to an *existing* wet scrubber is estimated to be about \$1,000 per pound of mercury removed. This cost is at least an order of magnitude lower than that for an activated carbon injection system. More significantly, the enhanced wet FGD system – *including the costs for the addition of a new wet scrubber* – can be competitive with activated carbon systems, depending on the mercury concentration in the coal and the amount of activated carbon required to meet emission targets.

It is important to note that this cost comparison takes no credit for the SO₂, H₂SO₄, HCl, or HF removal benefits of the addition of the scrubber. Further, the analysis does not take into account the potentially significant fuel cost savings made possible by the wet scrubber by enabling the utility to switch back to a higher-sulfur, local coal. An additional benefit of the scrubber approach is that no impact on ash utilization or disposal is anticipated. An activated carbon system may well result in higher ash disposal costs due to the presence of the carbon in the fly ash. Furthermore, installation of a spray cooling system and/or an additional fabric filter may be required to achieve high removal rates with activated carbon.

The B&W enhanced wet FGD process is expected to provide efficient mercury removal for coals that produce a high percentage of oxidized mercury – typically the eastern U.S. bituminous coals. When used in concert with an SCR system, it is expected to yield high mercury removal (~90%) on a wide variety of U.S. coals. Such a system is also capable of removing SO₂, NO_x, H₂SO₄, HCl, and HF with very high removal efficiencies. The highly interactive nature of these emissions control systems argues strongly for an integrated approach to future emissions control regulations for electric utilities.

Sorbent Injection. Based on testing conducted in the CEDF, limestone injection appears to offer a low-cost alternative to activated carbon injection for mercury control at modest levels of mercury removal (~50% mercury removal efficiency). In this regard, limestone injection for mercury control appears to be somewhat analogous to limestone injection for SO₂ control (a process commonly referred to as LIMB). In each case the limestone injection process offers modest removal efficiency at low capital cost, and relatively low operating cost. For electric

utilities, limestone injection for SO₂ control has largely been overshadowed by higher efficiency processes such as wet scrubbing due to the way in which SO₂ regulations have been promulgated. Whether or not low-efficiency, low-cost mercury removal processes find commercial application may well also depend on how mercury emissions are regulated.

Preliminary Assessment of Market. This activity focused on evaluating the existing U.S. coal-fired utility boiler population with respect to various design parameters (unit size and location, coal type, FGD system type, reagent type, extent of mercury oxidation, etc.) to quantify the potential impacts of B&W's control technologies on mercury emissions from U.S. utilities. The estimates are based on a detailed coal-fired utility plant database and mercury removal performance data obtained during pilot-scale testing.

Applying limestone injection to the currently-unscrubbed units, and enhanced wet FGD to the units with existing wet FGD systems, results in a 50% decrease in the U.S. mercury emissions rate, from 54 tons/year to 27 tons/year. The extreme case of applying the B&W enhanced wet FGD process in conjunction with SCR (for oxidation of elemental mercury, as well as NO_x removal) to all coal-fired units could result in total U.S. mercury emissions of 6.7 tons/year – a reduction of nearly 90%. As pointed out, above, this scenario would also result in dramatic reductions in U.S. emissions of SO₂, NO_x, H₂SO₄, HCl, and HF, and provide utilities with greater flexibility in purchasing coal supplies.

Fate of Mercury. A key consideration in the commercial viability of any mercury removal process is the fate of the captured mercury. To be an effective control technology, the captured mercury must remain sequestered in the solid byproduct. This is important for both the gypsum or sludge produced by the enhanced wet FGD process, and for the spent byproduct produced by the sorbent injection process. In an effort to determine the ultimate fate of mercury contained in the solid byproduct, and how the B&W control technologies might affect this fate, conventional wet chemistry methods and a new thermal stability technique developed during this project were used to characterize the byproduct.

Samples from several mercury test campaigns in the CEDF were used in the study, as were several samples obtained from two U.S. utilities – one burning an eastern bituminous coal and the other burning a blend of western subbituminous coals. The eastern plant has an ESP followed by a wet FGD system to control particulate and SO₂ emissions, respectively, although the scrubbing process is different than that tested in the CEDF. This plant provided three samples: an ESP ash, a dewatered wet FGD sludge, and a stabilized sludge that comprised a mixture of ESP ash, wet FGD sludge and lime. The western plant sent only a sample of ESP ash.

Significantly, *all samples tested* contained too little mercury to exceed Toxicity Characteristic Leaching Procedure (TCLP) limits even if all of the mercury had reported to the liquid phase, which it did not. For comparison purposes, human fingernail clippings were found to contain 83 times more mercury than the wet FGD sludge produced the B&W enhanced wet FGD system. Further, no mercury was ever detected in any liquid fraction, suggesting that no soluble form of mercury, such as HgCl₂, was present in any of the samples. Thermal stability testing indicated that all samples were stable (with respect to mercury content) up to at least 140 C, the temperature at which rotary kilns in wallboard plants operate.

Overall, the fate of mercury testing indicated that solid byproducts produced by conventional systems, as well as those produced by the B&W enhanced processes, appear to be suitable (with respect to mercury content) materials for wallboard and cement manufacture, and for disposal in landfills.

1.0 Introduction

1.1 Overview

The primary objective of the Advanced Emissions Control Development Program (AECDP) is to develop practical, cost-effective strategies for reducing the emissions of hazardous air pollutants (HAPs, or air toxics) from coal-fired boilers. This objective is being met by identifying ways to effectively control air toxic emissions through the use of conventional flue gas cleanup equipment such as electrostatic precipitators (ESPs), fabric filters (fabric filters), and wet flue gas desulfurization (wet FGD) systems. Development work initially concentrated on the capture of trace metals, hydrogen chloride, and hydrogen fluoride. Recent work has focused almost exclusively on the control of mercury emissions.

Work reported, herein, was conducted by McDermott Technology, Inc. (MTI), and The Babcock & Wilcox Company – a McDermott company (B&W), under an amendment (addition) to the original project workscope to permit a more thorough evaluation of mercury control concepts developed earlier in the project. The original workscope was conducted in three phases and was completed in July, 1999. The original three phases were jointly funded by the United States Department of Energy's National Energy Technology Laboratory (DOE), the Ohio Coal Development Office within the Ohio Department of Development (OCDO), and B&W. The additional workscope, conducted under the amendment, was funded by DOE. Detailed descriptions of the work completed under Phases I, II, and III are contained in the final reports for each of the phases.

1.2 Previous Work

Phase I (Facility Modification and Benchmarking) was aimed at providing a reliable, representative test facility to study air toxics. A full-flow ESP and partial-flow fabric filter and wet FGD system were added to the existing complement of flue gas treatment systems installed at the B&W Clean Environment Development Facility (CEDF). A schematic of the CEDF and project test equipment is provided in Figure 1-1. The CEDF is a unique testing facility with a rated capacity of 100 MBtu/hr (about the equivalent of a 10 MW_e electric plant). It simulates a

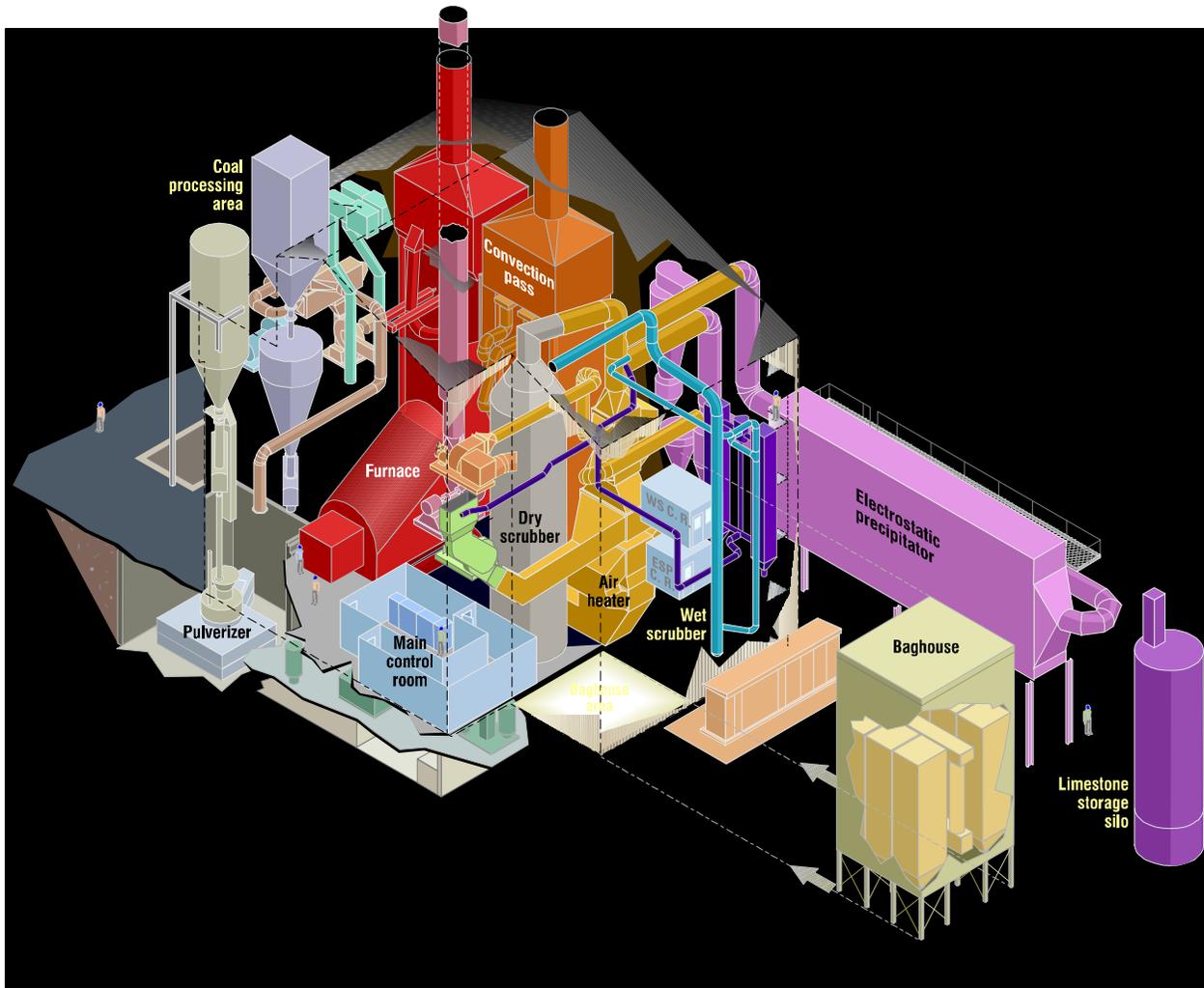


Figure 1-1 – Clean Environment Development Facility

large commercial generating station from the coal pile to the stack. For the added equipment, the general design philosophy was to install systems that would be representative of existing commercial systems, yet provide a high degree of flexibility in both operation and configuration. Other activities completed in Phase I included equipment verification, air toxics benchmarking and the establishment of an emissions database.

Air toxic benchmarking measurements were performed to quantify the air toxics emissions from the boiler and back-end flue gas cleanup equipment. Air toxics emissions were verified through comparison of the emissions from the CEDF with the emissions predicted by the trace element content of the coal and the draft emission modification factors (EMFs) established by the U.S.

Environmental Protection Agency (EPA). The EMFs were developed using data gathered at a number of commercial utility plant sites. The similarity between the predicted and measured emissions indicated that the air toxics emitted from the CEDF are representative of commercial units firing bituminous coal.

Three test campaigns were conducted in Phase II (Optimization of Conventional Systems). The first two campaigns were directed at the development of air toxics control strategies based on the use of conventional particulate and SO₂ control equipment. Campaign 1 focused on mercury speciation measurements, particulate- and vapor-phase trace metal emissions, and fine particulate emissions. Emphasis was placed on characterization of ESP and fabric filter trace element emissions control performance. The control of mercury emissions with a wet FGD system was broadly characterized during Campaign 2 under conditions representative of commercial scrubber operations. Campaign 3 provided data on the impacts of coal properties on mercury emissions for several Ohio steam coals. The impact of coal cleaning on mercury emissions was investigated through characterization of commercially-cleaned coals and their associated parent (uncleaned) coals. Two advanced measurement systems, a mercury monitor and a Fourier transform infrared spectrometry analyzer (FTIR), were also evaluated in Phase II.

Phase III (Advanced Concepts and Coal Comparisons) included investigations of advanced emissions control concepts, primarily for the purpose of reducing vapor-phase mercury emissions. Two different approaches were taken to address the two major segments of the coal-fired utility market:

- Scrubbed systems (primarily wet flue gas desulfurization), which represent about 25% of the coal-fired utility market. The majority of these scrubbed systems comprise an ESP followed by a wet scrubber.
- Unscrubbed systems, which represent about 75% of the utility coal market. The majority of these systems comprise an ESP, only.

Mercury species were tracked through the entire coal-utilization process including pre-combustion, combustion, and post-combustion processes for several Ohio coals. Commercial coal cleaning, which is used on the majority of coals fired east of the Mississippi, provided

average mercury emission reductions of 42% compared to the raw coal. Particulate control devices (ESPs and fabric filters) effectively removed the particulate-phase mercury, but the particulate-phase mercury was only a small fraction of the total mercury for the coals tested. Both the fabric filter and ESP provided negligible control of vapor-phase mercury. The fabric filter, however, did impact the speciation of vapor-phase mercury in the flue, resulting in a modest conversion of the elemental mercury to the oxidized form.

Control of mercury by an ESP with upstream sorbent injection was demonstrated during Phase III testing. Testing focused on sorbents of low cost relative to commercial activated carbons. Carbon injection is a commercially-proven technology for the control of mercury emissions from municipal solid waste incinerators. However, application of carbon injection technology to coal-fired utility boilers is projected to be expensive due to the low utilization of carbon expected for those systems. One low-cost sorbent (limestone) tested during Phase III provided 45 % and 56 % removal of total mercury at two cost-competitive stoichiometries, compared to an 18% average removal for baseline conditions with no sorbent injection. Carbon injection likewise provided improved control of mercury by an ESP, removing 56% of the total mercury in the flue gas at an activated carbon-to-mercury mass ratio of 9000 to 1.

Phase III testing related to wet FGD systems focused on enhancing control of mercury across wet scrubbers when operated downstream of an ESP. Testing during Phase II had consistently indicated less mercury removal for an ESP/wet FGD system as compared to a fabric filter/wet FGD system – *even though there was no significant difference in mercury removal or speciation across the particulate collectors*. Also, elemental mercury levels increased across the *scrubber* when an ESP was used upstream. Causes for these observations were hypothesized at the beginning of Phase III, and proposed methods for enhancing mercury control in the wet scrubber were tested. The hypotheses were based on the belief that the ESP can destroy gas-phase species that would otherwise react with the mercury in the scrubber, and thereby sequester the mercury in a solid precipitate, preventing the subsequent conversion of the oxidized mercury to the elemental form. Figure 1-2 illustrates the observed conversion of oxidized mercury species to the elemental form in a wet scrubber operating downstream of an ESP. This phenomenon is not

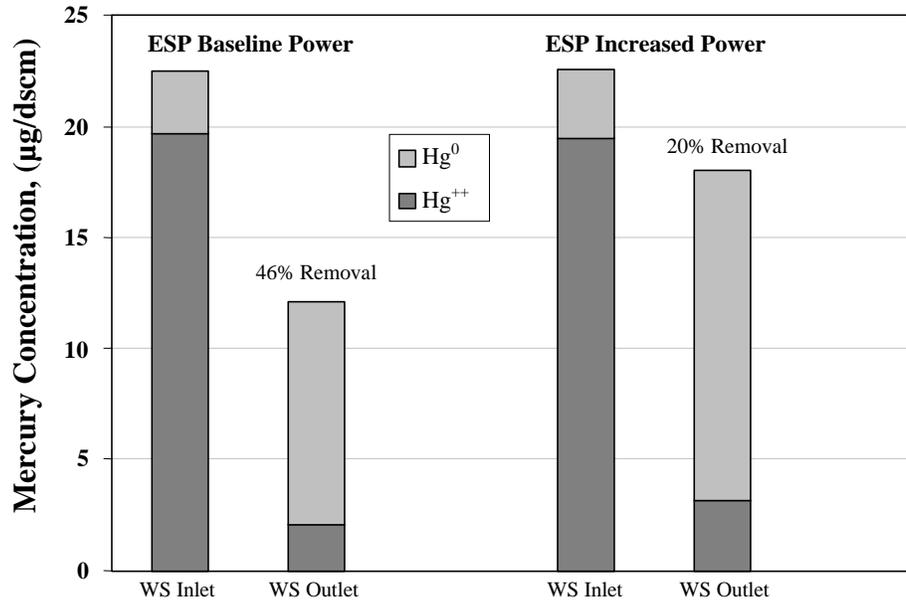


Figure 1-2 – Effect of ESP Power on Mercury Removal in Wet Scrubber

observed in the scrubber when operating downstream of a fabric filter. Figure 1-2 further illustrates the fact that the effect is dependent on the operating conditions in the ESP.

Several enhancements were identified to improve control of mercury in a wet FGD system downstream of an ESP. The baseline data used for comparison with the enhancements showed 46% removal across the scrubber when preceded by an ESP when firing a blend of Ohio 5, 6, & 7 coals. Three enhancements were evaluated to determine their potential for eliminating the effect of the ESP on mercury control in the scrubber. All three of the enhancements significantly improved mercury control across the wet scrubber and prevented increases in elemental mercury. Mercury removal increased to 80, 71, and 73% for the three enhancements, respectively.

1.3 Current Work

B&W considered the mercury control concepts developed during the original three phases of the AECDP, and described in the previous section, to have the potential to permit U.S. utilities to reduce mercury emissions from their coal-fired units in a very cost-effective manner. However, at the completion of the Phase III work, there remained a variety of issues that needed to be addressed before a detailed commercialization plan could be developed. Several of these issues

were addressed under the contract amendment, and are the subject of this report. They were addressed under two main activities or tasks: Concept Evaluation and Fate of Mercury.

1.3.1 Task 1 – Concept Evaluation

The objective of this task was to further evaluate the mercury emissions control concepts developed under Phase III. The enhanced wet FGD and limestone injection technologies were evaluated both technically and economically for potential application to coal-fired utility boilers.

Engineering Study / Conceptual Design. Preliminary (conceptual) process designs were developed for each of the mercury control concepts. These designs were based on the application of the technologies to representative commercial boilers, and were used to identify design uncertainties, as well as to quantify the sensitivity of performance and cost to design specifications. For each concept this activity included the preparation of a process flow diagram, material balance, major equipment list and budgetary equipment cost estimate. Estimated capital and operating costs were then developed and compared with other mercury control concepts such as activated carbon injection.

Preliminary Assessment of the Market. This activity was a follow-on to the preliminary boiler population study conducted earlier in the AECDP project. The evaluation included an updated utility boiler population survey, an assessment of existing environmental control equipment, and the potential for mercury emissions reductions using the B&W concepts.

1.3.2 Task 2 – Fate of Mercury

A key consideration in the commercial viability of any mercury removal process is the fate of the captured mercury. To be an effective control technology, the captured mercury must remain sequestered in the solid byproduct. This is an important consideration for both the gypsum or sludge produced by the enhanced wet FGD process, and for the spent sorbent/flyash byproduct produced by the limestone injection process. Work was done under this subtask to characterize the properties and stability of the byproducts produced by the mercury control concepts. This work involved chemical analysis of byproduct materials. Some of this work made use of

samples archived during earlier phases of the project. Samples collected at representative field sites were also evaluated.

2.0 Concept Evaluation

2.1 Recent Results from Other B&W Testing Programs

2.1.1 Enhanced Wet Scrubbing

Development work on the B&W enhanced wet FGD concepts identified during the first three phases of the AECDP continued under a separate project entitled “Mercury Control for Coal-Fired Boilers”. Project participants included the Ohio Coal Development Office within the Ohio Department of Development (under Grant Agreement CDO/D-98-7), Cinergy Corporation, B&W, and MTI. The objective of the project was to develop and optimize B&W’s wet FGD mercury removal enhancement technologies to the point where a commercial demonstration could be conducted. Extensive testing was conducted under the project, the results of which are detailed in several project milestone reports.

Of particular interest, here, is testing performed in the CEDF using a blend of Ohio 5 & 6 coals. This testing was done to evaluate the effectiveness of an alternate reagent – a reagent which mimics the chemical behavior of one of the reagents tested during the original AECDP, but which is lower in cost and more readily available in commercial quantities. Four tests were conducted with the alternate reagent. Mercury speciation measurements were performed in triplicate according to the Ontario Hydro method at the wet scrubber inlet and outlet for each test. Throughout the test campaign, vapor-phase mercury concentrations at the wet scrubber inlet remained steady, averaging 18.5 µg/dscm (micrograms per dry standard cubic meter). Mercury speciation at the wet scrubber inlet also remained relatively steady, with approximately 84% of the mercury reporting as oxidized mercury. Particulate mercury concentrations at the wet scrubber inlet averaged 0.38 µg/dscm, or approximately 2% of the total mercury present in the flue gas. For clarity, the particulate-phase mercury concentrations are not shown in the following two figures.

In Figure 2-1, the mercury removal and speciation results for the alternate reagent are compared with baseline (no additive) wet scrubber removal and speciation results. In the figure the feed

rate of reagent is reported as a multiple of the reagent feed rate used during the feasibility tests performed during the AECDP. For example, “1X” indicates that the feed rate used was the same as that used for the earlier AECDP tests. The test labeled “1XR” is simply a repeat of the “1X” test. Each set of bars represents the average inlet and outlet gas-phase mercury concentrations for a given test. Each bar is divided to show oxidized and elemental mercury concentrations. The numbers above the outlet bars show the average total mercury removals for each test. The error bars represent the maximum and minimum mercury concentrations for each set of triplicate measurements.

