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Evaluating the Thermal Stability of Mercury and Other Metals in Coal Combustion Residues Used in the Production of Cement Clinker, Asphalt, and Wallboard

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List of Acronyms

ACI	Activated Carbon Injection
ADA	ADA Environmental Solutions
ASTM	ASTM International ¹
BD	Below Detection
BML	Below Method Limit
CCR	Coal Combustion Residues
CVAA	Cold Vapor Atomic Absorption
DOE	Department of Energy
DRC	Dynamic Reaction Chamber
ELAN	Emulated Local Area Network
EPA	U. S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic Precipitator
FGD	Flue Gas Desulfurization
FIMS	Flow Injection Mercury System
HHV	Higher Heating Value
HMA	Hot Mix Asphalt
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LOI	Loss on Ignition
MDL	Method Detection Limit
MLQ	Minimum Level of Quantification
NA	Not Applicable
NETL	National Energy Technology Laboratory / DOE
NR	Not Recorded
NRMRL	National Risk Management Research Laboratory
NT	Not Tested
OH	Ontario Hydro
PRB	Powder River Basin
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
SCA	Specific Collection Area
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction

¹Previously ASTM was used as an acronym for American Society for Testing and Materials. The new name is ASTM International.

STI	Separation Technology Inc.
STL	Severn Trent Laboratories
TBD	To Be Determined
TPD	Temperature Programmed Desorption
USG	United States Gypsum Company
XRF	X-Ray Fluorescence

Executive Summary

Research is underway by the U.S. Environmental Protection Agency (EPA) to document changes that may occur to coal combustion residues (CCRs) as a result of implementation of mercury and multi-pollutant control technology at coal-fired power plants. This work was cited as a priority in EPA's Mercury Roadmap (<http://www.epa.gov/mercury/roadmap.htm>) to evaluate the potential for any cross-media transfers from the management of coal combustion residues resulting from more stringent air pollution control at coal fired power plants.

This report focuses on the potential for an increase in the volatilization of mercury and other metals from the utilization of CCRs in the production of cement clinker, asphalt, and wallboard. All three of these processes require heating during the production process. The four metals evaluated in this study are mercury (Hg), arsenic (As), selenium (Se), and lead (Pb) (Table E-1). Heating temperatures of the CCRs for this study were chosen to simulate actual conditions encountered in the cement, wallboard, and asphalt industries (Table E-2).

Table E-1. Boiling points and temperatures for 10 Pa (0.075 mm Hg) vapor pressure of Mercury, Arsenic, selenium, and lead

Element	Boiling Point (°C)	Temperature for Vapor Pressure of 10 Pa (°C)
Mercury	357	76.6
Arsenic	614	323
Selenium	685	279
Lead	1749	815

Table E-2. Typical maximum process temperatures of cement clinker kilns, asphalt, and wallboard manufacturing and laboratory testing temperatures

Process	Maximum Manufacturing Plant Temperature (°C)	Laboratory Testing Temperature (°C)
Cement Clinker Kiln	14,30	1,450
Asphalt Kettle	168	170
Wallboard Calciner Kettle*	162	120, 140, 160

*There are three processes in making wallboard that could result in Hg loss. However, the highest temperature that Hg is exposed to is during the calciner process.

Fly ash and flue-gas desulfurization (FGD) gypsum was obtained from a range of facilities in an attempt to span differences in air pollution control configuration and coal types. The samples evaluated include:

1. Fly ash from three different facilities evaluated by ADA-Environmental Solutions (ADA) under contract for the Department of Energy's (DOE's) National Energy Technology Laboratory (NETL) field evaluation program of sorbent to enhance mercury capture. At each of the three sites, the use of

activated carbon injection (ACI) was evaluated by adding powdered activated carbon upstream of existing particulate control. Samples analyzed include fly ash from three facilities with and without the use of ACI for a total of six fly ashes;

2. Fly ash from two facilities using selective catalytic reduction (SCR) for post-combustion control of NO_x and one utilizing selective non-catalytic reduction (SNCR) (four with SCR and one with SNCR, total of five samples); and
3. FGD gypsum kettle feedstock obtained from US Gypsum (two samples).
4. FGD gypsum material obtained from eight different power plants (eight samples).

A fixed-bed reactor design was used to simulate the thermal processes of concern in this study. Figure E-1 provides a schematic of the general setup for simulating asphalt manufacturing, wallboard manufacturing, and cement clinker manufacturing. For all simulations, samples consisting of various mixes and matrices were loaded into shallow-bed containers and placed in the reactor. The fixed-bed reactor used for the asphalt and wallboard simulation assays consisted of a horizontal quartz tube in a thermally controlled unit (furnace). In the case of the high temperature cement clinker manufacturing ($1450\text{ }^\circ\text{C}$), a Lindberg high temperature furnace was used.

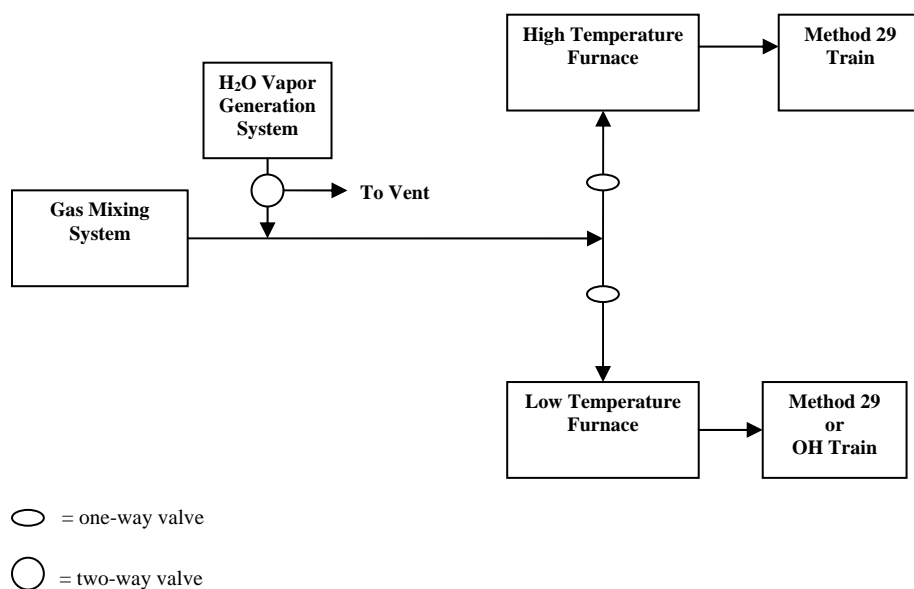


Figure E-1. Fixed-bed reactor design

In each simulation, the tests were performed in duplicate. Samples were exposed to a flow rate of 400 cc/min of inlet flue gas consisting of 14% CO_2 , 3% O_2 , 5.6% H_2O and 100 ppm NO_x , except for the wallboard simulation of the kettle calciner, in which the inlet gas consisted solely of N_2 , because the kettle calciners are indirectly fired and therefore the sample is not exposed to flue gases. The time in the fixed-bed reactor for each simulation was one hour. The samples placed in the fixed-bed reactor, as well as the temperatures in the processes, varied for each simulation. For mercury, the effluent of the reactor was sampled using a mini-impinger Ontario Hydro train. For sampling the other metals, a Method 29 mini-impinger train was used.

The making of cement involves the heating of various feedstocks in a cement kiln to make “clinker.” This clinker is ground with gypsum and transported to ready-mix concrete manufacturers. Various components are needed for feedstock including lime (CaO), iron oxide (Fe₂O₃), silica (SiO₂) or alumina (Al₂O₃). Fly ash can replace a portion of these, representing a maximum of about 5% (by weight) of the typical raw mix to the kiln. Other inputs typically include limestone (90%), iron ore (3%), and sand (2%). Cement kiln residence time is typically one to three hours, and temperatures reach over 1427°C (2600°F) (EPA, 2002). Cement simulation tests for arsenic, Se, and Pb desorption were performed in duplicate on the ADA fly ashes (baseline only). The tests show good reproducibility and indicate that virtually all of the metals tested are volatilized when exposed to high temperature as shown in Figure E-2.