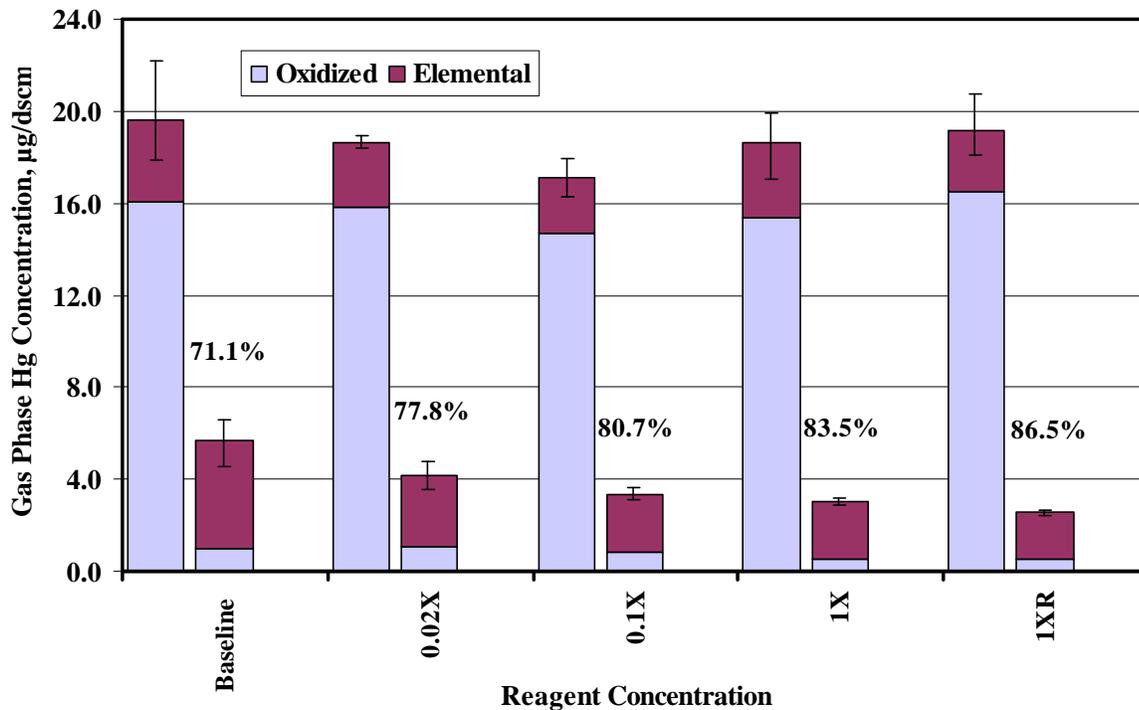


Figure 2-1 – Mercury Removal and Speciation with Alternate Reagent

As expected, the alternate reagent resulted in significant increases in mercury removal across the wet scrubber relative to baseline conditions. The same data, plotted in a different form in Figure 2-2, show that while comparable oxidized mercury removals were observed for each of the tests, the alternate reagent effectively suppressed the conversion of the captured oxidized mercury to the elemental form, thereby preventing its reemission as elemental mercury vapor. This was, of

course, the original objective of B&W's enhanced wet FGD process. Somewhat surprisingly, *elemental* mercury removal modestly increased with increasing reagent feed rate, as well.

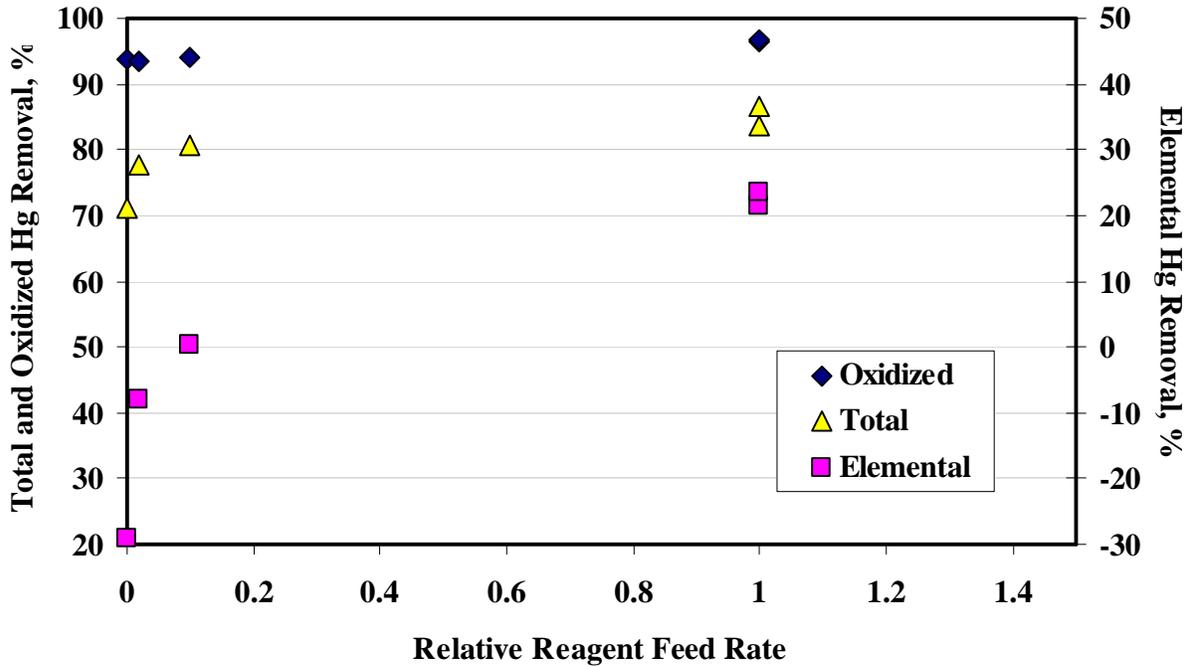


Figure 2-2 – Oxidized, Elemental and Total Mercury Removal Results

The results indicate that the alternate reagent has essentially the same effectiveness in improving mercury removal across the wet scrubber as that offered by the original reagent. The important point is that the alternate reagent is lower in cost and more readily available than the original reagent, and does not adversely affect either mercury removal performance or scrubber operation.

2.1.2 Improved Control of Elemental Mercury

As described, above, the B&W enhanced wet FGD process provides the means for controlling up to 86% of the vapor-phase mercury emitted during the combustion of Ohio coals. There are three primary factors that contribute to this success:

- Ohio coals – as well as other eastern U.S. bituminous coals – exhibit the property whereby approximately 70 to 85% of the vapor-phase mercury is emitted in the oxidized form (presumably HgCl_2).
- A conventional lime/limestone scrubber provides the ability to effectively capture the oxidized form of mercury.
- The B&W process prevents the conversion of the captured oxidized mercury in the scrubber back to the elemental form, thereby precluding its reemission.

As impressive as these results are, it is unlikely that this approach, alone, will yield mercury removal efficiencies in excess of 90% for coals that produce a larger percentage of elemental mercury. To achieve this level of control, a way must be found to reduce the emissions of elemental mercury. This problem can be addressed by:

- Decreasing the percentage of elemental mercury, or by
- Capturing the elemental mercury, directly.

While B&W is currently investigating concepts for the direct capture of elemental mercury, the focus of the work done under this project was to identify potential means for decreasing the fraction of elemental mercury in the flue gas. Two of the methods identified for effecting the oxidation of elemental mercury were subsequently tested under the “Mercury Control for Coal-Fired Boilers” project. The first involved the use of a conventional catalyst for the selective catalytic reduction (SCR) of NO_x . The second involved injecting a calcium chloride solution into the combustion zone of the furnace.

SCR Catalysts. It has long been recognized that conventional SCR catalysts have a tendency to oxidize SO_2 to SO_3 . Testing was performed under representative SCR conditions to determine whether or not the catalysts also promote the oxidation of elemental mercury.

Calcium Chloride Injection. This approach is based on the empirical observation that western coals low in chloride content tend to produce less oxidized mercury than eastern bituminous coals that are characteristically higher in chloride content. This led to the idea of artificially

increasing the chloride content of the coal by, for example, coating the coal with a solution of calcium chloride to promote the formation of HgCl_2 .

All testing was conducted in the Small Boiler Simulator (SBS) while firing an Ohio Mahoning 7 coal. For the CaCl_2 injection test one set of triplicate Ontario Hydro sampling was conducted. An EPA Method 26 sampling procedure was also conducted to quantify the amount of chloride present in the flue gas. No incremental conversion of elemental mercury was observed when injecting a calcium chloride solution into the SBS combustion zone. The amount of calcium chloride injected was comparable to a coal containing 3000 ppm chloride.

Mercury speciation results for the tests where the flue gases were exposed to SCR catalyst are presented in Figure 2-3. The flue gases were exposed to the catalyst at typical SCR catalyst temperatures (approx. 750 F). Each bar in the figure represents a single Ontario Hydro sample train and is identified either as an *SCR* train (flue gas has contacted the SCR catalyst) or a *Reference* train (flue gas is untreated). Each pair of bars represents a simultaneous pair of Ontario Hydro sample trains. The bars are divided to indicate the amount of oxidized and elemental mercury present in the flue gas. The numerical percentage above each bar represents the percent of oxidized mercury present in the flue gas.

It can be seen from the data that at typical SCR operating temperatures substantial incremental mercury oxidation is achieved. For the three sets of data the average percentage of oxidized mercury increased from 50.9% untreated to 93.4% in the presence of the SCR catalyst. Further, in each set the total mercury present is similar, indicating that the gas-phase mercury is remaining in the gas phase (and not, for example, adsorbing onto the catalyst surface). It should be pointed out that while significant effort was expended to ensure that the catalyst conditions tested closely simulated commercial conditions, these results must be verified at full scale.

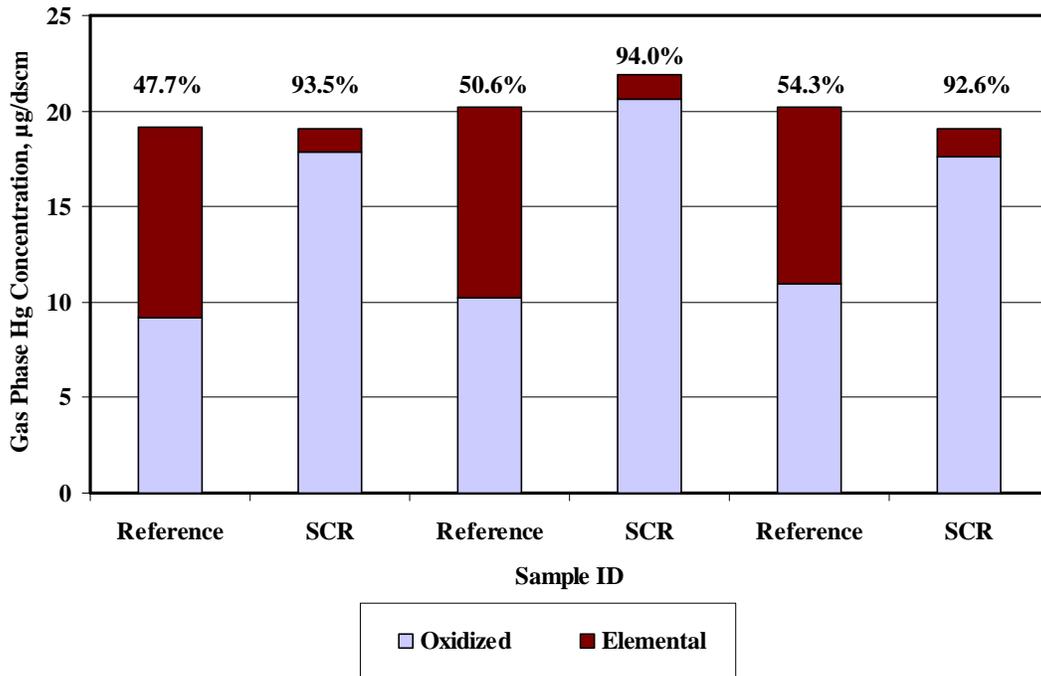


Figure 2-3 – Effect of SCR Catalyst on Mercury Speciation

2.2 Conceptual Design

2.2.1 Overview

Preliminary (conceptual) process designs were developed for each of the mercury control concepts. These designs were based on the application of the technologies to representative commercial boilers, and were used to identify design uncertainties, as well as to quantify the sensitivity of performance and cost to design specifications. For each concept this activity included the preparation of a process flow diagram, material balance, major equipment list and budgetary equipment cost estimate. Estimated capital and operating costs were then developed and compared with other mercury control concepts such as activated carbon injection.

2.2.2 Unscrubbed Systems

Approximately seventy-five percent of today's coal-fired power plants are not equipped with flue gas desulfurization systems. Most of these plants are equipped only with electrostatic precipitators for the control of particulate emissions. With mercury emissions regulations for the electric power industry pending, B&W has been working to develop cost-effective mercury capture technologies for this segment of the power plant market.

Activated carbon injection is a method of mercury control that is currently used at municipal solid waste (MSW) plants. It is cost-effective for the control of mercury in MSW plants and medical waste combustors. Its cost-effectiveness for coal-fired power plants is somewhat uncertain. Flue gas mercury concentrations at coal-fired power plants are typically one to two orders of magnitude lower than those at waste-to-energy plants, and mercury species found at the two types of facilities can also differ significantly.

Preliminary studies on utility flue gas have indicated that carbon injection can be used to remove mercury from coal-fired flue gas. However, significant mercury removal – especially removal of elemental mercury – seems to require injection at very high carbon-to-mercury stoichiometries. The resultant low utilization of the relatively expensive sorbent may make activated carbon injection a very expensive proposition for power plant operators. In hopes of finding a low-cost

alternative to activated carbon, B&W and MTI have evaluated the effectiveness of limestone as a mercury removal sorbent.

AECDP Limestone Injection Test Results. Several tests were conducted during Phase III of the AECDP to evaluate the effectiveness of limestone as a mercury removal sorbent. These tests were conducted in B&W's CEDF. The limestone chosen for the tests was a high purity ($\text{CaCO}_3 > 95\%$) limestone with a mass mean diameter (D_{43}) of 15 microns and a Sauter mean diameter (D_{32}) of 5.6 microns. Two limestone flow rates were tested: 0.35 and 0.04 moles Ca/mole S. The flow rates are expressed in moles Ca/mole S for comparison with typical limestone flow rates used for SO_2 removal. The limestone flow rates used to target mercury were much lower than those used for targeting SO_2 (typically in the range of 1.4 – 2.0 moles Ca/mole S). An upper-furnace injection temperature of 2100-2300 F was chosen as the optimum range to calcine the limestone (CaCO_3) to lime (CaO). It was assumed that the resulting CaO would be more reactive by analogy with results for limestone injection for the removal of SO_2 . An ESP operating at 350 F was used for particulate control during the limestone injection tests.

Figure 2-4 illustrates results for a limestone feed rate equivalent to 0.04 moles Ca/mole S. The total mercury in the flue gas at the ESP inlet with and without limestone injection is about the same. Limestone injection substantially increases the particulate-phase mercury, which is subsequently removed by the ESP – providing an overall mercury removal of 45%. Without limestone injection, baseline mercury removal was about 18% for the coal tested. A somewhat higher mercury removal of 56% was achieved at the higher calcium stoichiometry of 0.35 moles Ca/mole S (Figure 2-5). The mercury removal provided by limestone injection appears to be a result of the capture of oxidized mercury onto the particulate phase. Limestone injection had no apparent effect on the elemental mercury.

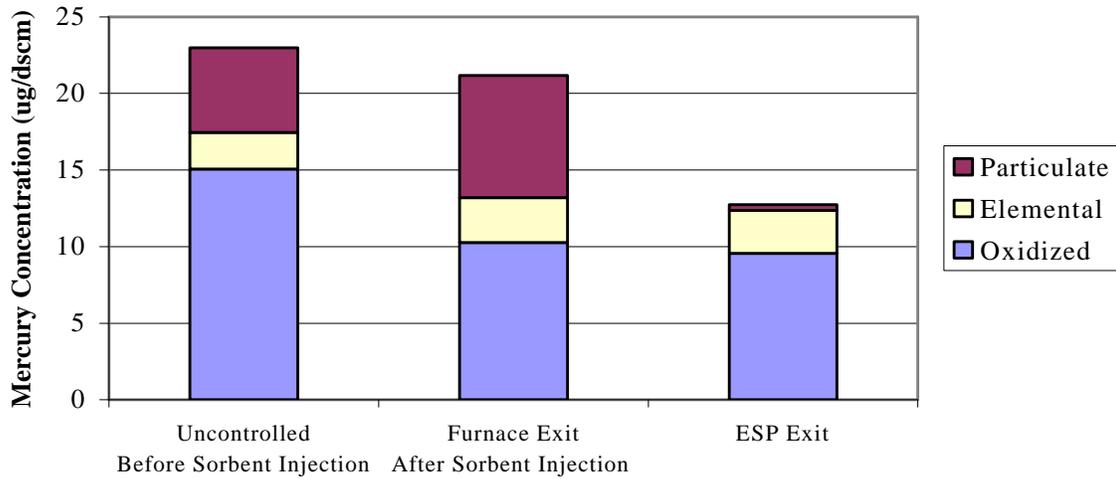


Figure 2-4 – Limestone Injection Mercury Capture at Ca/S = 0.04 mol/mol

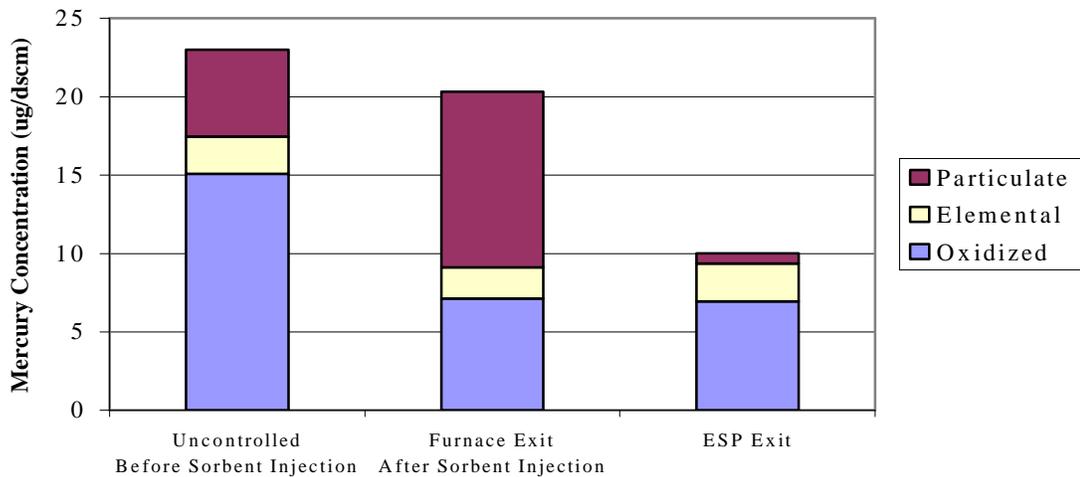


Figure 2-5 – Limestone Injection Mercury Capture at Ca/S = 0.35 mol/mol

System Description. The conceptual upper-furnace limestone injection system design is sized for a 400 MW_e power plant burning a high-sulfur bituminous coal. System mercury removal performance is based on the results presented, above, from the AECDP. A Ca/S stoichiometry of 0.35 mole Ca / mole S was used for the design. It should be noted that this may not be the optimum limestone feed rate for the system. Further testing aimed at optimization of the limestone system is needed.

Coal Analysis. The design fuel is a high-sulfur bituminous coal. A complete fuel analysis is listed in Table 2-1.

Table 2-1 – Coal Analysis

Component % by Weight	
Carbon	62.14
Hydrogen	4.27
Sulfur	3.40
Oxygen	7.59
Nitrogen	1.20
Moisture (Water)	11.65
Ash	9.75
Mercury	0.20 ppm
Heating Value	11336 Btu/lb

System Schematic and Mass Balance. An overall mass balance for the system is presented in Table 2-2. With a coal mercury content of 0.20 ppm, 0.058 lb/hr mercury is entering the system with the coal. With a system mercury removal of 56%, 0.032 lb/hr mercury would be exiting the system in the solid by-product and 0.026 lb/hr mercury would be exiting the system in the flue gas. A schematic diagram of the system is presented in Figure 2-6.

Table 2-2 – System Mass Balance

Component	Units	Coal	Furnace before Limestone Injection	Limestone Feed	Transport Air	Furnace Exit
Temperature	F	175	2200	70	225	700
GAS STREAMS			A		B	C
CO ₂	lb/hr		646,163			650,431
O ₂	lb/hr		472,235		232	472,228
SO ₂	lb/hr		19,119			18,163
H ₂ O	lb/hr		182,259		13	182,272
N ₂	lb/hr		1,810,755		766	1,811,521
TOTAL GAS FLOW	lb/hr	0	3,130,531	0	1,011	3,134,615
SOLIDS STREAMS		1		2		3
CaCO ₃	lb/hr			9,709		
CaO	lb/hr					4,605
Inerts	lb/hr			405		405
CaSO ₄	lb/hr					2,029
Ash	lb/hr		25,435			25,435
Coal	lb/hr	289,670				
TOTAL SOLIDS	lb/hr	289,670	25,435	10,114	0	32,474
TOTAL FLOW	lb/hr	289,670	3,155,966	10,114	4,050	3,167,089

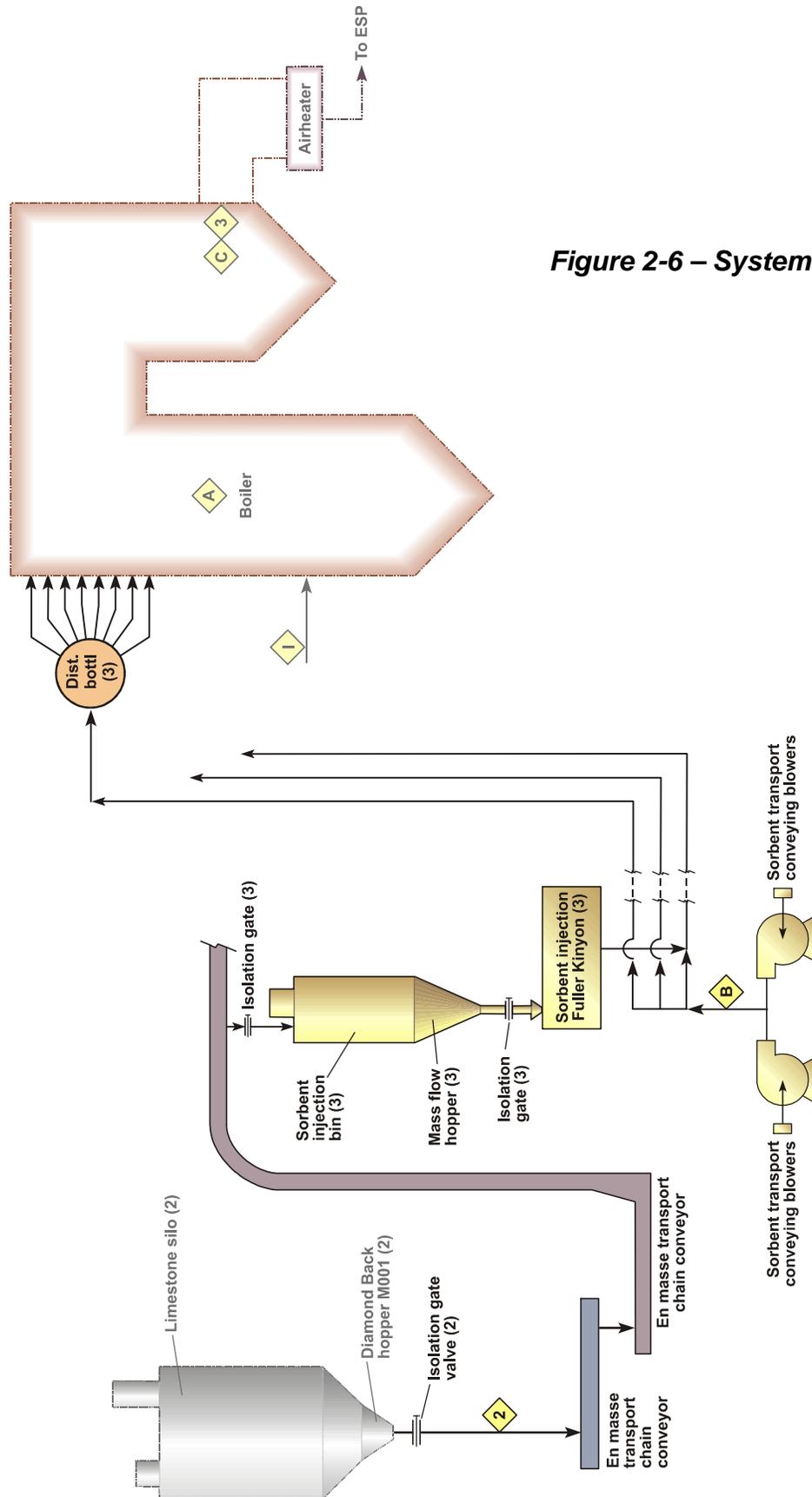


Figure 2-6 – System Schematic

Limestone Reagent Transport System. The sorbent handling system consists of the equipment between the limestone silo outlet and the limestone injection bins as listed in Table 2-3. Prepared ground sorbent, sized to 100% passing 325 mesh, is purchased from a supplier, delivered to the plant and stored in two limestone silos. Each silo is sized to contain 500 tons or the equivalent of 96 hours of full boiler load operation. The bottom of each silo is equipped with a “diamond back” hopper to facilitate uninterrupted flow of the fine powdered solids from the silo. Two isolation gate valves located at the bottom of the hoppers isolate the flow of limestone from the silo to a single 43 ton/hr “en masse” transport chain conveyor. The conveyor delivers the limestone to three limestone injection bin(s). Each of the three bins holds 27 tons of limestone which is equivalent to an 8-hour supply at full load.