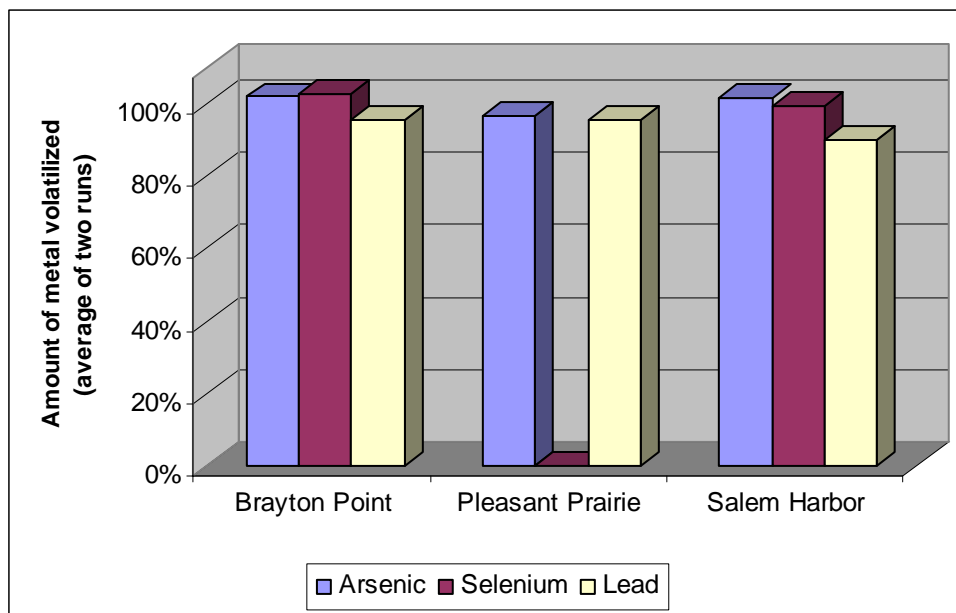


Figure E-2. Results of high-temperature cement kiln simulations

Note: Se levels for Pleasant Prairie Baseline fly ash were below minimum detection levels; therefore, no volatility results are presented.

Hot mix asphalt is a combination of 95% aggregate (e.g., stone, sand, or gravel) bound together by asphalt cement, a product of crude oil. Fly ash can make up approximately 5% of the total aggregate weight, replacing natural fillers such as hydrated lime or stone dust (EPA, 2002). Asphalt manufacturing consists of a very short residence time mixing process (about one minute), a long residence time storage process (several hours), and then application. The storage process occurs at temperatures of about 5 °C higher than the mixing process. Asphalt is delivered to the paving machine at approximately the same temperature as it is stored. Therefore, the most important step (in terms of thermal desorption) is the storage step. Storage temperatures typically range from 127 °C to 143 °C for binder grade PG46-28 and 157 °C to 168 °C for binder grade PG82-22.

Results for duplicate asphalt simulation tests at 170 °C using the ADA fly ashes are presented in Figure E-3. Results shown are normalized for mercury measured after completion of the simulation tests. In all cases, the majority of the mercury was retained in the solid after simulation, with minimal measured volatilization of mercury (<10% in all cases). Generally, the addition of ACI increased the tendency for mercury to be retained in the solids at the temperature tested. Total absolute mercury volatilized from samples with activated carbon injection was <1% for all samples tested.