Table 2-3 – Limestone Reagent Transport System Major Equipment List

COMPONENT	QUANTITY	CAPACITY PER UNIT
Limestone silo	2	500 ton
Isolation gate valve	2	10114 lb/hr
Transport chain conveyor	1	43 ton/hr
Limestone injection bins	3	27 ton/hr

Sorbent Injection System. The sorbent injection system begins at the bottom of the three injection bins and ends at the injection ports on the boiler furnace walls as listed in Table 2-4. The isolation gate valves, located at the inlets and outlets of the injection bins, isolate the sorbent reagent feed, and allow for maintenance of equipment downstream without interruption of the system operation or the need to empty the bin above. The rate of limestone flow from the injection bins is determined by the rate of the three pumps. Each pump is designed to deliver 2 tons/hr of the powdered limestone.

Limestone flows from the injection bins to the pneumatic pick-up bottles of the pumps, where compressed air is combined with the solids to form a dilute-phase solid transport mixture. The air-transported solids are delivered pneumatically to the injection points. The pumps isolate the

transport lines from the downspout of the injection bins and prevent the transport air from fluidizing the sorbent in the bins. The solids are transported in a dilute phase at a rate of 10 pounds of solids per pound of air.

The transport air is provided by one of two 100%-flow conveying blowers. The transport air picks up the sorbent from the pumps and delivers it to three distribution bottles located adjacent to the front wall of the boiler. The distribution bottles receive the sorbent from the transport lines through one pipe line and distribute it evenly to eight pipes located on top of the bottle. The injection lines deliver the limestone to the appropriate temperature zone of the boiler. The feed and distribution lines are made of appropriate material to withstand the erosive action of the transported solids.

Table 2-4 – Sorbent Injection System Major Equipment List

COMPONENT	QUANTITY	CAPACITY PER UNIT
Injection bins isolation inlet gate valves	3	3371 lb/hr
Injection bins isolation outlet gate valves	3	3371 lb/hr
Fuller Kinyon pumps	3	2 tons/hr
Conveying / injection blower	2	225 scfm
Distribution bottles	3	3371 lb/hr

2.2.3 Scrubbed Systems

System Description. The conceptual enhanced wet FGD system is sized for a 500 MW_e power plant burning an eastern U.S. bituminous coal. System mercury removal performance is based on the results presented in Section 2.1.1, above, which presented performance results for the “alternate reagent”. The reagent is delivered by tank truck to the plant as a 25% by weight solution in water. This reagent solution has a density of approximately 10 lbs/gallon, and is alkaline with a pH of 9-12. While this additive is listed as a hazardous substance, it is not listed as a carcinogen or potential carcinogen, and no exposure limits have been established by OSHA. Gas can evolve from this additive solution as a decomposition product. Therefore, the tank truck is not vented during off-loading, but is kept under positive pressure with plant air. Tank truck unloading personnel are equipped with appropriate respirators and protective clothing.

System Schematic and Mass Balance. The enhanced wet FGD process comprises such a minor addition to a conventional wet scrubber that a detailed mass balance and major equipment list are unneeded. The recommended plant storage for the reagent is a closed vessel having a vent pipe equipped with a caustic scrubber. The tank may be fabricated from either plastic or 18-8 stainless steel. To minimize construction and set-up at the plant site, the additive feed/metering system is skid-mounted, producing a small footprint. The skid is connected to the plant water and wet FGD absorber recirculation piping. Stainless steel piping is used to connect the components on the skid to the wet FGD system.

Two identical additive injection/metering pumps are mounted on the skid providing 100% redundancy. The pumps are equipped with variable frequency controllers to permit a wide range of turndown. The skid is also equipped with a dilution water connection/control system for added flexibility in adjusting additive feed concentration. A calibration tube is provided upstream of the pumps to check pump delivery rates. A pulsation dampener, having a flexible elastomeric bladder/diaphragm and a gas-pressurized upper chamber, is located in the pumps’ common discharge line to facilitate a more uniform feed flow. Also provided are flow meters, flow control valves, pressure regulating valve, pressure gauges, and a pressure relief valve. Figure 2-7 illustrates the proposed equipment arrangement on the skid. All equipment, pipe and

fittings are fabricated of 316 stainless steel, with elastomeric components suitable for the process conditions, where required.

Only minor modifications to the existing (or new) wet FGD equipment is required. A tie-in at the suction of each absorber recirculation pump is required for the introduction of the reagent solution. Recirculation pump hydraulics are used to mix the reagent solution with the recycle slurry prior to its discharge through the absorber internal spray nozzles.

No changes to the operation and/or maintenance of the wet FGD system are expected as a result of the reagent injection system for mercury removal. The incremental increases in operation and maintenance labor for the reagent solution off-loading, storage and pumping/metering are minimal, and should be easily handled by existing plant shift personnel. Since very small amounts of additive solution (approximately 12 gallons/hour for a 500MW_e plant) will be injected into the scrubber, no impact on by-product (gypsum) quality is anticipated.

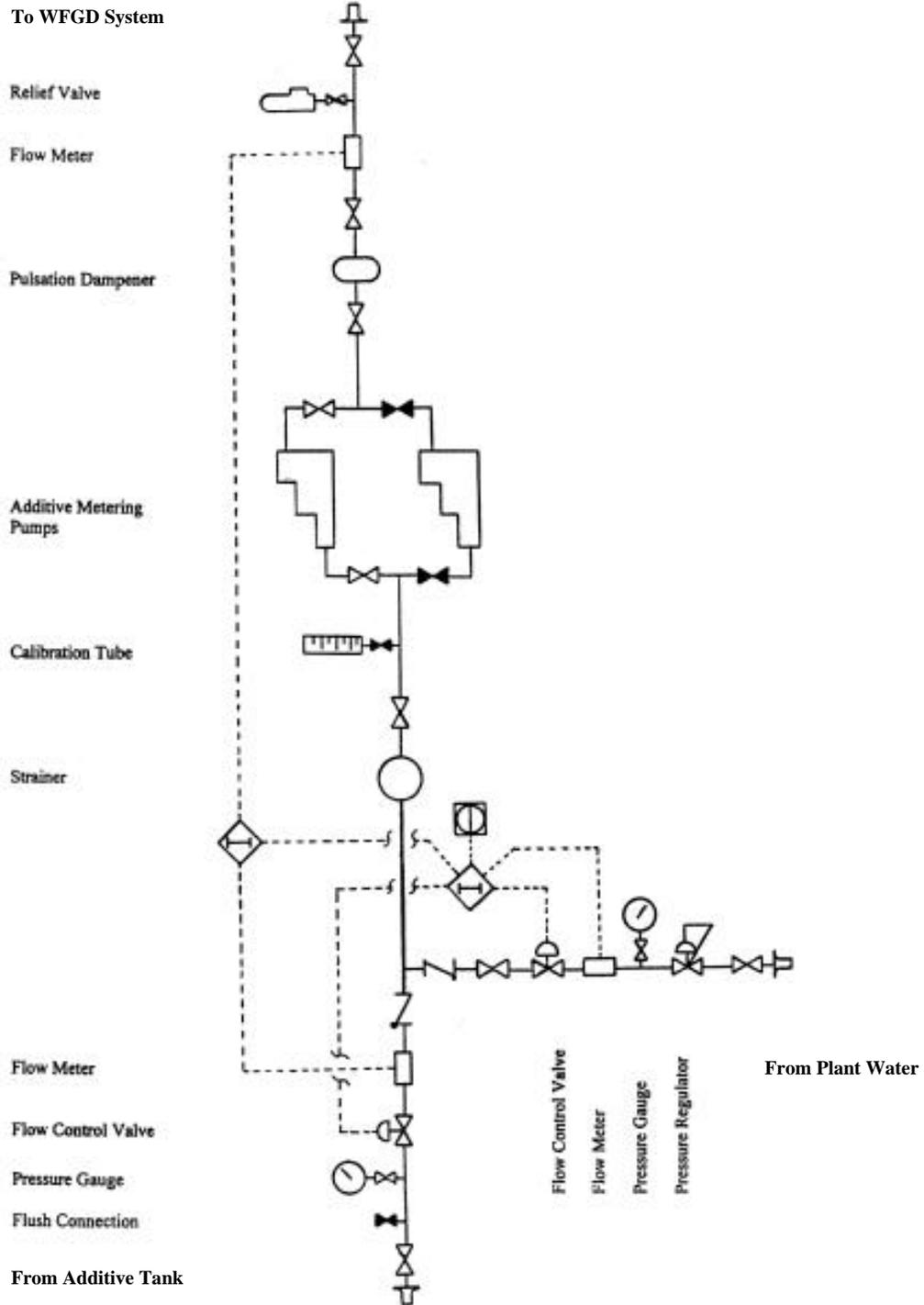


Figure 2-7 – Enhanced Wet FGD Equipment Schematic

2.3 Cost Analysis

2.3.1 Unscrubbed Systems

Based on the design described in Section 2.2.2, annual levelized costs were estimated for a limestone injection system installed at a 400 MW_e coal-fired plant. The costs were calculated based on the total capital requirement, distributed over a 15-year life, plus yearly operating and maintenance costs. EPRI's (Electric Power Research Institute) TAGTM *Technical Assessment Guide* (EPRI Report P-6587-L) was used as the basis for the calculations. The starting point for the total capital requirement was the installed equipment cost – all other capital costs were determined by applying factors to the installed equipment cost. Included as other capital/investment costs were engineering, general facilities, project contingency, process contingency, pre-production costs, inventory costs and a one-time licensing fee.

Yearly operating costs included the sorbent (10,100 lbs/hr @ \$25/ton delivered), parasitic power (168 kW @ \$0.067/kW-hr), and incremental ash disposal costs (7,050 lbs/hr @ \$20/ton), as well as a substantial capital carrying charge. A unit capacity factor of 65% was assumed for the calculation of variable operating costs. Incremental costs for operation, maintenance, and supervision were also included as fixed operating costs. The estimated total levelized cost for the system is \$2,700,000/yr or \$10.40/kW (annual basis). An assumed mercury removal efficiency of 56% yields an incremental mercury removal (relative to the 18% baseline removal) cost of about \$21,000/lb Hg. The limestone flow rate for this case corresponds to 0.35 moles Ca/mole S in the coal, or about 175,000 lbs/lb Hg.

A similar estimating procedure yielded a mercury removal cost of \$17,500/lb Hg for an activated carbon injection system. This estimate assumes an activated carbon cost of \$0.53/lb. Costs for the activated carbon itself represent about 70% of the total cost. The levelized costs for activated carbon injection are based on a carbon-to-mercury mass ratio of 9000:1. When tested in the B&W CEDF, this flow rate of carbon yielded a mercury removal efficiency of 56% when firing bituminous coal.

The limestone and carbon injection cases illustrated, above, result in similar mercury removal efficiencies at similar annual costs. However, a second limestone injection test in the CEDF

conducted at a limestone flow rate equivalent to a Ca/S molar ratio of 0.04 (or about 20,000 lbs limestone/lb Hg) yielded a mercury removal efficiency of 45%. This results in a significantly lower removal cost than the previous cases. More extensive parametric testing with both sorbents would be required to quantify the relative economics over a range of coal types, removal efficiencies, and operating conditions.

Limestone injection seems to offer a low-cost alternative to activated carbon injection for mercury control at modest levels of mercury removal. It may be particularly effective where a fabric filter is used for particulate control. A fabric filter provides for more intimate contact between the sorbent and flue gases than does an ESP. Of course this same characteristic of fabric filter systems may also improve performance of the activated carbon process.

Limestone injection for mercury control appears to be somewhat analogous to limestone injection for SO₂ control (a process commonly referred to as LIMB). In each case the limestone injection process offers modest removal efficiency at low capital cost, and relatively low operating cost. For electric utilities, limestone injection for SO₂ control has largely been overshadowed by higher efficiency processes such as wet scrubbing due to the way in which SO₂ regulations have been promulgated. Whether or not low-efficiency, low-cost mercury removal processes find commercial application may well depend on how mercury emissions are regulated.

2.3.2 Scrubbed Systems

Annual levelized costs were estimated for B&W's enhanced wet FGD process installed at a 500 MW_e coal-fired plant. The costs were calculated comprising the total capital requirement, distributed over a 20-year life, and yearly operating and maintenance costs. EPRI's (Electric Power Research Institute) TAGTM *Technical Assessment Guide* (EPRI Report P-6587-L) was used as the basis for the calculations.

The starting point for the total capital requirement was the installed equipment cost – all other capital/investment costs were determined by applying factors to the installed equipment cost. Included as other capital costs were engineering, general facilities, project contingency, process contingency, pre-production costs, inventory costs and a one-time licensing fee. Yearly operating costs included the reagent, water, and parasitic power costs, as well as a substantial carrying charge. Since existing plant operating personnel can easily assume the duties of operating and monitoring the B&W system, no costs were included for additional operating labor.

The levelized cost for the B&W enhanced wet FGD mercury removal process added to an *existing* wet scrubber is estimated to be \$1,000 per pound of mercury removed. This cost is significantly lower than that reported, above, for the activated carbon injection system – \$17,500/pound of mercury removed. The cost of mercury removal for the B&W process is only 5.7% of the cost of using activated carbon.

The cost for activated carbon injection is based on a carbon:mercury mass ratio of 9000:1, which yielded an incremental mercury removal of 38% in tests conducted in the CEDF. Reported values for C:Hg ratios necessary to achieve 90% mercury removal range from 6000:1 to in excess of 30,000:1. Figure 2-8 provides a comparison between activated carbon injection over a range of C:Hg ratios with the B&W process *including the levelized costs for the addition and operation of a new wet FGD system*. Assumptions for this comparison include (in addition to those made for the calculations, above):

- Plant Size: 500 MW_e, 75% capacity factor
- Coal Mercury Concentration: 0.05 to 0.25 ppm
- Wet Scrubber Capital Costs: \$6.00/kW
- Wet Scrubber Material Costs: \$1.00/kW
- Wet Scrubber Personnel Costs: \$4.00/kW
- Baseline Mercury Removal in Scrubber: 50%
- Particulate-Phase Mercury: 20% of total

It can be seen that the levelized costs for the B&W process (including the cost of the wet scrubber) are more-or-less independent of the mercury concentration in the coal. This is due to the relative costs of the wet scrubber (\$11/kW) compared to the incremental cost of the enhanced mercury removal system – \$0.08/kW to \$0.42/kW, depending on the mercury concentration in the coal. It is important to note that the B&W enhanced wet FGD system – *including the costs for the addition of a wet scrubber* – can be competitive with activated carbon systems, depending on the mercury concentration in the coal and the mercury emissions target.

It is also important to note that this comparison takes no credit for the SO₂, H₂SO₄, HCl, or HF removal benefits of the addition of the scrubber. Further, the analysis does not take into account the potentially significant fuel cost savings made possible by the wet scrubber by enabling a utility to switch back to a higher-sulfur local coal. An additional benefit of the scrubber approach is that no impact on ash utilization or disposal is anticipated. The activated carbon system may well result in higher ash disposal costs due to the presence of the carbon in the fly ash. Furthermore, installation of a spray cooling system and/or an additional fabric filter may be required to achieve high removal rates with activated carbon.

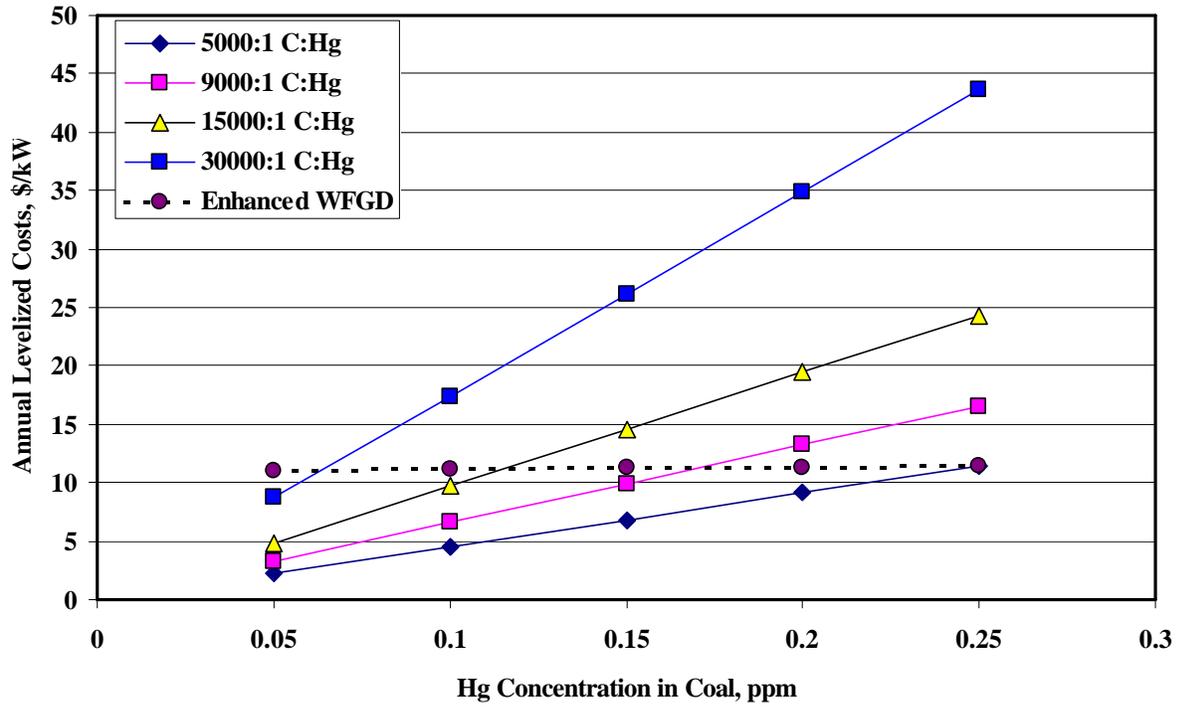


Figure 2-8 – Annual Cost Comparison for Wet FGD and Activated Carbon

2.4 Preliminary Assessment of the Market

This activity focused on evaluating the existing U.S. coal-fired utility boiler population with respect to various design parameters (unit size and location, FGD system type, reagent type, extent of mercury oxidation, etc.) to quantify the potential impacts of B&W's control technologies on mercury emissions from U.S. utilities. The estimates are based on a detailed coal-fired utility plant database and data obtained during pilot-scale testing.

A summary of the current U.S. coal-fired utility boiler population is shown in Table 2-5. The units are arranged by geographic location (east or west of the Mississippi River), coal type, FGD type (if applicable), and particulate control device (PCD). The categorical breakdowns are based on EPA-supplied data. The six highlighted rows correspond to the six largest categories and represent 85% of the total U.S. generating capacity. For simplicity, the various mercury removal impact scenarios are calculated using only these six categories. These scenarios also assume that no fuel switching occurs. Three mercury removal impact scenarios are shown in the table and represent:

- **Current:** The amount of mercury removal currently achieved with existing pollution control equipment.
- **Enhanced w/o Oxidation:** The amount of mercury removal possible with the application of B&W's control technologies (sorbent injection for unscrubbed units, enhanced wet FGD for units equipped with wet scrubbers).
- **Enhanced w/Oxidation:** The amount of mercury removal possible with the application of the B&W control technologies *and* the application of a technology capable of oxidizing 80% of the elemental mercury in the flue gas prior to (upstream of) the mercury removal process.

To be effective, oxidation of the mercury needs to be effected upstream of the mercury removal process. The use of SCR catalyst for mercury oxidation, for example, is expected to impact mercury removal in the enhanced wet FGD process since the SCR unit is located upstream of the wet scrubber. The effectiveness of the SCR approach for the sorbent injection process, on the other hand, is not known. The sorbent is injected into the flue gases in the upper furnace (well upstream of the SCR), and removed from the flue gases in the particulate collector (downstream

of the SCR). The impact of mercury oxidation across the SCR on mercury removal by the sorbent is therefore dependent on the temperature window in which the mercury is adsorbed by the sorbent. Unfortunately, the time-temperature relationship for mercury removal by the limestone is currently unknown.

For each of the three scenarios illustrated in the table, a weighted-average removal (and corresponding estimated emission rate) is calculated based on the installed generating capacity for each category. For example, the “Current” weighted-average mercury removal is 35%, resulting in an estimated emission rate of 54 tons/yr of mercury. This estimate agrees well with the generally-reported emission rate of 50 to 55 tons/yr of mercury.

Table 2-5 – U.S. Coal-fired Generating Market Summary

Location	Coal Type	FGD Type	PCD Type	MW	% of Total MW	Hg Removal Impact Scenarios		
						Current	Enhanced w/o Hg ⁰ Oxidation	Enhanced w/ Hg ⁰ Oxidation
Scrubbed Units								
East	Bit	Wet	ESP	39,345	12.8	63%	80%	92%
East	Bit	Wet	Other	3,496	1.1			
East	Bit	Dry	ESP	160	0.1			
East	Bit	Dry	Other	3,017	1.0			
East	Sub	Wet	ESP	1,954	0.6			
East	Sub	Wet	Other	44	0.0			
West	Bit	Wet	ESP	2,305	0.8			
West	Bit	Wet	Other	1,498	0.5			
West	Bit	Dry	Other	1,256	0.4			
West	Sub	Wet	ESP	13,412	4.4	57%	72%	91%
West	Sub	Wet	Other	9,867	3.2	57%	72%	91%
West	Sub	Dry	ESP	1,562	0.5			
West	Sub	Dry	Other	4,588	1.5			
West	Lig	Wet	ESP	8,726	2.8			
West	Lig	Dry	Other	1,380	0.4			
Scrubbed Totals				92,610				
Unscrubbed Units								
East	Bit	NA	ESP	109,659	35.7	18%	66%	79%
East	Bit	NA	Other	2,974	1.0			
East	Sub	NA	ESP	45,431	14.8	39%	63%	82%
East	Sub	NA	Other	1,807	0.6			
West	Bit	NA	ESP	2,438	0.8			
West	Bit	NA	Other	864	0.3			
West	Sub	NA	ESP	40,858	13.3	39%	63%	82%
West	Sub	NA	Other	6,795	2.2			
West	Lig	NA	ESP	1,031	0.3			
West	Lig	NA	Other	2,430	0.8			
Unscrubbed Totals				214,287		Weighted-Average Removal		
U.S. Totals				306,897		35%	68%	83%
						Estimated Emission Rates, ton/yr		
						53.8	26.9	14.2

The results presented in Table 2-5 illustrate several key considerations for improving mercury removal performance for coal-fired utilities:

- Two-thirds of U.S. generating capacity is supplied by bituminous and subbituminous coal-fired units equipped with an ESP, only. Improved mercury control for these units will have a major impact on the nationwide emissions rate.
- Applying B&W's enhancement technologies to both scrubbed and unscrubbed units results in a 50% decrease in the emissions rate, from 54 tons/yr to 27 tons/yr.
- Combining B&W's control technologies with an oxidation technology capable of oxidizing 80% of the elemental mercury results in a further reduction of 50%, down to 14 tons/yr. This reduction is due in large part to the conversion (and capture) of the large amount of elemental mercury generated by the subbituminous coal-fired units. As described, above, this scenario assumes an as-yet unidentified method for oxidizing mercury in such a way as to improve mercury capture for the sorbent injection process.
- Even with the high levels of oxidized mercury generated in the oxidation-based scenario, sorbent injection removes less mercury than enhanced wet FGD.

Table 2-6 further illustrates the importance of mercury oxidation technologies for high levels of mercury removal on a national scale. In the table, the results of the three scenarios, above, are repeated along with two additional scenarios (again, no fuel switching is included). The two additional scenarios are:

- All Enhanced WFGD w/o Oxidation: In this scenario, all units (both scrubbed and unscrubbed) are equipped with B&W's enhanced wet FGD process.
- All Enhanced WFGD w/Oxidation: In this scenario, all units are equipped with B&W's enhanced wet FGD process *and* an oxidation technology capable of converting 80% of the elemental mercury to oxidized mercury.

Table 2-6 – Impact of Elemental Hg Oxidation

Scenario Number	1	2	3	4	5
	Current	Enhanced w/o Hg ⁰ Oxidation	Enhanced w/ Hg ⁰ Oxidation	All E-WFGD w/o Hg ⁰ Oxidation	All E-WFGD w/ Hg ⁰ Oxidation
Weighted-Average Removal	35%	68%	83%	76%	92%
Estimated Emission Rate, tons/yr	53.8	26.9	14.2	19.6	6.7

The results shown in Table 2-6 indicate that utilizing enhanced wet FGD for all units without a mercury oxidation technology (Scenario 4) yields higher mercury removals than the combination of sorbent injection for unscrubbed units and enhanced wet scrubber control for scrubbed units (Scenario 2). It can also be seen that mercury removal can be dramatically increased with the addition of an oxidation technology (Scenarios 2 versus 3 or Scenarios 4 versus 5). The emission rate for Scenario 5 is equivalent to an average plant removal (from as-fired coal to stack) of 92%, compared to an average plant removal of 76% in the absence of an oxidation technology.

In lieu of a viable elemental mercury oxidation technology, a potential option for increasing the level of oxidized mercury (and subsequently increase mercury removal efficiency) would be for plants currently firing low sulfur, subbituminous coal to switch to higher sulfur bituminous coal and install a B&W enhanced wet FGD system. Specifically, this option would target eastern plants that switched to a western subbituminous coal to meet SO₂ emissions requirements. As described, above, western coals typically generate significantly higher percentages of elemental mercury than do eastern coals – a significant disadvantage with respect to mercury removal.

As presented in Section 2.3.2, B&W’s enhanced wet FGD process may be cost-competitive with an activated carbon system – even when the entire cost of the wet scrubber is included in the mercury removal cost. For some plants, it may be cost-effective for these plants to switch back

to the local high sulfur coal (with its significantly lower shipping costs and higher oxidized mercury formation) and install an enhanced wet FGD system for SO₂ and mercury control, as opposed to installing an activated carbon system for mercury control, alone. This approach has the additional advantages of reducing H₂SO₄, HCl, and HF emissions.

The potential impact of this option is shown in Table 2-7, wherein four scenarios are shown. The first represents the current emissions as shown in Table 2-5. Scenario 2 assumes that all units currently equipped with wet scrubbers apply B&W’s enhanced wet FGD process. Scenario 3 includes Scenario 2 *plus* the assumption that all unscrubbed eastern units currently firing subbituminous coal (45,431 MW_e from Table 2-5) switch to an eastern bituminous coal *and* install an enhanced wet FGD system. Scenario 4 includes Scenario 3 *plus* the assumption that all unscrubbed eastern units currently firing low sulfur bituminous coal (109,659 MW_e from Table 2-5) switch to a higher sulfur (and presumably less expensive) bituminous coal *and* install an enhanced wet FGD system. It can be seen that, even without a viable mercury oxidation technology, B&W’s enhanced wet FGD process can have a significant impact on national mercury emissions levels.

Table 2-7 – Impact of Coal Switch + B&W’s Wet FGD Process

Scenario Number	1	2	3	4
	Current	Scrubbed Units w/ Enhanced WFGD	Scenario 2 + East Sub Switch	Scenario 3 + East Bit Switch
Weighted-Average Removal	35%	39%	46%	73%
Estimated Emission Rate, tons/yr	53.8	50.6	44.7	22.9

3.0 Fate of Mercury

3.1 Overview

The objectives of this task were to investigate the ultimate fate of mercury contained in coal combustion products (CCP) and how emerging mercury control technologies may affect this fate. Previous sections of this report illustrate that much of the mercury released during coal combustion can be adsorbed using an injected sorbent which is subsequently removed with the fly ash, or can be absorbed in a downstream flue gas desulfurization unit. However, little work has been done to determine if the mercury removed with the CCP is in a stable form, or a form that can be leached into ground water or vaporized in subsequent treatment or utilization processes. The use of sorbents or additives to remove mercury may also affect the suitability of CCP for reuse.

This task focuses on the main methods of disposal and reuse for CCP. CCP can be divided into two categories:

- Ash, which includes fly ash, bottom ash, and slag
- FGD waste, which includes all forms of FGD sludge, but mainly the gypsum produced in wet scrubbers that employ limestone forced oxidation systems

The American Coal Ash Association publishes a breakdown of all CCP produced in the U.S. each year and how much of this material is recycled for other uses. In 1998, the main use for ash was in the cement/grout industry (13%) and most of the rest was landfilled (66%). A small percentage was used for other purposes. For FGD wastes, a large portion was landfilled (91%), and some was used in the wallboard industry (6%). Therefore, work under this task is focused on the fate of mercury as it applies to landfills and the cement and wallboard industries.

Section 3.2 of this report focuses on conventional chemical characterization, like the Toxicity Characteristic Leaching Procedure (TCLP), EPA Method 1311. Samples from pilot-scale tests were evaluated via the TCLP for their mercury leaching characteristics. Section 3.3 of the report presents the development and results of a new procedure to test the thermal stability of mercury

compounds in CCP waste. Both the cement and wallboard processes employ heating steps that could release the mercury captured in the CCP wastes if the mercury compounds are not suitably inert. The procedure is based on the use of a mercury analyzer that can detect low levels of mercury in the off gas from heated CCP waste samples.

3.2 Conventional Chemical Testing

This section presents the results of conventional wet chemistry testing on various CCP waste samples. The main procedure used is the Toxicity Characteristic Leaching Procedure (TCLP), EPA Method 1311. This method involves a 20:1 dilution of a small sample of CCP waste in a weak acid solution. The solution is then analyzed to determine if mercury has leached from the sample. For these types of materials, the TCLP limit is 0.2mg Hg/l. Materials with concentrations below this limit are acceptable for landfill without additional treatment.

Waste samples from pilot tests conducted in October, 1999, were collected from the wet scrubber and ESP for each test run. These samples were filtered, and the solid and liquid fractions were analyzed for total mercury. According to the TCLP method, a sample can contain up to 4mg Hg/kg and still meet TCLP limits because of the 20:1 dilution. For these tests, if the solids contained less than 0.2mg Hg/kg, a TCLP was not done because the subsequent dilution would reduce the mercury concentration well below the TCLP limit.

Table 3-1 illustrates the results of the tests. Column 1 is the test number. Column 2 shows the Test ID used by MTI. The final letter in the ID corresponds to the particular Ontario Hydro sample train (triplicates were performed for each test condition) during which the sample was collected. Shaded cells indicate that the sample was further tested for thermal stability as explained in the next section. Column 3 shows the code used by MTI to identify which technology was being tested without divulging proprietary information. Column 4 shows the solids content (in percent) of the slurry samples. Column 5 shows the total mercury contained in the solid portion of the samples. This column shows that “non-detects” were obtained for all but three samples. Columns 6-8 show the total mercury contained in the solid portion of the samples for additional tests that will be explained below. Column 9 shows the total mercury contained in the liquid portion of the samples. For the slurry samples, no mercury could be detected in the

filtrate. For two of the ESP ash samples (which were taken during sorbent injection tests), subsequent TCLP tests showed that the mercury was below the detection limit of 0.01mg Hg/l. This is important because it shows that the form of mercury in these samples is not soluble (e.g., not HgCl₂) and that the solubility was not affected by the use of the mercury control technologies.

Table 3-1 – Results of Mercury Analyses on October Waste Samples

Wet Scrubber Sludge Analysis				Hg in Solids, mg/kg dry				Filtrate
Test	MTI ID	Code	% solids	Std 1	Std 2	HNO ₃	HNO ₃ /HCl	mg/l
1	WS-1C	Baseline	38.9	#N/A	0.072	0.064	0.069	<0.00050
2	WS-2B	App1 0.1x	39.2	#N/A	0.074	0.074	0.064	
3	WS-3C	App1 0.01x	39.1	#N/A	0.069	0.072	0.079	
4	WS-4C	App1 1.0x	48.0	#N/A	0.075	0.081	0.081	
5	WS-5C	Alt App1	48.8	#N/A	0.160	0.160	0.160	
6	WS-6C	App2 0.25x	52.3	#N/A	0.130	0.130	0.140	<0.00050
7	WS-7B	Alt App1+App2	52.6	0.21	0.190	0.190	0.190	<0.00050
8	WS-8C	App1+App2	52.7	#N/A	0.150	0.150	0.160	<0.00050
9	WS-9C	App2 0.125x	54.8	#N/A	0.093	0.091	0.100	<0.00050
ESP Ash Analysis					TCLP			
SI-1	SI-1C	Sorb1 350F		#N/A	0.038	0.031	0.031	
SI-2	SI-2B	Sorb2 250F		0.22				<0.01
SI-3	SI-3C	Sorb3 750F		0.34				<0.01

= Tested by Thermal Decomposition

Method Key:

Std1 = SW846-7471

Std2 = SW846-7471 w/high mass sample

HNO₃ = 50% HNO₃ at room temp for 60 min

HNO₃/HCl = 50% HNO₃/HCl at room temp for 60 min

Filtrate = SW846-7470A / EPA 245.2

TCLP = SW846-1311

If meeting TCLPs limits were the only goal of this study, testing would have stopped at Column 5. However, in order to study the effect of the various mercury control technologies on waste characteristics, additional information was needed from the samples. Therefore, the basic analytical technique used to determine total mercury was revised by increasing the initial sample

size to decrease the detection limits, thus producing the results shown in Column 6 (Std 2). This column shows that the mercury concentration in the wet scrubber module gradually increased during the test. This is predicted by mass balance calculations that indicate a steady-state mercury level of 0.5mg Hg/l should eventually be reached. The drop shown in Test 9 was caused when half the slurry in the recirculation tank was dumped in preparation for Test 9.

The analytical procedure for total mercury calls for a very aggressive (and costly) digestion step because it was originally designed to completely dissolve all the various species in fly ash. The original procedure involves heating the sample in a sealed container for 1 hour in aqua regia (a mixture of concentrated hydrochloric (HCl) and nitric (HNO₃) acids). However, because of the low volatility of mercury, it is unlikely that any would be present in the fly ash particles that form at high temperatures in the upper furnace. Therefore, the digestion step was simplified to determine if the mercury compounds could be digested with weaker acids and in shorter times. The new procedure used a 50% acid solution and no heating (Columns 7&8 in Table 3-1). The digestion step was further studied to determine the minimum digestion time required. If adopted, this procedure would be less costly, less time consuming and safer to perform.

Figure 3-1 presents a comparison of the three digestion procedures. The good agreement between the methods suggests that the mercury is not strongly tied up within fly ash or gypsum and is relatively easy to digest. Also, no differences were detected in the mercury concentration for digestion times ranging from 5 min to 60 min. This does not imply that the mercury will leach in landfills. A 50% nitric or hydrochloric acid solution is much stronger than rainwater or the dilute acetic acid solutions used in TCLP test. However, this does imply that the mercury is not strongly bound with the fly ash or gypsum particles.

The same types of analyses were performed on samples from tests conducted in April of 2000. Table 3-2 illustrates the results. Again, the total mercury in the samples was far below a level that would necessitate further TCLP tests. In addition, no mercury could be detected in the filtrate, indicating that the mercury compound(s) formed in the waste through the use of the various mercury control technologies are relatively insoluble.

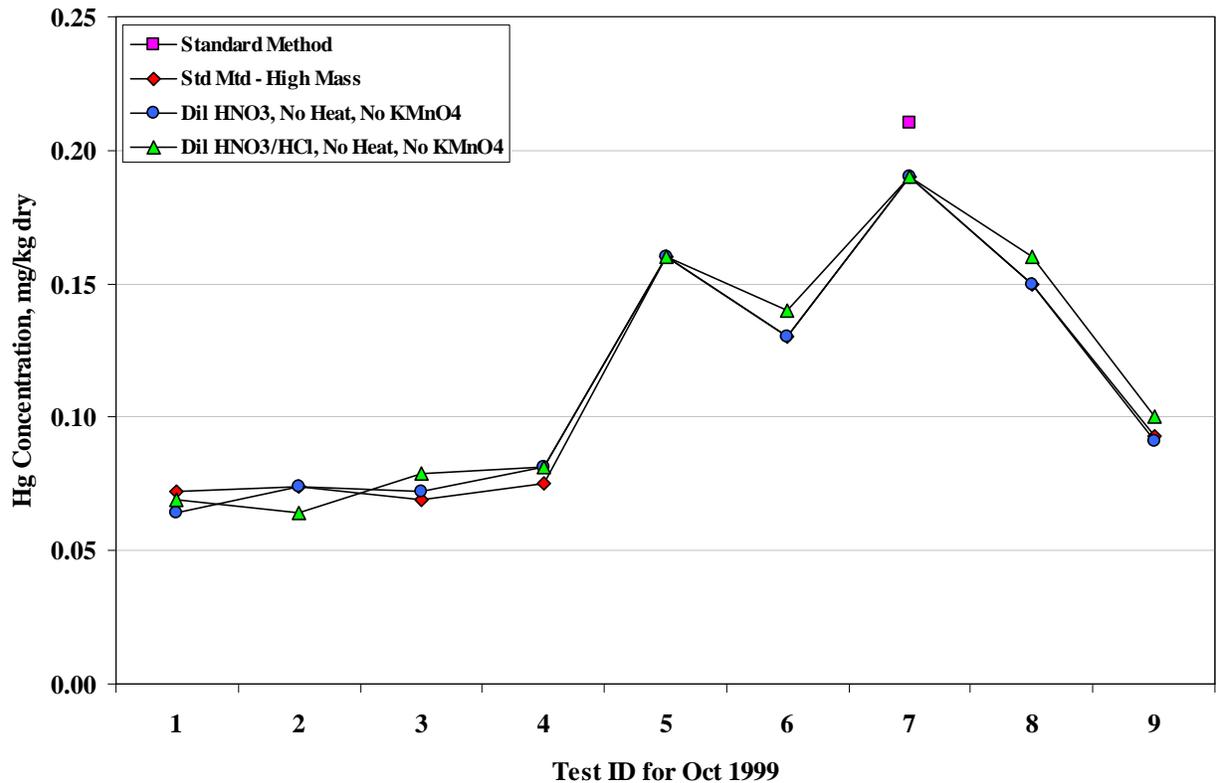


Figure 3-1 – Hg Concentrations in Wet Scrubber Hydroclone Underflow Slurry

The combined results of all the conventional chemical analyses show that, at least for the B&W mercury removal technologies tested, the mercury compound(s) formed are:

- insoluble by TCLP standards
- are present at levels far below the TCLP limits

and thus acceptable for disposal in a landfill.

Further speculation hints that the mercury removed in the wet scrubber forms a fine particulate, perhaps mercury sulfide (HgS). However, more tests are needed to confirm this. If the form of mercury could be determined, then much could be inferred about its fate in landfills (HgS is

insoluble in water and weak acids) and in the cement and wallboard industries (HgS has a relatively low vapor pressure at the processing temperatures of interest). The section below discusses the development and results of a thermal stability method that may provide more clues as to what mercury compounds are present in CCP wastes.

Table 3-2 – Results of Mercury Analyses on April Waste Samples

Wet Scrubber Sludge Analysis			Hg in Solids, mg/kg		Filtrate
Test	MTI ID	Code	% solids	Std 2	mg/l
1	WS2-2A	Base	45.0	0.130	<0.00050
2	WS2-2C	Alt App1A-1x	43.0	0.140	<0.00050
3	WS2-3C	Alt App1A-0.1x	44.0	0.180	<0.00050
4	WS2-4C	Base	47.0	0.150	<0.00050
5	WS2-5C	Alt App1A-0.02x	49.0	0.180	<0.00050
6	WS2-6B	Alt App1-1x	49.0	0.170	<0.00050
7	WS2-7B	Base	50.0	0.170	<0.00050
8	WS2-8B	Alt App1A-1x	50.0	0.200	<0.00050
9	WS2-9C	App2-Mix	53.0	0.140	<0.00050
ESP Ash Analysis					
9	WS2-9C	Base		<0.10	

= Tested with Hg CEM by Thermal Decomposition

Method Key:

Std1 = SW846-7471

Std2 = SW846-7471 w/high mass sample

Filtrate = SW846-7470A / EPA 245.2

TCLP = SW846-1311

3.3 Thermal Stability Tests

The results presented, above, indicate that the mercury in wet scrubber sludge, with or without the application of enhanced mercury removal technologies, exists in a form that is insoluble in the weak acid used in the TCLP method. Calculations also show that the mercury content in most coals is so small that, even if all the mercury ended up in the scrubber sludge in a soluble form, the sludge would still meet TCLP limits. Therefore, the focus of this study shifted to the development of a method to determine the thermal stability of mercury compounds in CCP wastes. If successful, the information could be used to predict the fate of mercury in any subsequent disposal or reuse application.

Normal wet chemistry and other analytical methods cannot be used to distinguish the various mercury compounds in CCP wastes because they are present in such small amounts. However, MTI recently purchased a mercury analyzer from PS Analytical that is capable of detecting mercury at very low concentrations in gas streams. The analyzer was used to develop a method to detect, as a function of temperature, the evolution of mercury from samples of CCP waste.

Figure 3-2 shows the vapor pressure curves for Hg and several simple mercury salts that may exist in CCP waste. The figure shows that different mercury compounds have significantly different vapor pressures at any given temperature. Theoretically, these differences could be used to help determine what mercury compounds exist in CCP waste – if the compounds exist as such. Adsorbed or absorbed forms of mercury and its compounds would significantly complicate the situation, of course. The the following sections describe the apparatus used in the thermal stability study, how standards were prepared and tested, problems encounter during the development of this method, and finally, the results of tests on samples from pilot tests at MTI and from several utility sites. In all, over 130 tests were conducted as part of this study.

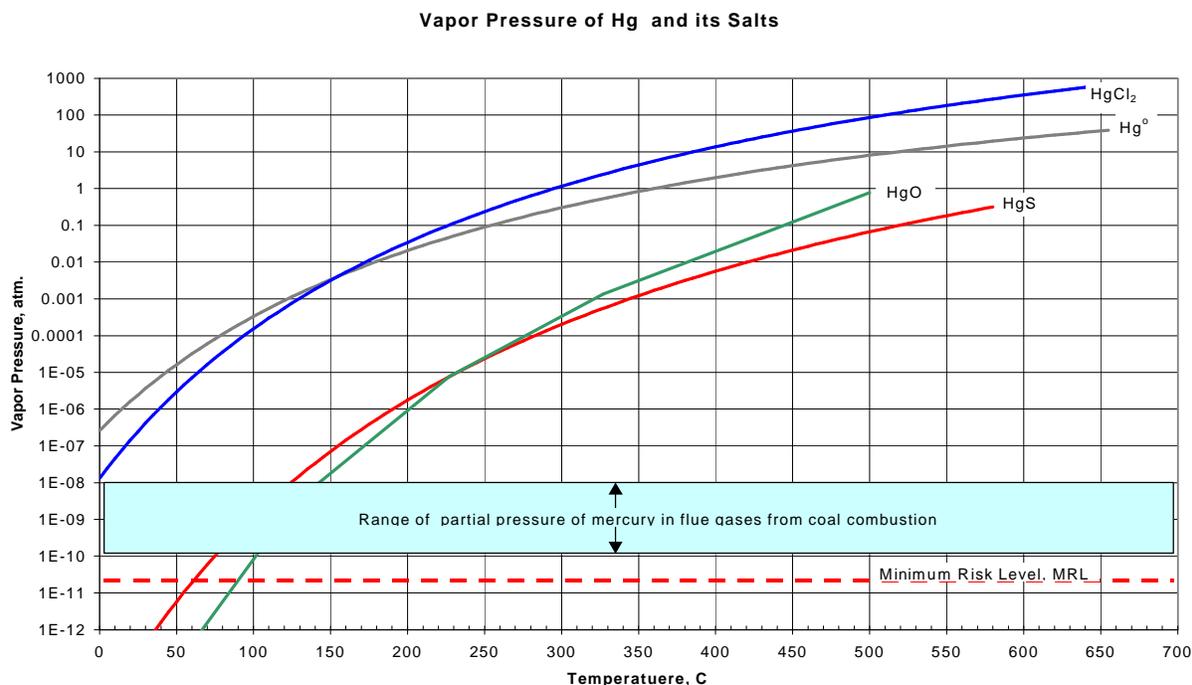


Figure 3-2 – Vapor Pressure of Hg and Select Hg Salts

3.3.1 Apparatus and Method

A schematic of the thermal stability test apparatus is shown in Figure 3-3. It consists of an argon source, an argon flow meter, a temperature-controlled tube furnace, a high temperature furnace, an impinger to convert all mercury to elemental mercury (Hg^0), a chiller to remove water vapor, space to test various traps and filters, and a PS Analytical Mercury Analyzer (PSA).

Temperature is measured at the sample location and in the pyrolyzer. Argon flow is held at 250 ml/min throughout each test. Test samples are placed in a glass sample boat (preheated to 800 C to purge mercury) and placed in the control oven. The samples are first heated to 140 C to evaporate all liquid water and evolve the waters of hydration of gypsum, and then to 600 C at a rate of 6 C/min. The temperature of 140 C was chosen to simulate the temperatures within the rotary kiln of a typical wallboard plant. This is the highest temperature to which most CCP wastes are typically exposed. Gases from the control oven then flow through the pyrolyzer to convert gaseous mercury compounds to elemental mercury. Mercury concentration in the gas is then measured by atomic fluorescence in the PSA and the data displayed and stored as a function of time and temperature.