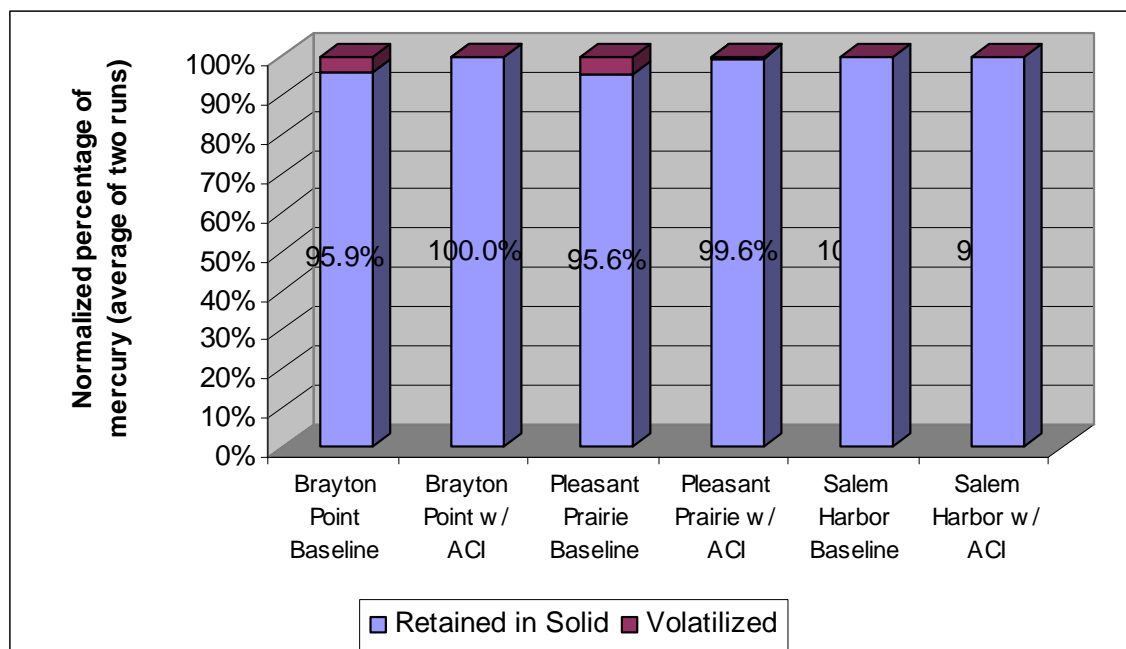


Figure E-3. Normalized results of asphalt simulations tests for ADA fly ashes

Asphalt simulations were run at 170 °C using fly ashes from six facilities (in addition to the ADA samples). Four of the fly ashes were obtained with and without post-NO_x combustion control in use (Facility A and B). None of these samples had ACI in use. Except for Facility M with a mass balance of 74%, the non-ADA fly ashes have a mercury mass balance ranging from 92.5 to 101%. Figure E-4 shows the results of these experiments that have been normalized by adjusting the mass balance to 100%. As was the case for the ADA fly ashes, Facility A and Facility E showed minimal mercury loss upon heating. Facility B, however, demonstrated high mercury volatility (~70-90% loss upon heating).

There was no obvious reason for the higher loss of mercury seen for the Facility B fly ash. Perhaps the type of SCR catalyst in use at Facility B may have interacted with the fly ash making the mercury less tightly bound. Additional testing is needed to evaluate this using a wider range of samples

Asphalt simulation tests at 170 °C for the Brayton Point and Facility B fly ashes showed no measurable volatilization of arsenic, Se, and Pb at the temperature tested during duplicate runs.