Prior to testing, the oven was carefully probed with a separate thermocouple placed inside of an empty sample boat to determine the position at which the oven temperature coincided with the sample temperature. This was necessary because it was felt that any metallic thermocouple placed in the oven during an actual test could interfere with the mercury measurement.

Figure 3-4 shows that at a position of 4.75 inches from the leading edge of the heating element the sample temperature coincided very well with the oven temperature. The center of the sample boat was placed at this position for all tests after Nov 5, 2000 – which includes all of the data presented in this report.

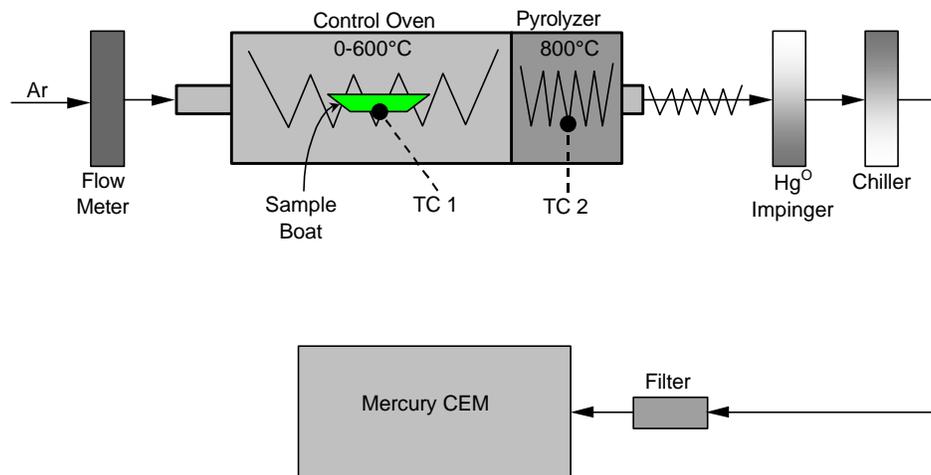


Figure 3-3 – Thermal Stability Test Apparatus

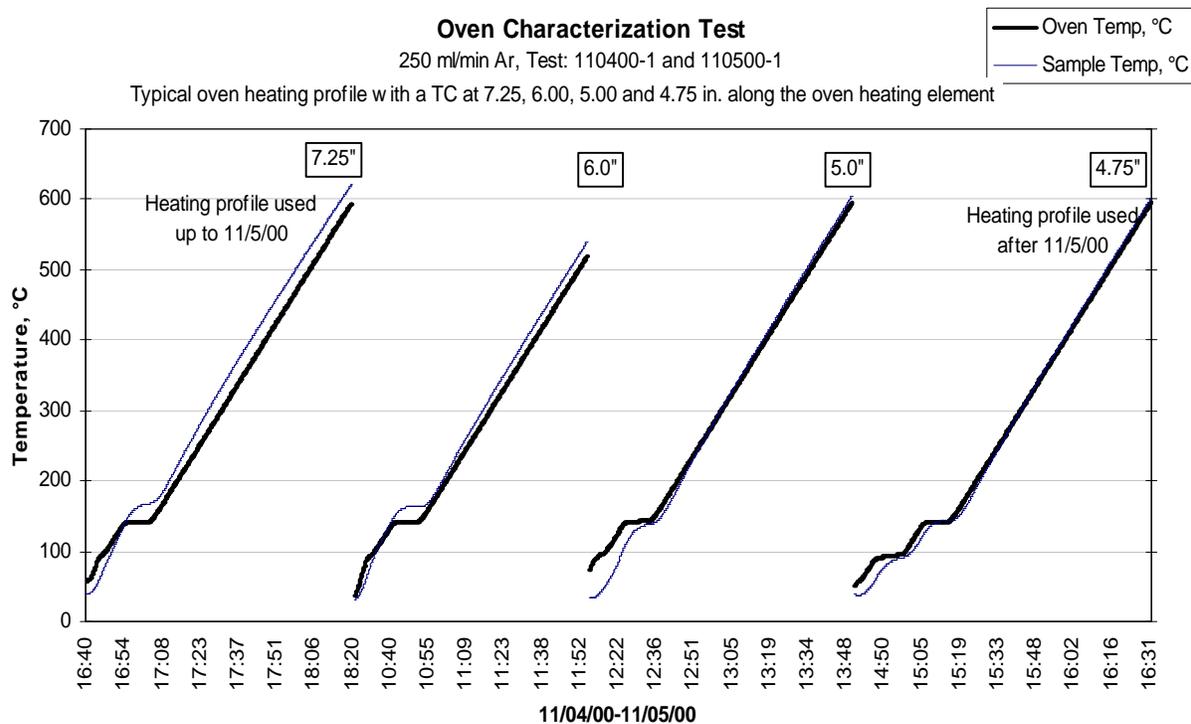


Figure 3-4 – Oven Characterization Test

3.3.2 Preparation and Testing of Standards

Standards made from pure mercury compounds were prepared and tested in order to generate plots for comparison with CCP wastes. It was beyond the scope of this study to test all possible mercury compounds, so several of the most likely compounds that may form in the wet scrubber environment were chosen: mercuric chloride (HgCl_2), mercuric sulfide (HgS), mercuric sulfate (HgSO_4) and mercuric oxide (HgO). Good test practices also call for the periodic testing of a blank, in this case either an empty sample boat or a boat filled with alumina (Al_2O_3) that was previously baked at 800 C, pure gypsum or distilled water.

At first, the standard compounds were dissolved in the appropriate acids and diluted to about 1 ppm. However, subsequent tests gave poor results. A new method was therefore developed whereby the mercury compounds were ground and diluted with pure alumina. The alumina was prebaked at 800 C. The target concentration was about 1 ppm Hg. These standards produced

reliable and reproducible results in subsequent tests. They were also used in later tests to spike waste samples in an attempt to identify particular mercury compounds.

Figure 3-5 shows the thermal stability curve (TSC) produced during a typical test. This test represents a blank consisting of an empty sample boat that had been washed and prebaked in a muffle furnace (as was done for all tests). The title indicates the sample tested, the flow rate of argon, the composition of the impinger solution, the heat rate of the sample and the test ID. The x-axis shows the date and time of the test. The left-hand y-axis shows control oven temperature in degrees Celsius. The temperature curve for this test shows that the sample was quickly heated from room temperature to 100 C, held at 100 C for 30 min, heated at 6 C/min to 140 C, held at 140 C for 10 min, then heated to 400 C at 6 C/min. The control oven has 12 programmable heating rates and pauses. The heating curve was often changed depending on what type of material was being analyzed, but in general the rate of heating was typically 6 C/min.

The right-hand y-axis shows mercury concentration. No units are given because the software controlling the mercury analyzer was not written for the case in which the gold trap is bypassed, as was done for this study. However, it is roughly equivalent to $\mu\text{g}/\text{Nm}^3$. A precise calibration method will be developed if the results of this study warrant further development. Furthermore, the most important information to be gained from this study is the temperature at which mercury is detected, the general shape of the mercury curve and the relative area under the curve. Exact concentrations are only needed if this method were to be used to measure the exact amount of mercury in the samples, for which there are already adequate wet chemistry techniques. The value of the mercury concentration for this test shows a “background” concentration of about 7. The “background” level is a consequence of not being able to precisely calibrate the instrument. The overall conclusion is that Figure 3-5 shows that no mercury was evolved from the sample boat.

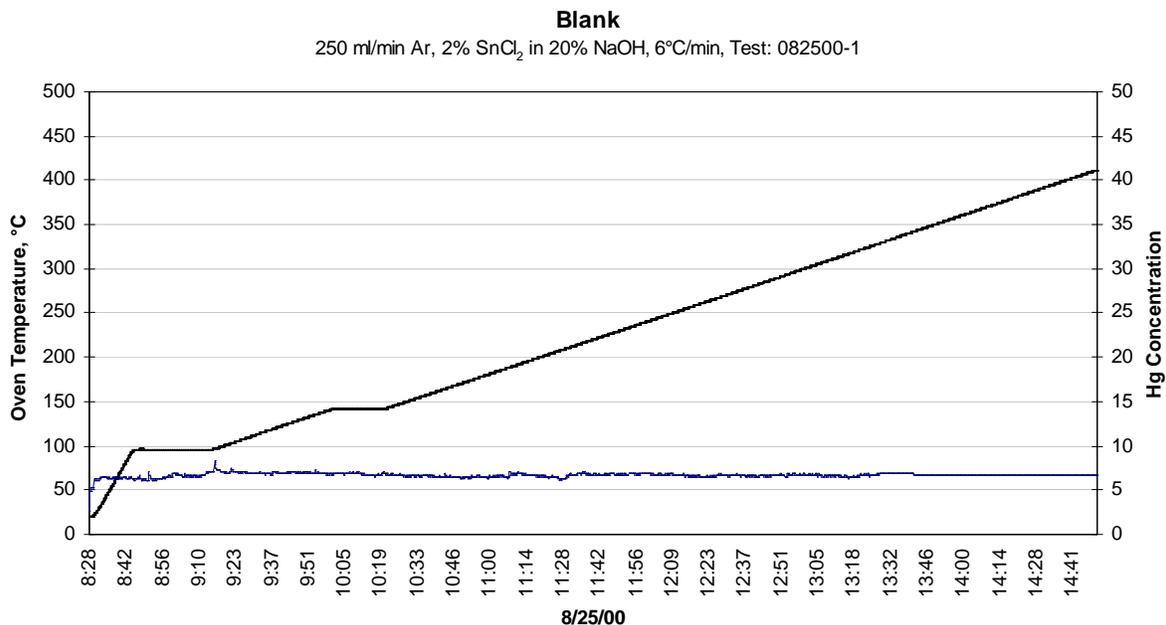


Figure 3-5 – Blank Sample Boat

Figure 3-6 shows the TSC for laboratory-grade gypsum. The small peak at 200 C may represent some mercury contamination in the sample or it may be caused when the waters of hydration released from the sample free some mercury that had deposited in the apparatus (this phenomenon will be further discussed, below). The area under the mercury curve is also given. It can be proportioned with the sample weight given in the title to determine a *relative* mercury concentration.

Figure 3-7 shows the TSC for three sample weights of a HgSO₄ standard. This figure shows that the area under the curve can be used to compare the relative amounts of mercury in the samples. The sample weights tested were equivalent to about 1x, 0.5x and 0.25x and this corresponded well to the areas under the curve of 0.999, 0.496 and 0.245, respectively.

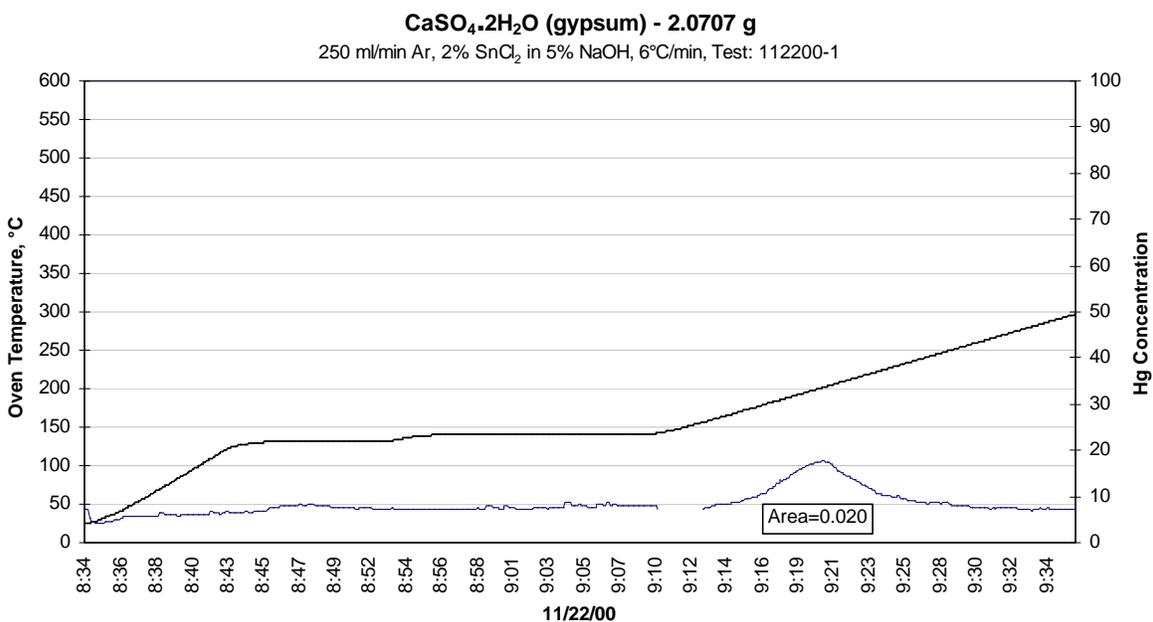


Figure 3-6 – Gypsum Blank

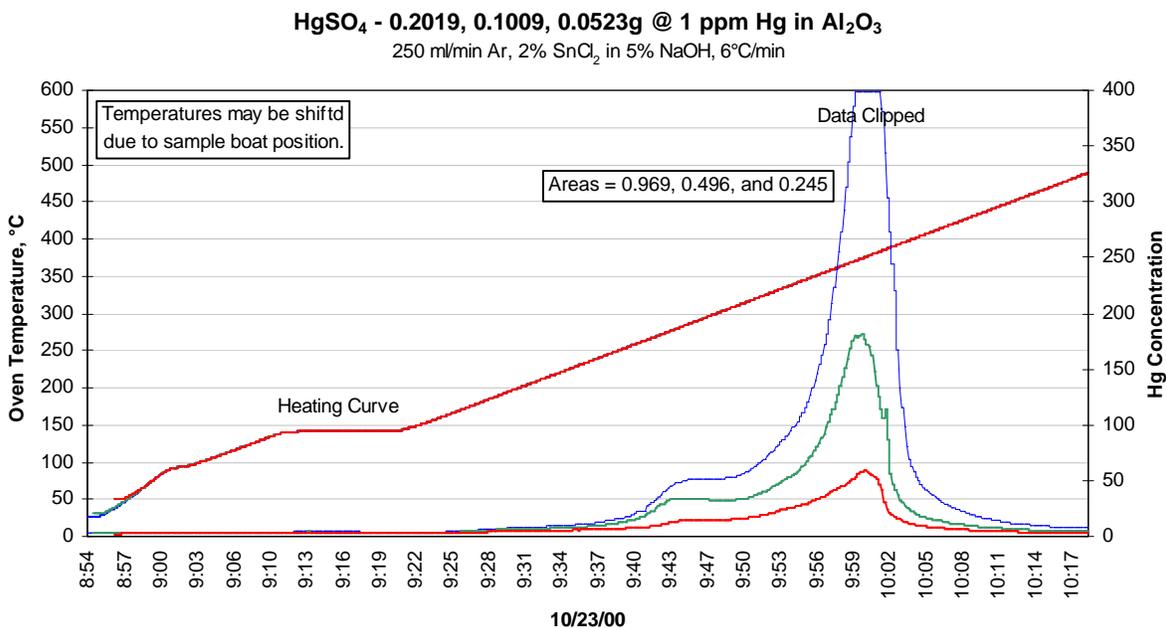


Figure 3-7 – Multiple TSCs for the HgSO₄ Standard at Various Sample Weights

Figures 3-8 through 3-11 show the TSCs for the HgCl₂, HgO, HgSO₄, and HgS standards, respectively. The figures shows several interesting things. First, in all cases, only a small fraction of the total mercury is evolved up to 140 C. The samples evolve mercury according to somewhat different time-temperature relationships. The curves are in general agreement with the vapor pressure data presented in Figure 3-2. Unfortunately, as reported by this method, three of the four compounds chosen for this study evolve mercury at similar peak temperatures (~300 C).

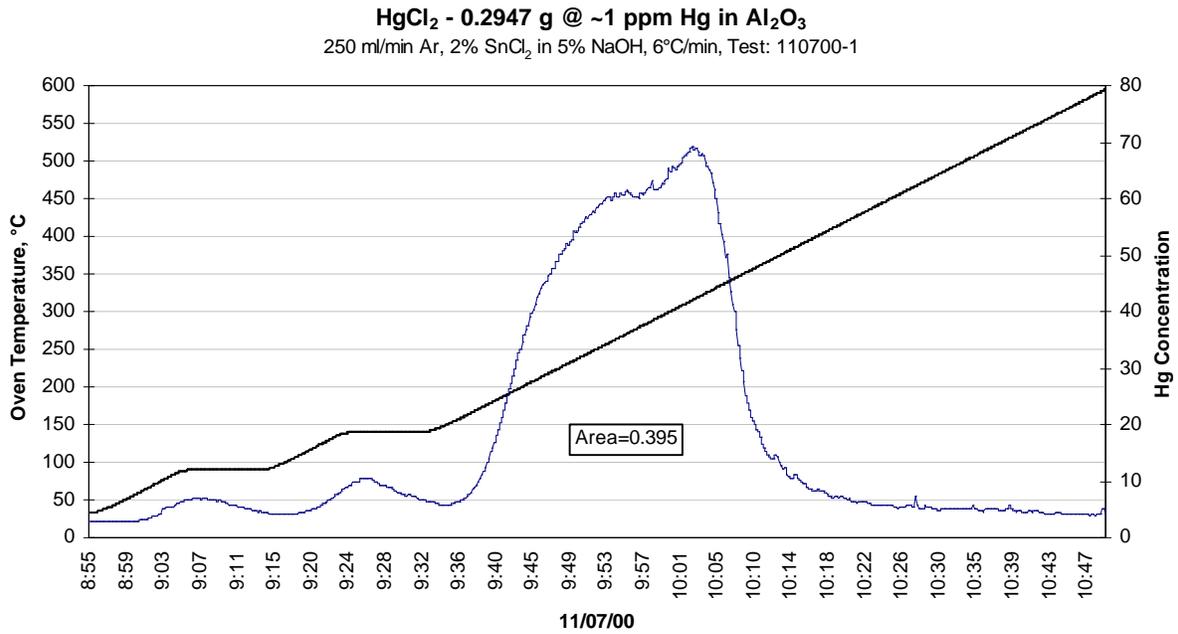


Figure 3-8 – TSC for the HgCl₂ Standard

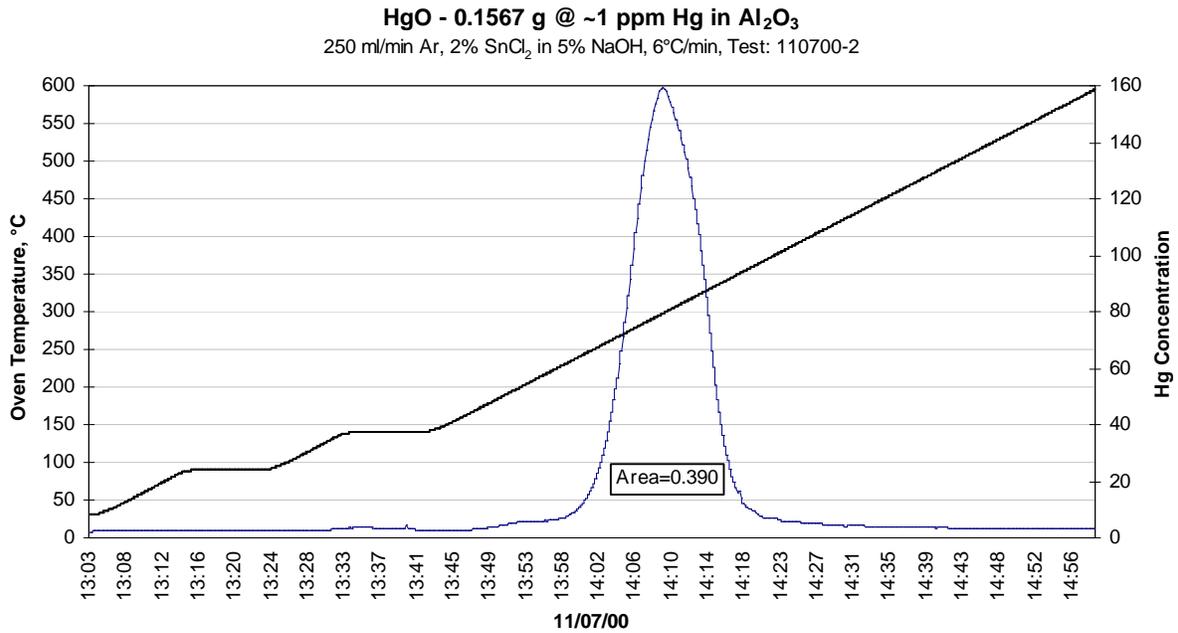


Figure 3-9 – TSC for the HgO Standard

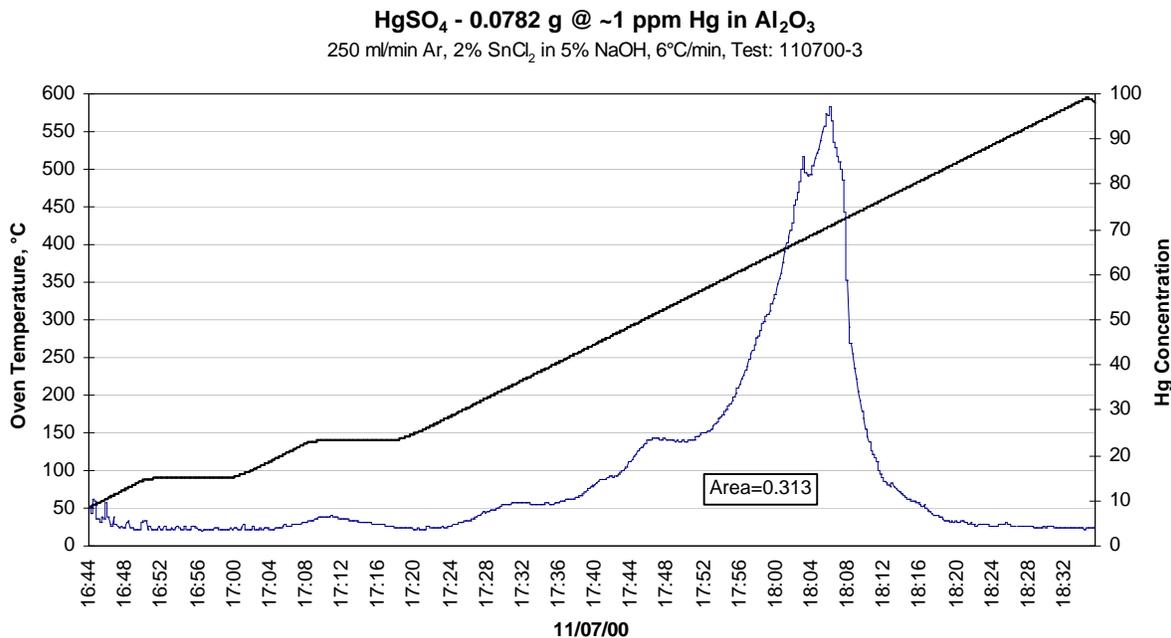


Figure 3-10 – TSC for the HgSO₄ Standard

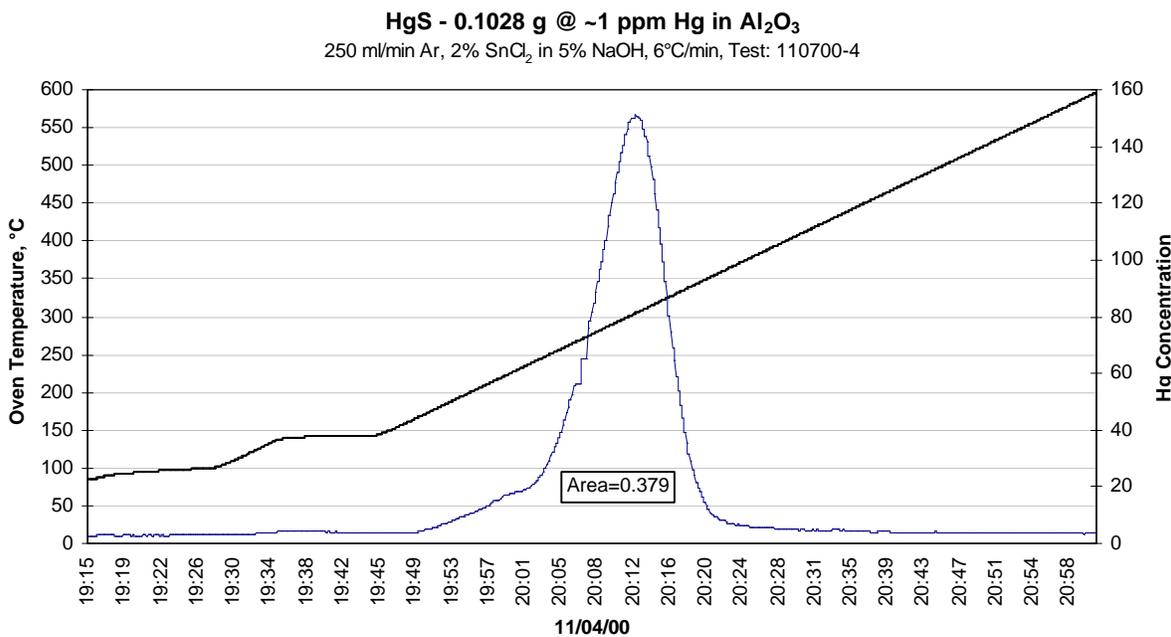


Figure 3-11 – TSC for the HgS Standard

Figure 3-12 shows the TSC for a combination of the HgCl_2 and HgS standards. The figure shows the effect of having multiple compounds within the same sample with similar expected peak temperatures. This demonstrates the difficulty in using this technique if the CCP wastes contain multiple compounds – even when the compounds are well-defined.

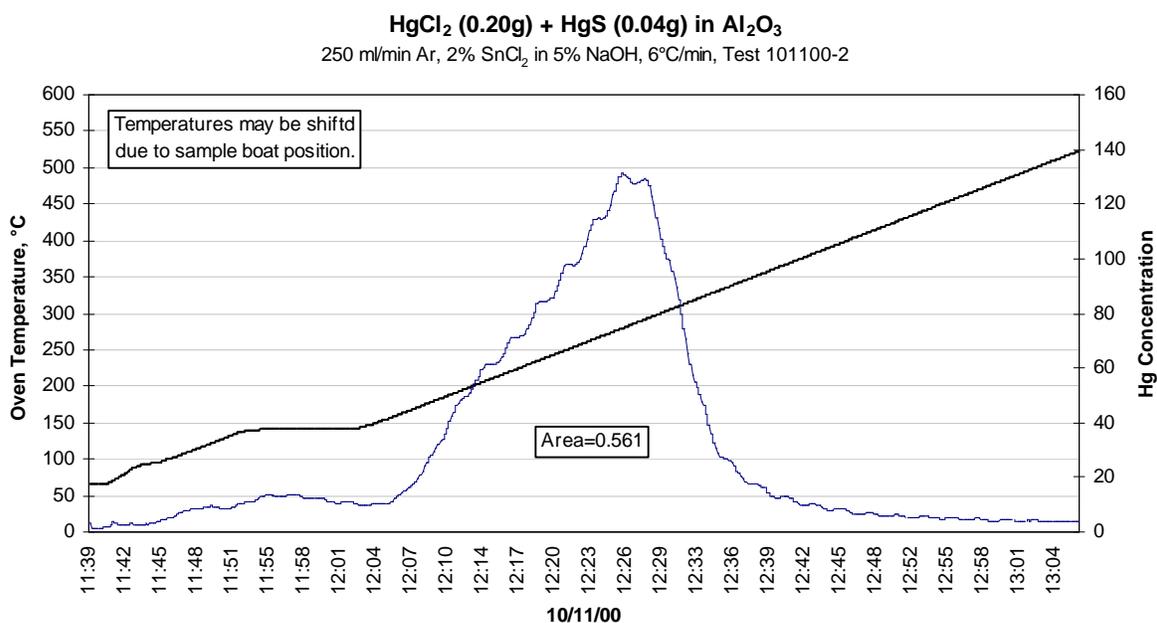


Figure 3-12 – TSC for the Combined HgCl_2 and HgS Standards

3.3.3 Method Development

Upon completion of standard development, the next step involved testing select waste samples from pilot-scale tests. The samples chosen (highlighted earlier in Tables 3-1 and 3-2) are a representative cross-section of the B&W mercury control technologies described in earlier sections of this report. However, early results with the TSC method were very disappointing as shown in Figure 3-13. The TSC produced from the wet scrubber samples produced dozens of poorly-defined, sharp and broad peaks. Worse yet, many of the peaks occurred at very low temperatures that would indicate the presence of some form of highly volatile mercury compound.

However, the area under these peaks was much larger than could be accounted for by the total mercury in the sample as measured by standard methods. Furthermore, the peaks were not reproducible and could often be generated by using only distilled water (see Figure 3-14) – hence these mysterious peaks were dubbed “water spikes”.

Many explanations were put forth to explain the peaks. Test procedures were modified and different kinds of filters were added to ascertain their cause. After dozens of tests, it was determined that mercury was depositing in the apparatus. This mercury was then released when water from the test sample (either liquid water or waters of hydration) was vaporized into the argon stream. The exact mechanism by which this occurs is not known. It could be a chemical reaction, steam stripping, or possibly some impact of the steam on the temperature profile within the apparatus.

In an attempt to eliminate mercury deposition within the test apparatus, further tests identified two cool zones: one between the exit of the pyrolyzer and heated sample hose and, more significantly, one between the exit of the heated sample hose and the inlet of the impinger. The apparatus was modified to eliminate the cool zones as best as possible. The test procedure was also modified to include vaporizing a sample boat of distilled water at the beginning and end of each test, called a “steam flush”. However, even with these changes, the water spikes could not be completely eliminated. It is believed that this effect could be eliminated in the future by further design modifications.

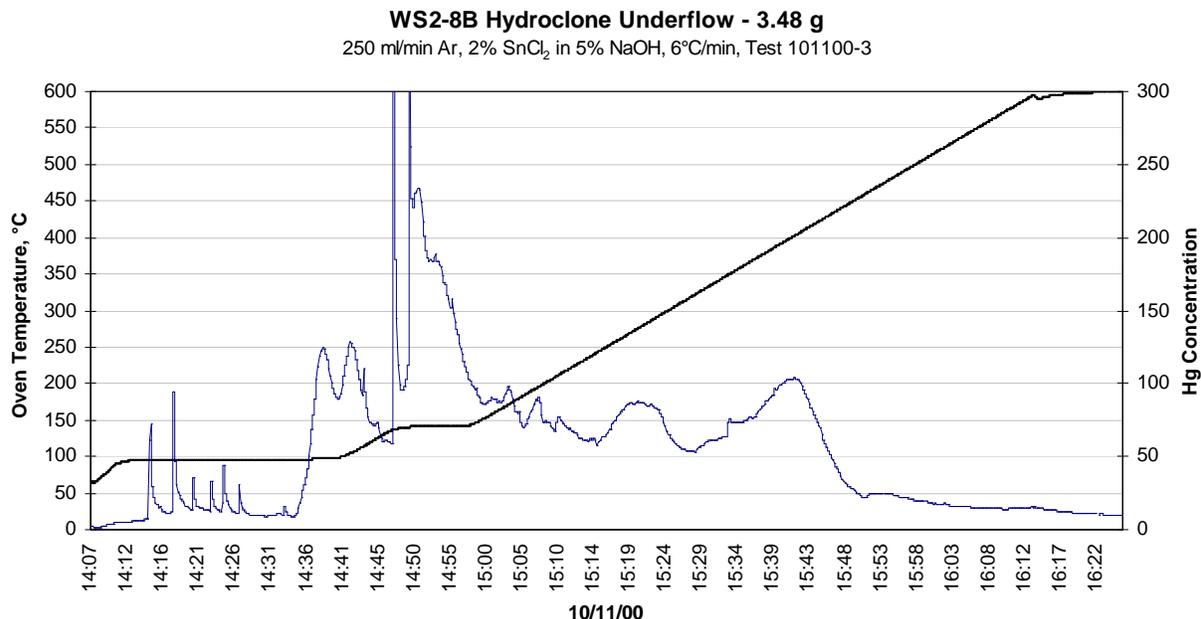


Figure 3-13 – “Water Spikes” for a Typical Wet Scrubber Sludge

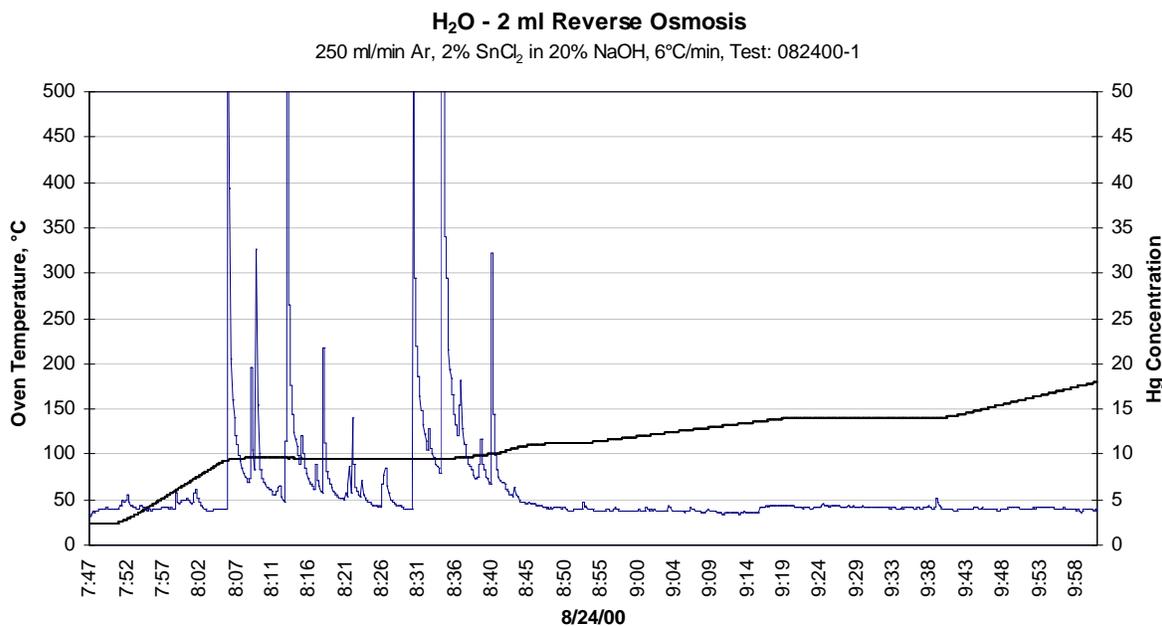


Figure 3-14 – “Water Spikes” from Distilled Water

3.3.4 Pilot-Scale Sample Testing

This section presents results of thermal stability testing for samples from several pilot-scale test programs conducted at MTI's Alliance Research Center. Results from samples obtained from commercial utility plants are reported in Section 3.3.5. Table 3-3 shows what samples were tested. The data is presented by showing the pilot data for the ESP ash, then the pilot data for the wet FGD sludge, and finally the data from the utilities.

Table 3-3 – Sample List for Thermal Stability Testing

April 1998 AECDP Phase III Test Series

Test	Type	MTI ID	Code		% Hg Rem
10	WFGD Sludge	10C	App1		71
11	WFGD Sludge	11C	App2		73
					ESP Rem
10	ESP Ash	10	Baseline for Ash		20
13	ESP Ash	13A	Sorb Inj 1		53

Oct 1999 Phase I Test Series

Test	Type	MTI ID	Code	Hg, mg/kg	% Hg Rem
1	WFGD Sludge	WS-1C	Baseline	0.072	47
5	WFGD Sludge	WS-5C	Alt App1	0.160	77
7	WFGD Sludge	WS-7B	Alt App1+ App2	0.190	80

April 2000 Phase II Test Series

Test	Type	MTI ID	Code	Hg, mg/kg	% Hg Rem
1	WFGD Sludge	WS2-2A	Baseline	0.130	71
6	WFGD Sludge	WS2-6B	Alt App1	0.170	84
8	WFGD Sludge	WS2-8B	Alt App1A	0.200	87
9	ESP Ash	WS2-9C	Baseline for Ash	<0.10	

Utility Samples

Eastern Bituminous
ESP Ash
WFGD Sludge
Landfill Waste
Western Subbituminous Blend
ESP Ash

Misc.

Fingernails

ESP Ash Samples. The first two TSCs for the pilot-scale samples, Figures 3-15 and 3-16, represent ESP ash before and after a sorbent injection test, respectively. Figure 3-15 shows that 5.1g of ash produced a single peak with an area of 1.14 and a peak temperature of about 400 C. The only standard with these characteristics is HgSO₄, however the shapes of the two curves are not similar.

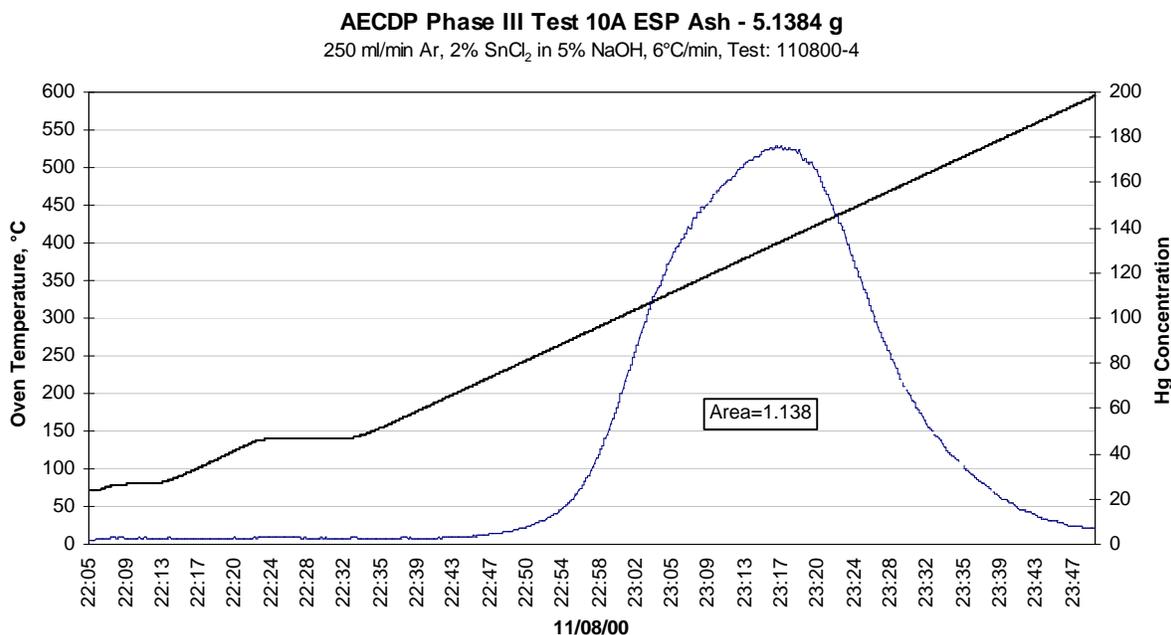


Figure 3-15 – TSC for ESP Ash (Baseline)

The TSC in Figure 3-16 has several interesting characteristics. It shows that sorbent injection changed the TSC in that a new, and more dominant, peak formed with a peak temperature of 300 C. The new peak produced an area of 0.43 with a sample size of only 0.50g. A relative mercury concentration can be calculated for the ash samples by dividing the total area under the curve by the mass of the sample. The baseline ash had a relative mercury concentration of 0.2215 (1.138/5.138). The ash from the sorbent injection test had a relative mercury ratio of 1.292 (0.652/0.5046), which is approximately 6 times higher than baseline sample and is consistent with the increased mercury removal shown for these tests in Table 3-3. The new peak suggests the presence of HgO or HgS, but could simply be the result of a desorption process of

these or some other mercury compound(s). The drawn out shoulder on the back of the new peak corresponds to the peak in Figure 3-15. This helps explain the mercury removal mechanism for this particular sorbent. It appears that the mercury in the flue gas combines with the sorbent to produce a solid-phase product, without significantly affecting the baseline mercury removal of the ash.

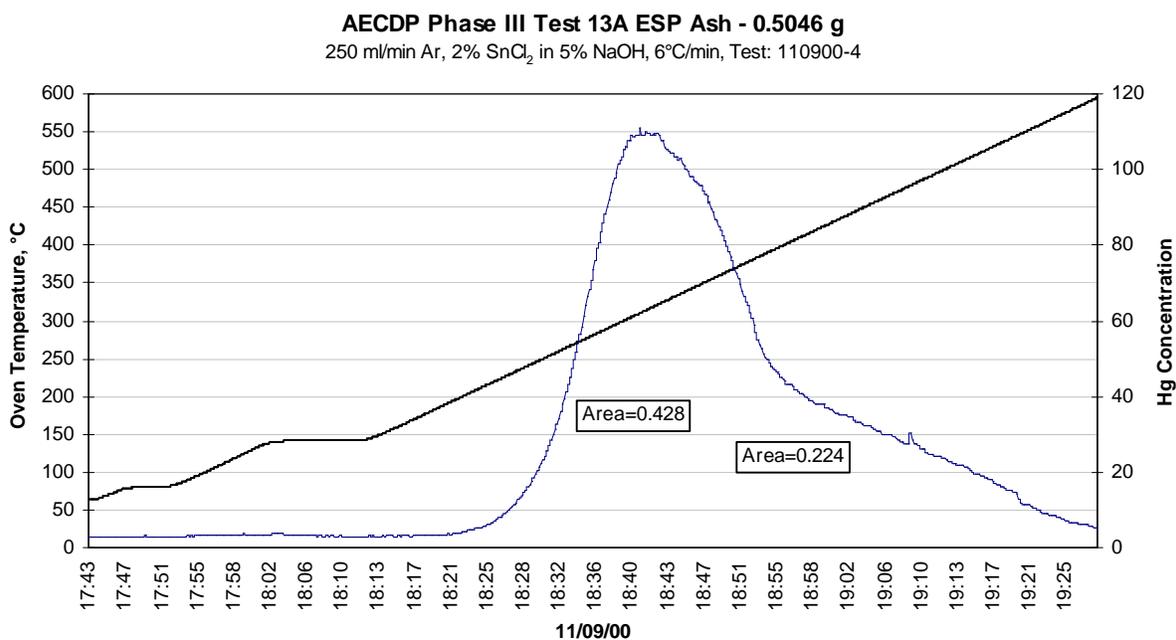


Figure 3-16 – TSC for ESP Ash (Sorbent Injection)

Figure 3-17 shows the TSC for an ESP ash sample from the April testing. No sorbent injection tests were conducted during this test series, so this figure corresponds to another baseline ESP mercury removal condition. The sample contained very little mercury as 5.3g of sample only produced an area of 0.1. The sharp peak on the right side of the graph, labeled “steam flush” is the first example presented of the mercury released at the end of the test by vaporizing a sample boat of distilled water. For this particular test, the mercury released during the flush represents about 26% of the total mercury evolved from the sample.

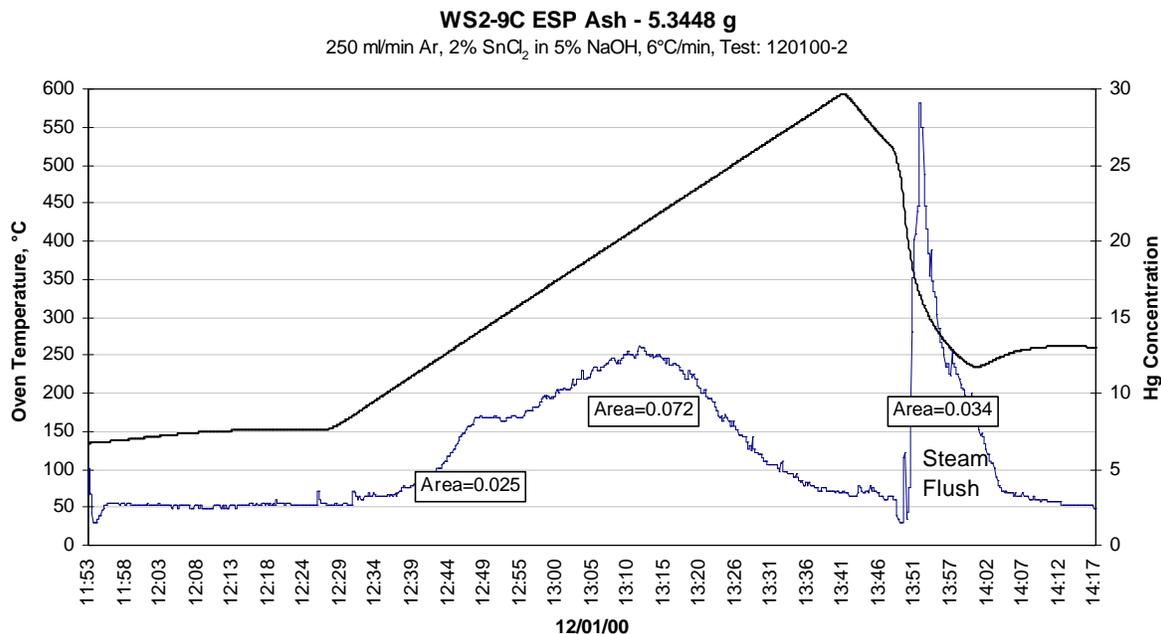


Figure 3-17 – TSC for WS2-9C ESP Ash (Baseline)

The important result from the work with the ESP ash samples is that no mercury is evolved at temperatures below about 150-200 C. This is true for both the baseline and sorbent injection test conditions.

Wet FGD Samples. Figures 3-18 and 3-19 show the baseline TSCs for wet FGD slurry for the October and April tests, respectively. Both curves seem to show that the slurry contains two mercury forms, one with a peak temperature of about 300 C, and one with a peak temperature of about 400 C. In both cases, the first peak is smaller than the second peak. The first peak suggests the presence of HgO or HgS, and the second peak resembles the behavior of the HgSO₄ standard, but there is no way to positively identify the compounds. These curves also show that a small amount of mercury is released below 140 C. It's hard to discern whether these small peaks represent a volatile mercury compound or are just a remnant of the “water spike” phenomenon, but in either case, they are a small fraction of the total mercury in the samples. The steam flushes at the end of each test yielded 17% and 10% of the total mercury, respectively.