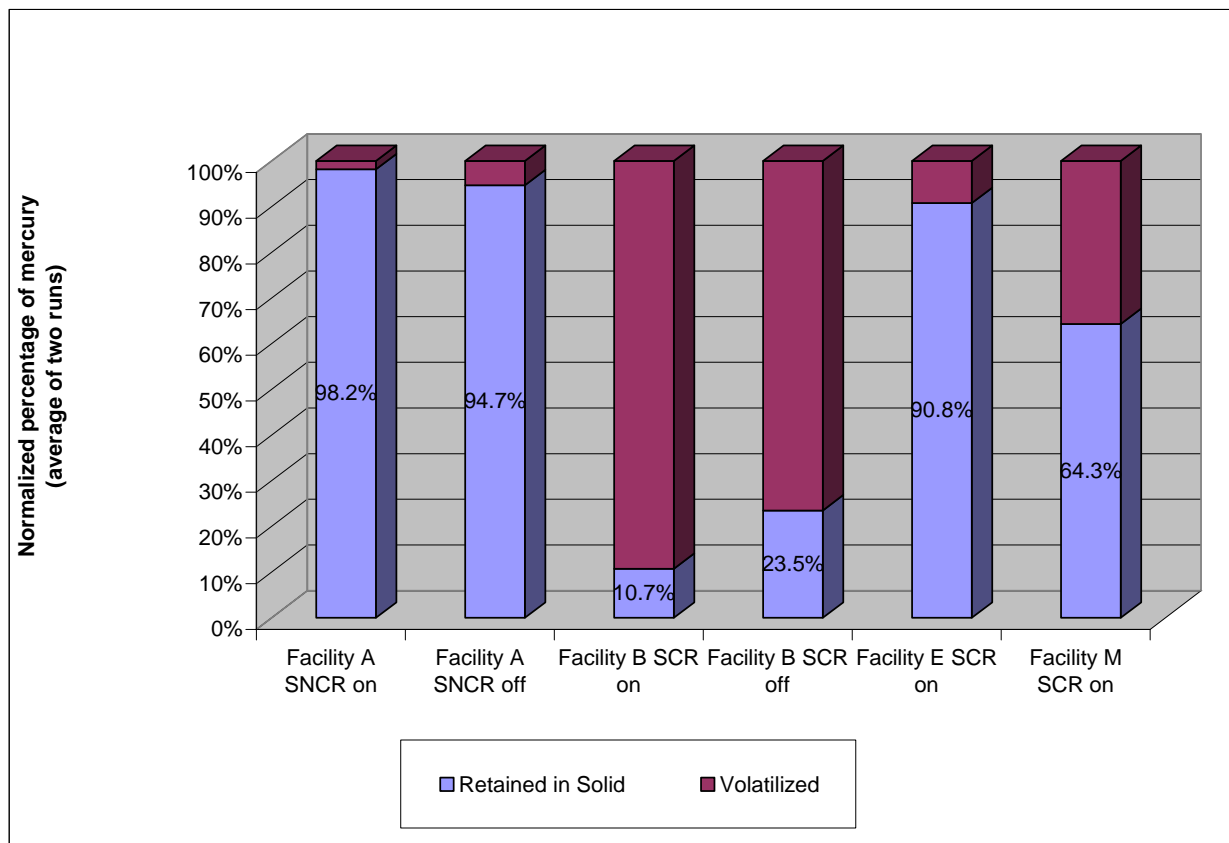
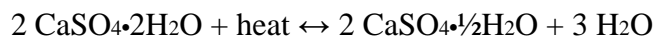


Figure E-4. Normalized results of asphalt simulation tests for non-ADA fly ashes

Wallboard is made using calcium sulfate which can be mined as natural rock or obtained from a coal-fired power plant using flue-gas desulfurization (FGD) gypsum. The first step in the process to make wall board is to dry the gypsum so that it contains no free moisture – only chemically bound waters of hydration. This material is referred to as “land plaster”. The next step is to calcine the land plaster in a kettle for about one hour to form calcium sulfate hemi hydrate (i.e., stucco or plaster of Paris) according to the following reaction:



The stucco is mixed with water and additives to form slurry that is extruded between two sheets of paper to form wallboard. The final step is to dry the wallboard prior to processing and stacking it as final product. Any potential loss of mercury is assumed to occur during the thermal processes with losses most likely to occur during the calcining step. The highest temperature that FGD gypsum is exposed to is 128°C. Losses could also occur in the gypsum dryer and the finished wallboard dryer. However, the maximum temperatures that FGD gypsum is exposed to in the dryers is less than calcining (77 to 110°C). (Sanderson et al., 2008)

Sanderson et al., (2008) provide the most extensive study to date on the fate of Hg when FGD gypsum is used as feedstock for wallboard production. This work was conducted by U.S. Gypsum Corporation (USG). Testing of full-scale production facilities is considered more reliable than laboratory testing to simulate wallboard production. However, the study did not include other metals. Therefore, laboratory

simulation of wallboard production was conducted as part of this study. Results from Sanderson et al., (2008) indicate that the process where Hg loss is more likely to occur is the kettle calciner. Therefore, laboratory simulation of wallboard production was conducted evaluating Hg and other metals with the focus on trying to simulate potential loss across the kettle calciner. Only FGD gypsum samples were used in this simulation since this is the material used in the production of wallboard (and not fly ash). This research was conducted in two phases. The first phase resulted in unacceptable mass balance for Hg. The results for the other metals are considered acceptable. Consequently, additional testing was conducting in a second phase using more recent FGD samples.