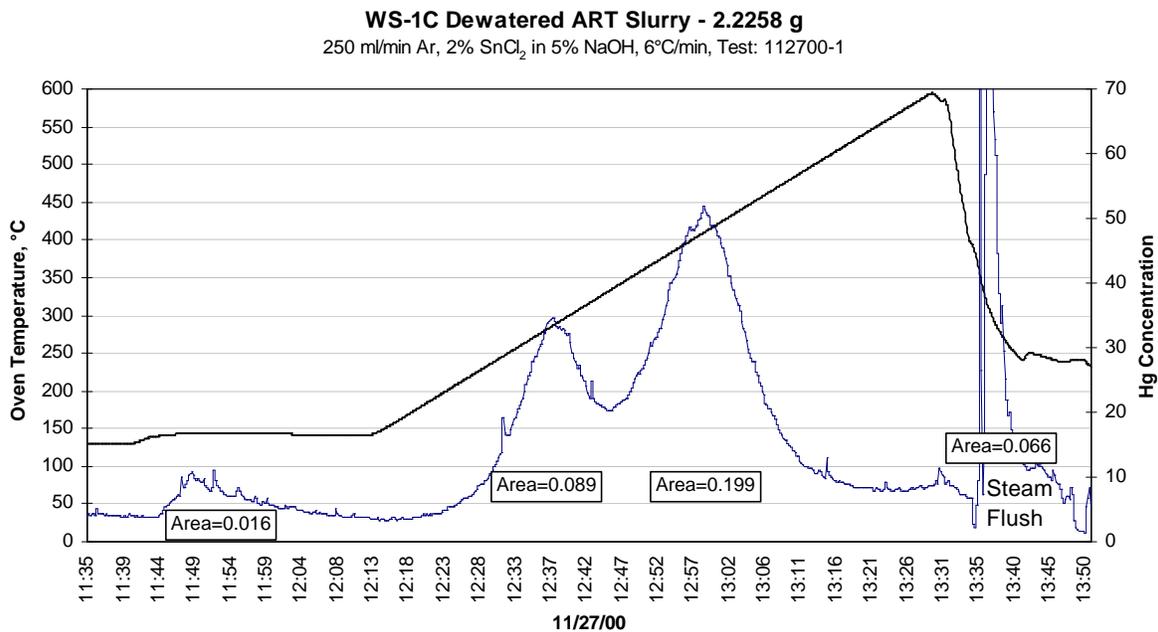


Figure 3-18 – TSC for WS-1C Wet FGD Sludge (Baseline)

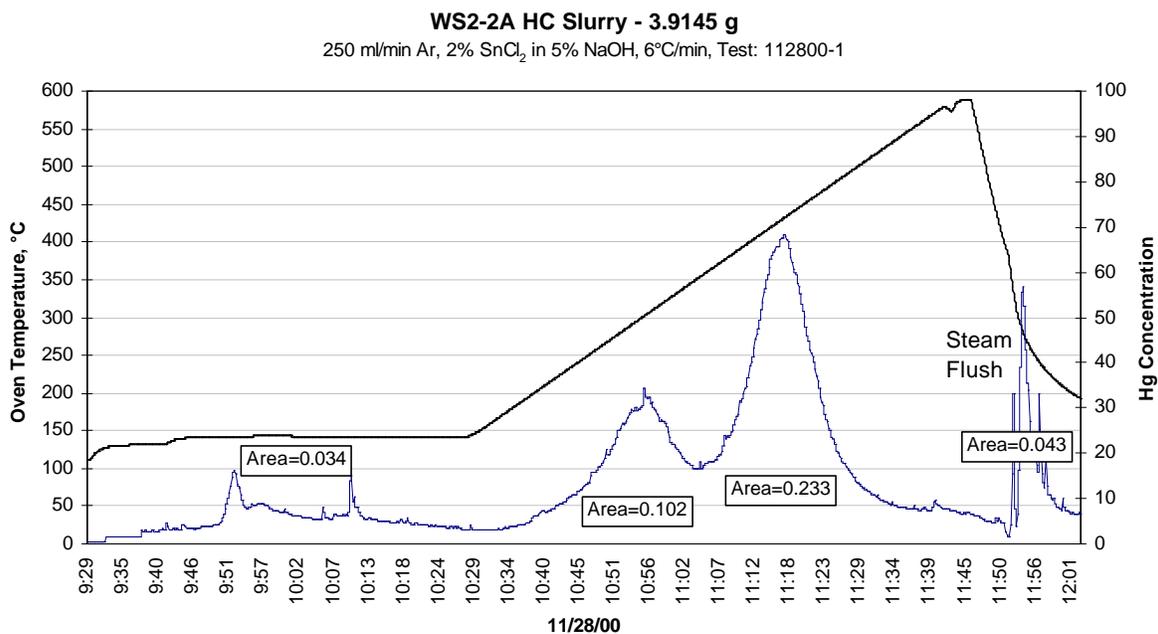


Figure 3-19 – TSC for WS2-2A Wet FGD Sludge (Baseline)

Figures 3-20 through 3-25 illustrate the TSCs for various pilot-scale wet FGD sludges obtained during testing of B&W's enhanced wet FGD process (using a variety of approaches and reagents). In general, the curves show two peaks similar to the baseline peaks, except that the first peak is generally larger in area. This seems to suggest that the enhanced processes are favoring the formation of only one form of mercury.

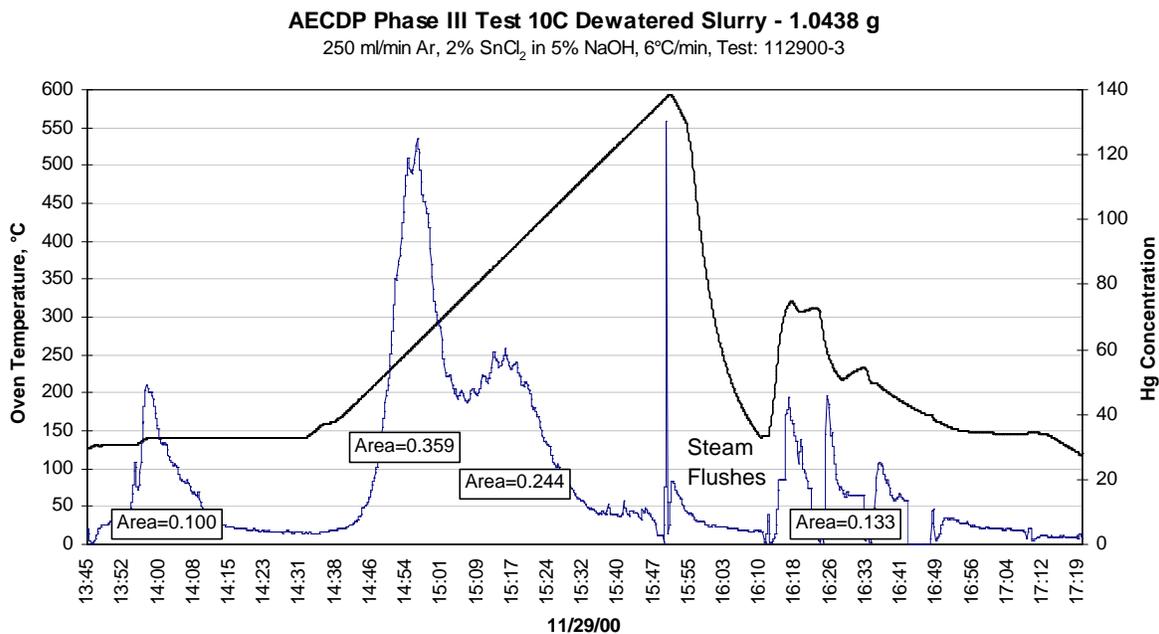


Figure 3-20 – TSC for AECDP Phase III Test 10C Wet FGD Sludge (App1)

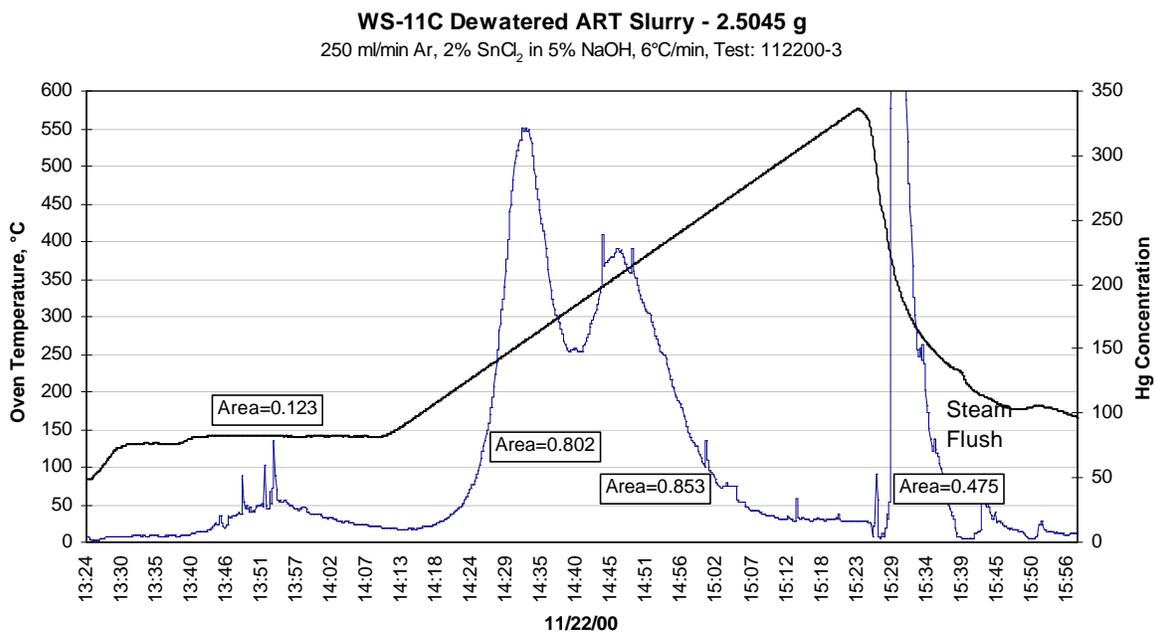


Figure 3-21 – TSC for AECDP Phase III Test 11C Wet FGD Sludge (App2)

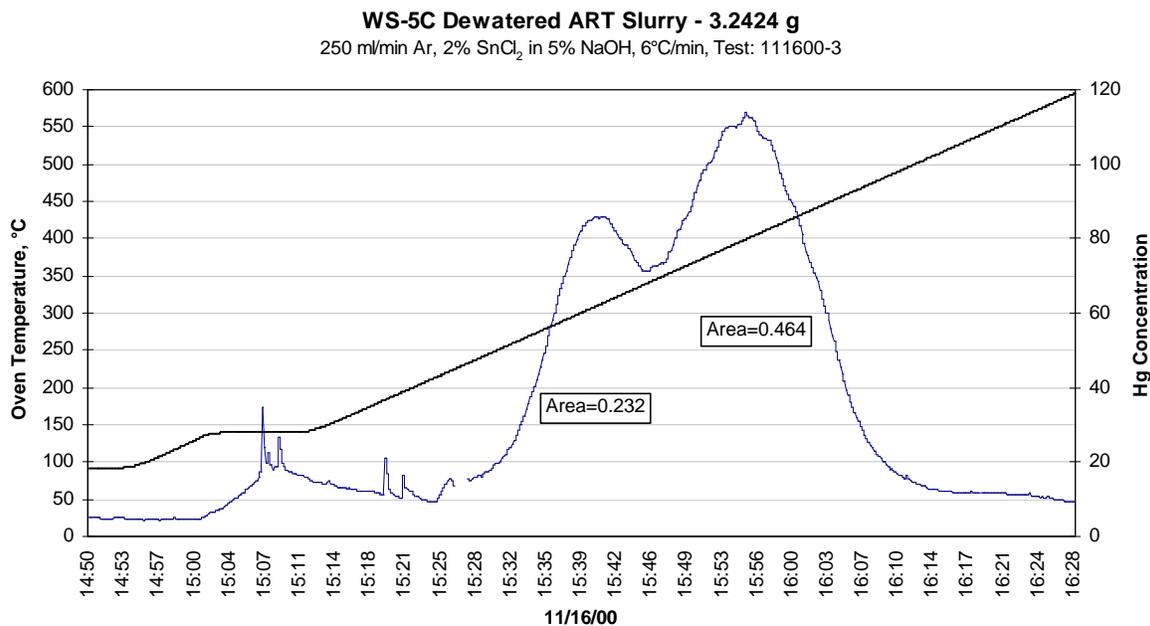


Figure 3-22 – TSC for WS-5C Wet FGD Sludge (Alt App1)

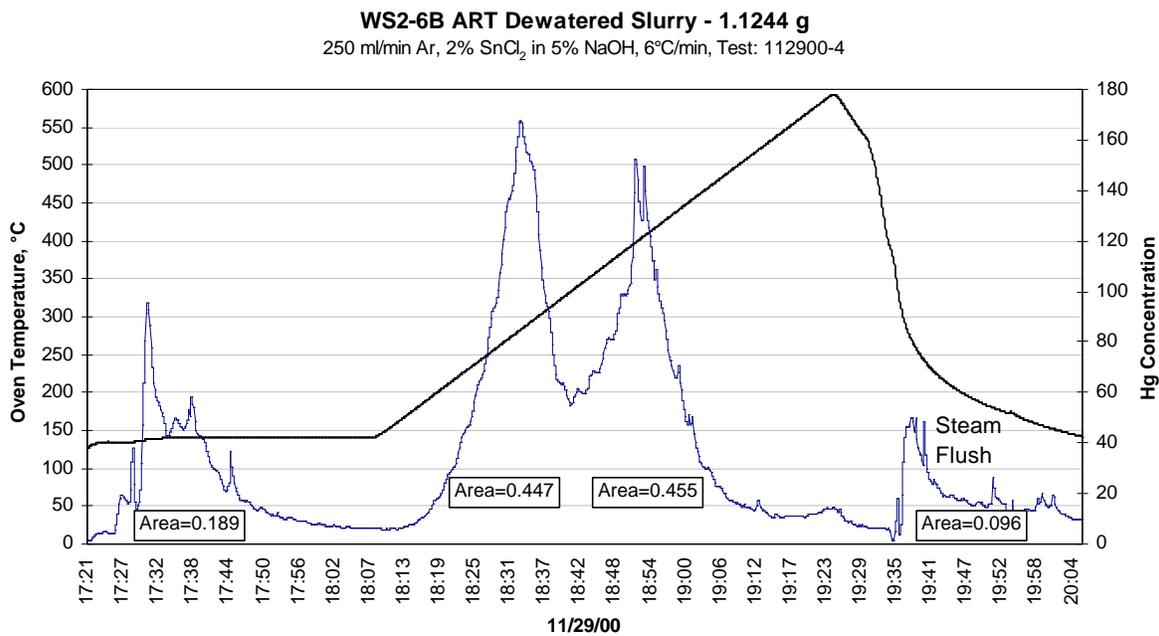


Figure 3-23 – TSC for WS2-6B Wet FGD Sludge (Alt App1)

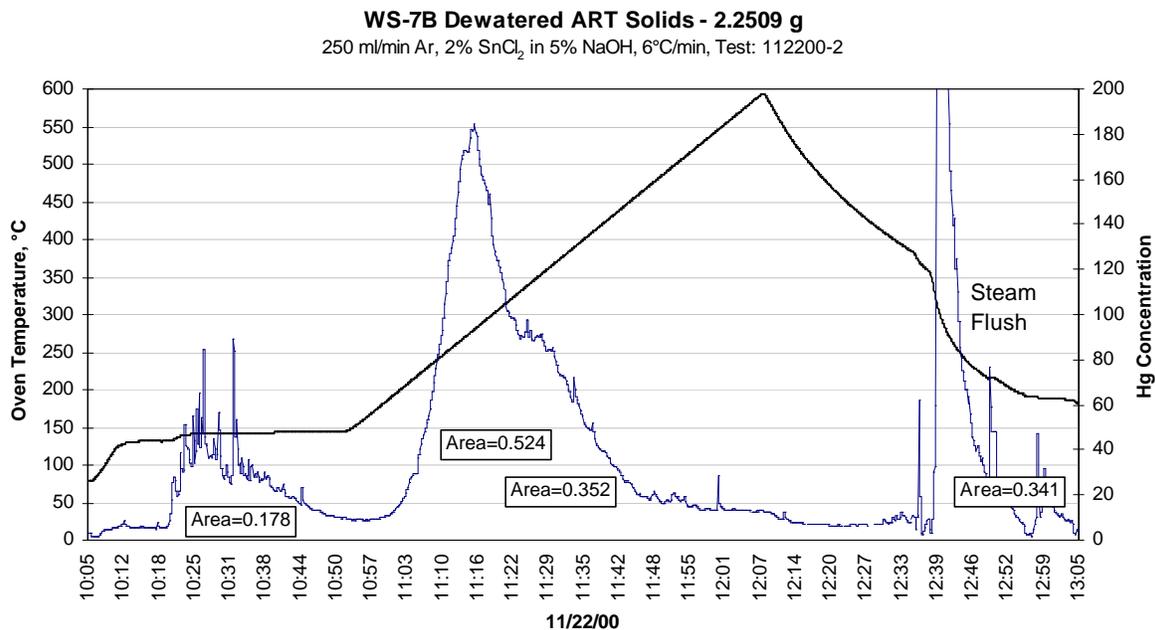


Figure 3-24 – TSC for WS-7B Wet FGD Sludge (Alt App1 + App2)

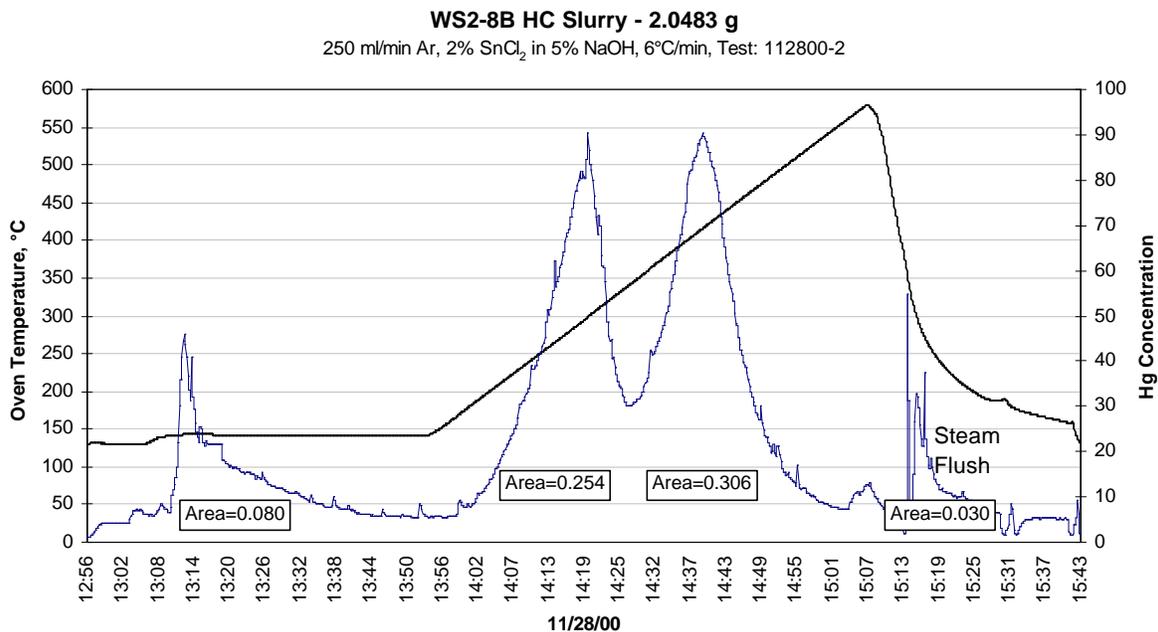


Figure 3-25 – TSC for WS2-8B Wet FGD Sludge (Alt App1A)

Miscellaneous Samples. For general comparison purposes, and to illustrate the sensitivity of the method, Figure 3-26 shows the TSC for a sample comprising a co-author's fingernail clippings. This author was not involved in the preparation or handling of any of the pure mercury compounds used to make the standards. The main peak in this TSC has a peak temperature of 340 C, which does not correspond well with any of the standards. However, the most interesting finding in this run is that the resulting peaks for the fingernails had a combined area of 1.58. Dividing by the mass of the fingernail clippings gives a relative mercury concentration ratio of 26.6 (1.58/0.0594). This means that the mercury concentration in the fingernail sample was 83 times greater than in the wet FGD slurry, illustrating how little mercury there is in CCP wastes, with or without enhanced mercury control.

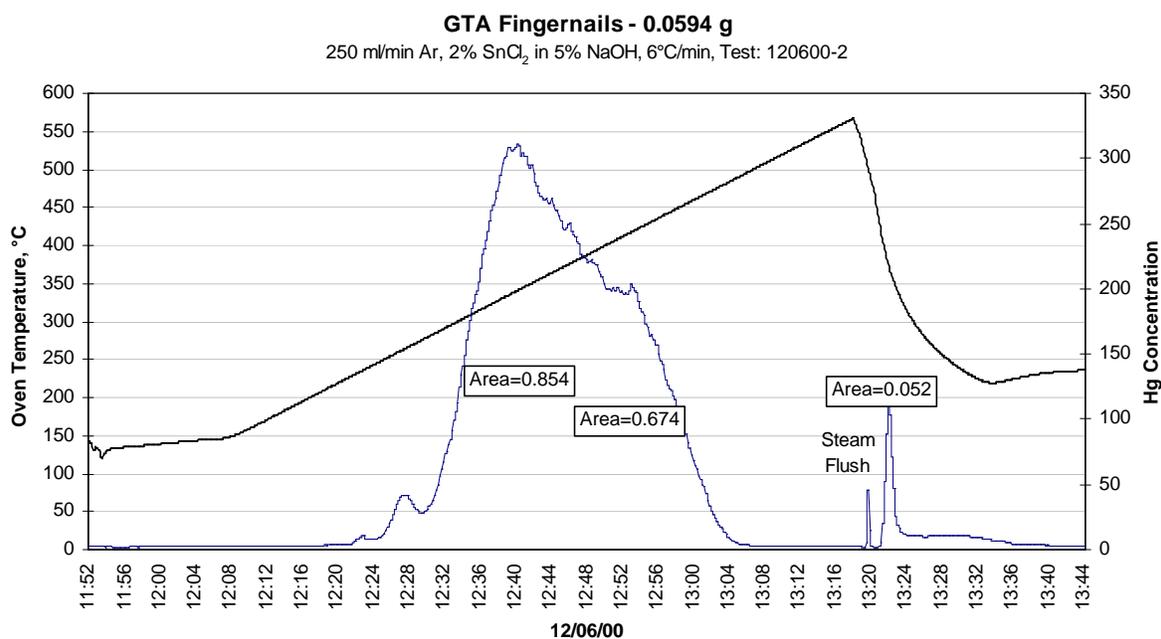


Figure 3-26 – TSC for Co-author's Fingernails

3.3.5 Commercial Plant Samples

With help from the American Coal Ash Association, CCP waste samples were obtained from two utilities, one burning an eastern bituminous coal and the other burning a blend of western subbituminous coals. The eastern plant uses an ESP and wet scrubber to control particulate and SO₂ emissions, although the scrubber chemistry is different than that for B&W testing in the CEDF. This may effect the mercury compound(s) formed in the scrubber as will be discussed below. This plant provided three samples: an ESP ash, a dewatered wet FGD sludge and a stabilized sludge that consists of a mixture of ESP ash, wet FGD sludge and lime. The western plant sent only a sample of ESP ash.

Figures 3-27 and 3-28 show the TSCs for the two ESP ash samples. The eastern ash (Figure 3-27) produced a broad peak at 330 C to 400 C. The relative mercury concentration ratio for this ash is 0.44. This is about twice as high as the pilot-scale ash shown earlier in Figure 3-15. The western ash (Figure 3-28) contained almost no mercury. A 20g sample had to be used to produce even a modest peak on the TSC. The peak temperature for this ash was about 280 C and the relative mercury concentration was only 0.0014. The differences between these two ashes could be due to differences in coal constituents, like mercury, chlorine and calcium, as well as the operating conditions of the boiler and ESP.

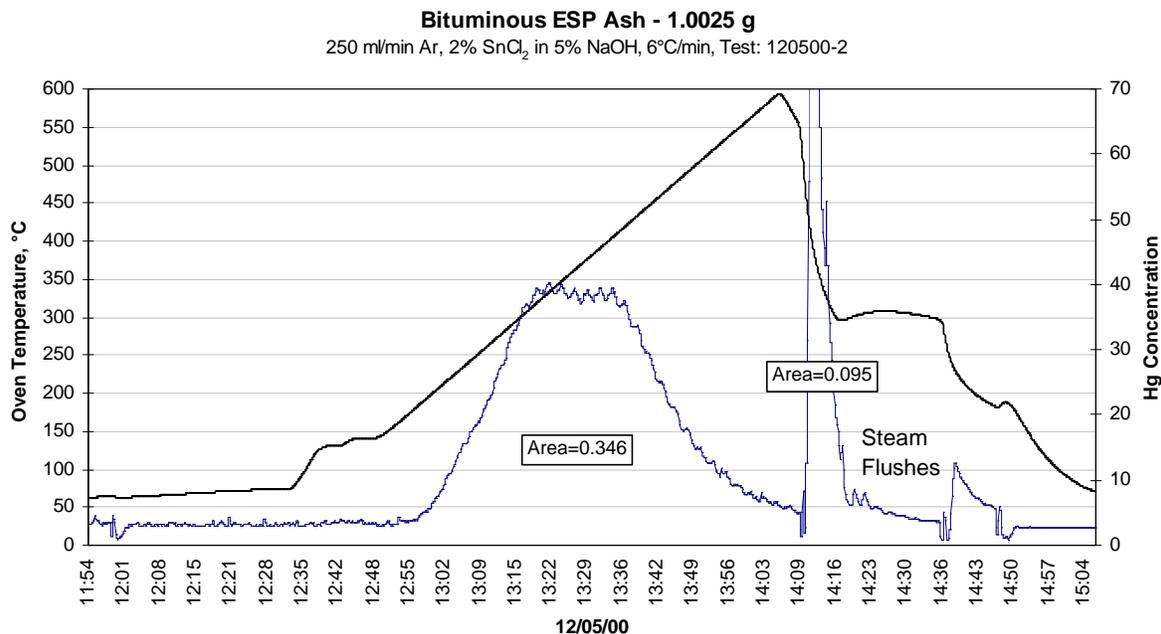


Figure 3-27 – TSC for an Eastern Bituminous Coal ESP Ash

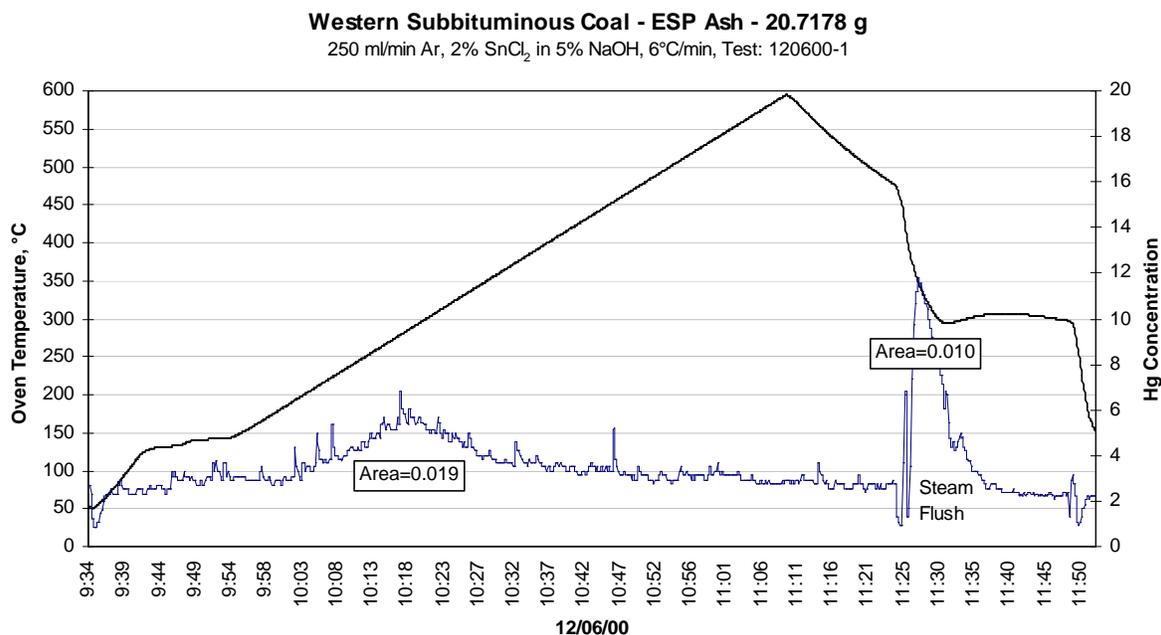


Figure 3-28 – TSC for a Western Subbituminous Coal Blend ESP Ash

Figures 3-29 and 3-30 show the TSCs for the eastern wet FGD and stabilized sludge, respectively. These materials appear to contain a mercury compound with a peak temperature of only 200 C, which is much lower than any recorded for the standards or the pilot-scale sludges. This difference is likely due to the fact that the scrubbers that produced the samples were operated very differently. However, additional samples from other sites would be needed to confirm this. The wet FGD sludge has a relative mercury concentration of 1.05, which is 3.3 times higher than the pilot-scale wet FGD sludge shown earlier in Figure 3-25. However, this is well within the range of mercury found in different coals. Also, the utility scrubber was likely operating at steady state, whereas the CEDF scrubber had not attained steady-state mercury concentration in the slurry (calculated to be about 2.5 times higher than the reported value).

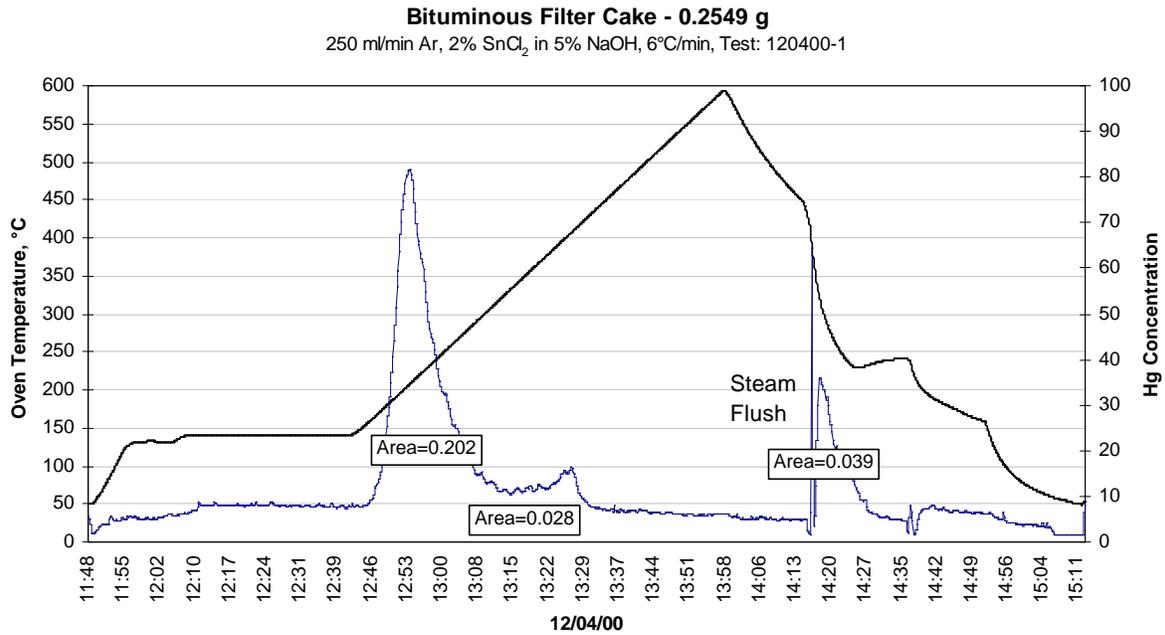


Figure 3-29 – TSC for an Eastern Bituminous Coal Wet FGD Sludge

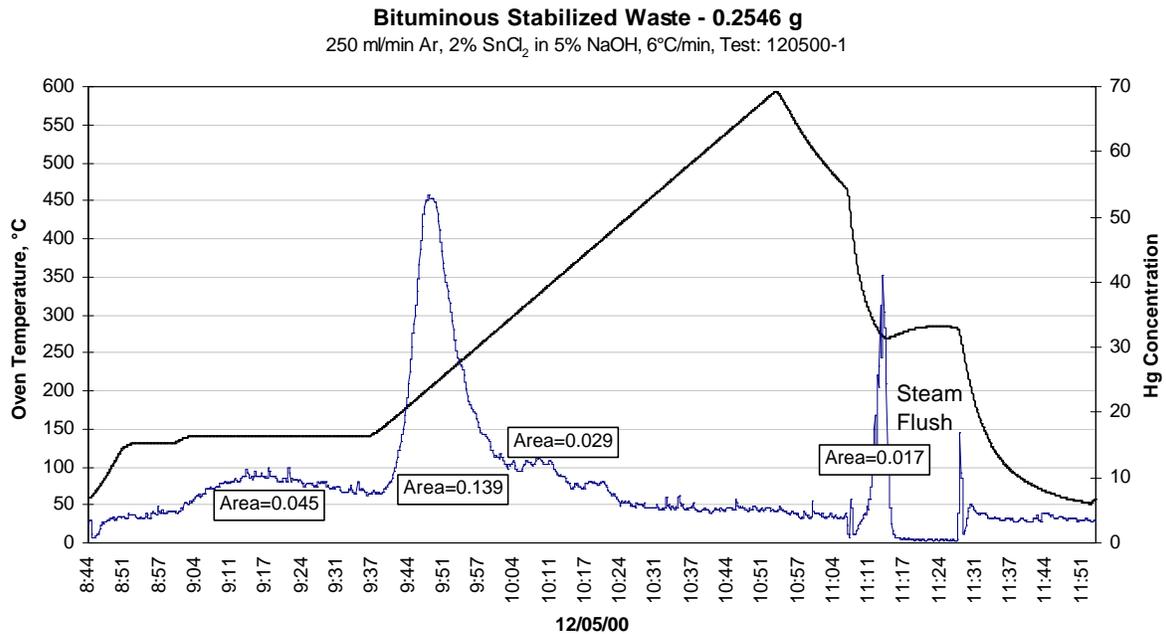


Figure 3-30 – TSC for an Eastern Bituminous Coal Landfill Waste

3.3.6 Sample Spikes

Several TSC tests involved the addition of standards (known compounds) to a typical wet FGD sludge to determine the effect on the resulting TSC. It was hoped that new peaks would form or that existing peak heights would increase in correspondence to which standard was used. Four samples were prepared by adding appropriate amounts of the standards to typical wet FGD slurry (Figure 3-25) and mixing overnight. Figures 3-31 to 3-34 show the TSCs for the four spiked samples. In each case, only the first peak increased in area. This was attributed to chemical reactions between the standards and slurry. This, again, illustrates the limitations of the method in identify individual mercury compounds.

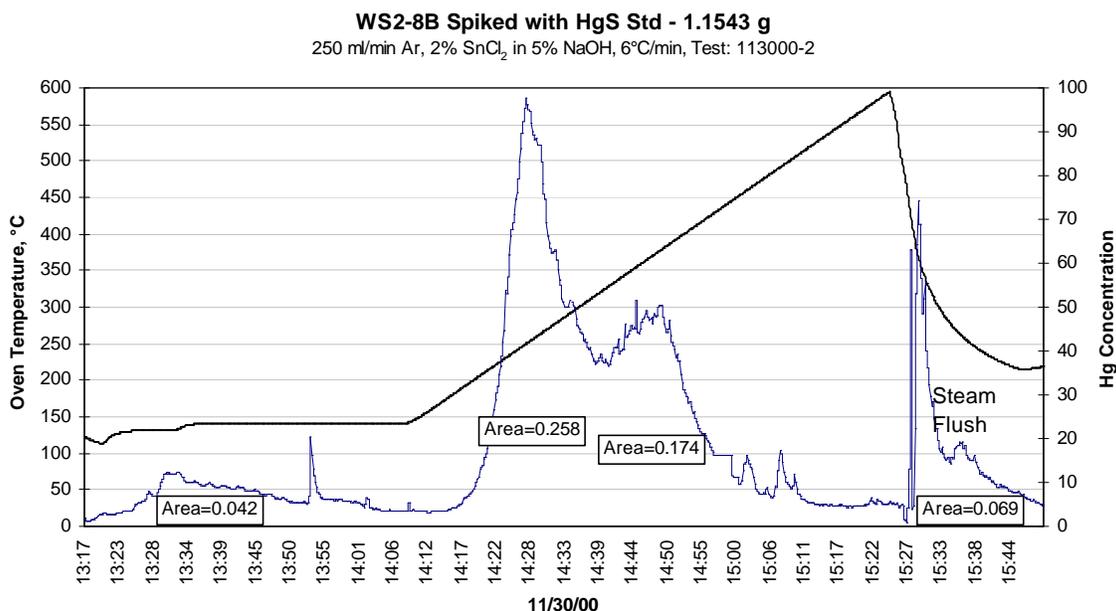


Figure 3-31 – TSC for MTI Wet FGD Slurry Spiked with HgS Standard

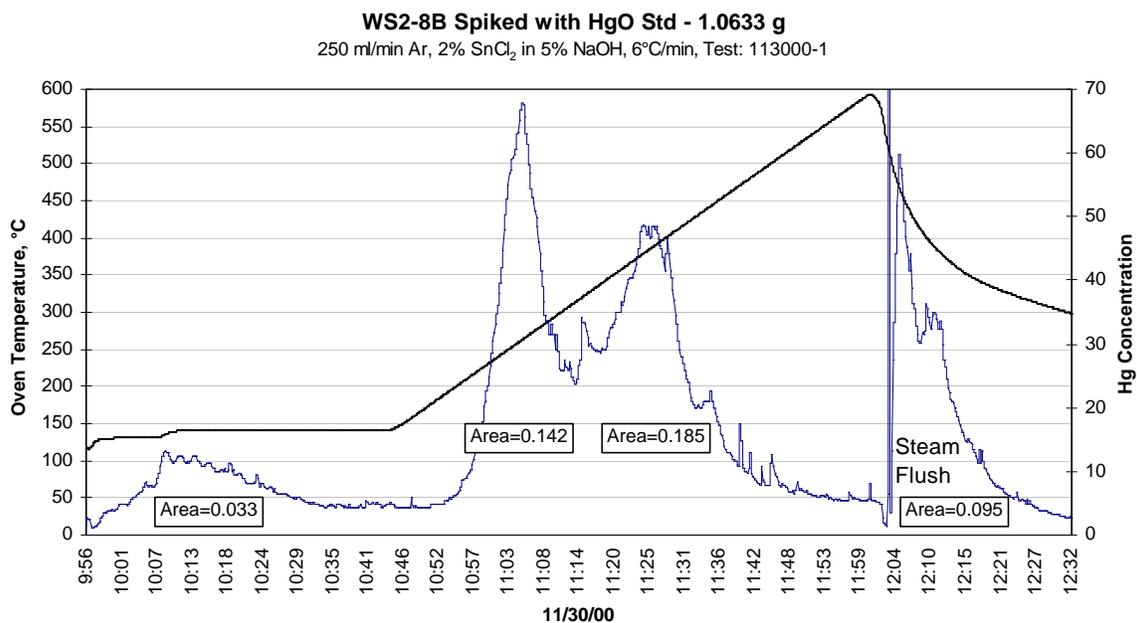


Figure 3-32 – TSC for MTI Wet FGD Slurry Spiked with HgO Standard

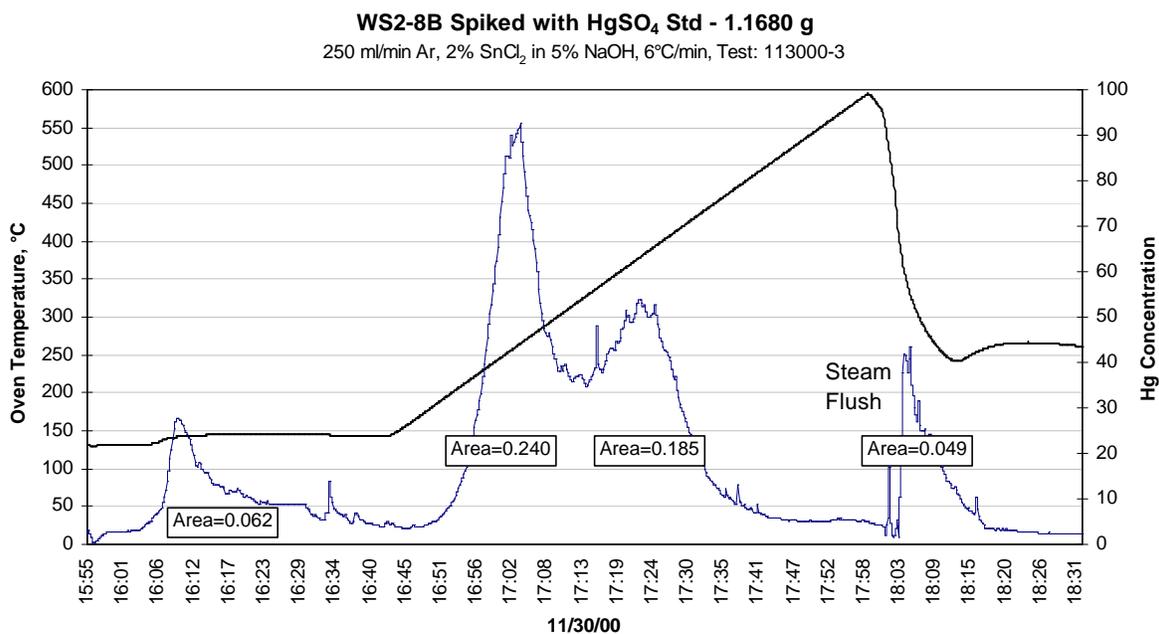


Figure 3-33 – TSC for MTI Wet FGD Slurry Spiked with HgSO₄ Standard

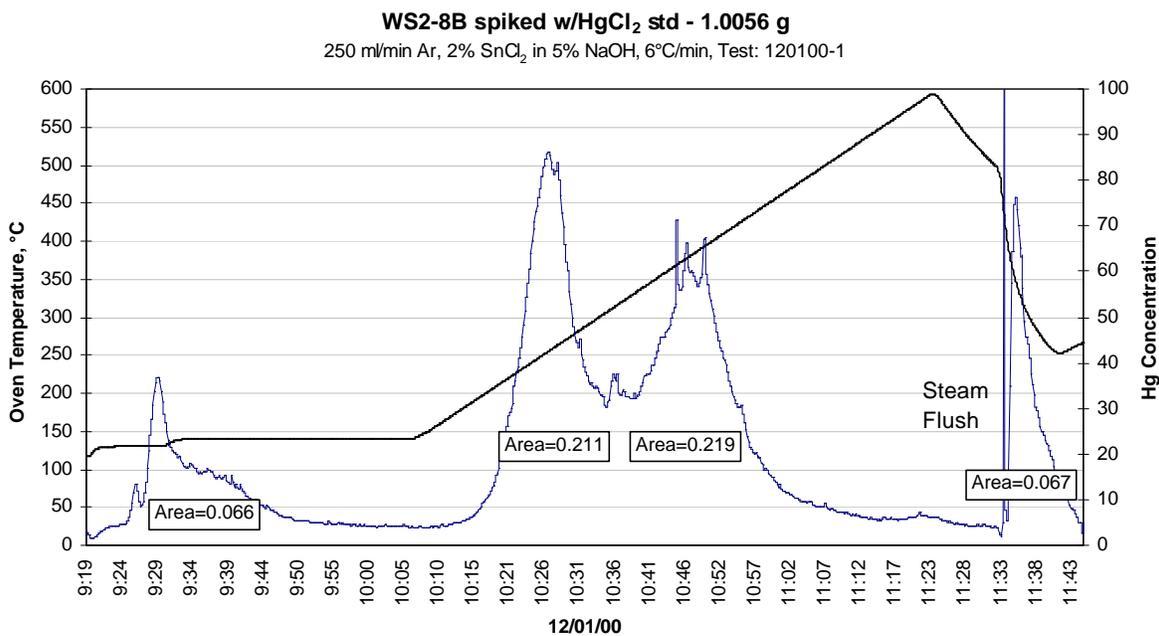


Figure 3-34 – TSC for MTI Wet FGD Slurry Spiked with HgCl₂ Standard

3.4 Fate of Mercury – Summary

All CCP samples tested contained too little mercury to exceed Toxicity Characteristic Leaching Procedure (TCLP) limits – even if all of the mercury had reported to the liquid phase, which it did not. For comparison purposes, human fingernail clippings were found to contain 83 times more mercury than the wet FGD sludge produced by either the conventional or B&W enhanced wet FGD system. Further, no mercury was ever detected in any liquid fraction, suggesting that no soluble form of mercury, such as HgCl_2 , was present in any of the samples. Thermal stability testing indicated that all samples were stable (with respect to mercury content) up to at least 140 C, the temperature at which rotary kilns in wallboard plants operate.

Overall, the fate of mercury testing indicated that solid byproducts produced by conventional systems, as well as those produced by the B&W enhanced processes, appear to be suitable (with respect to mercury) materials for wallboard and cement manufacture, and for disposal in landfills.

4.0 Acknowledgements

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5.0 References

Advanced Emissions Control Development Program, Phase I Final Report, U.S. Department of Energy DE-FC22-94PC94251, Ohio Coal Development Office CDO/D-922-13, February 29, 1996.

Advanced Emissions Control Development Program, Phase II Final Report, U.S. Department of Energy DE-FC22-94PC94251, Ohio Coal Development Office CDO/D-922-13, April 21, 1998.

Advanced Emissions Control Development Program, Phase III Final Report, U.S. Department of Energy DE-FC22-94PC94251, Ohio Coal Development Office CDO/D-922-13, July 28, 1999.

Mercury Control for Coal-Fired Utilities, Milestone Report #1, Ohio Coal Development Office CDO/D-98-7, March 15, 2000.

Mercury Control for Coal-Fired Utilities, Milestone Report #2, Ohio Coal Development Office CDO/D-98-7, February 13, 2001.

Mercury Control for Coal-Fired Utilities, Technical Report –Amendment for Hg Speciation Testing, Ohio Coal Development Office CDO/D-98-7, March 15, 2001.