The first phase of testing suggests that As and Se are more likely retained in the FGD gypsum and less likely to be volatilized during the kettle calcining process. The second phase of testing provided improved Hg mass balance results. The results (Figure E-5) indicate potential Hg loss of 9 to 48%. The USG results from wallboard manufacturing facilities indicate Hg loss across the kettle calciner (excluding the Texas lignite sample) of 2 to 50%. This is considered confirmation of the previous USG research and emphasizes the variability across samples that may be attributed to how the wet scrubber is operated. However, additional research is needed to better understand the parameters that might affect Hg loss across a production facility.

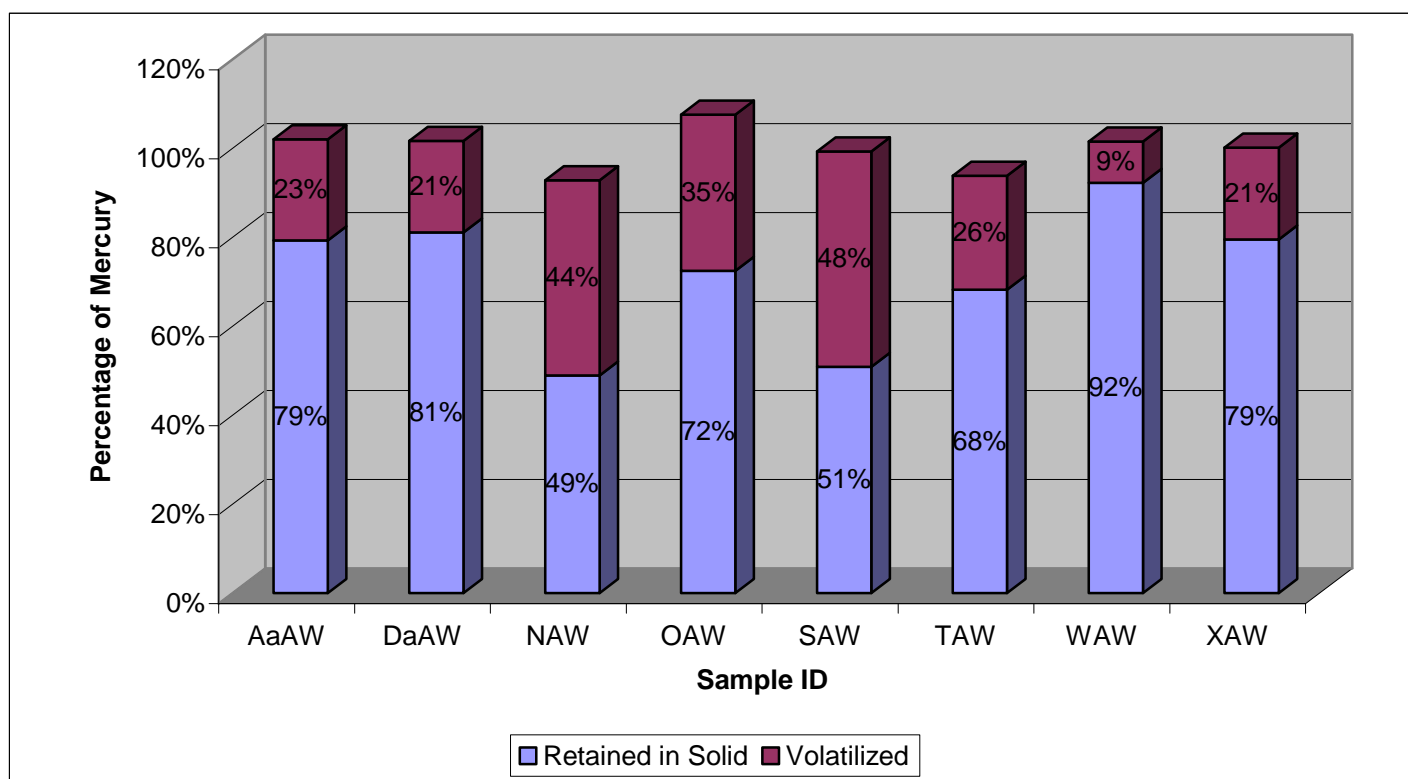


Figure E-5. Results for wallboard simulation tests on gypsum samples.

The results from this laboratory study demonstrate the varying degree of volatility for mercury, arsenic, Se and Pb in CCRs depending on the process temperature being used. A high temperature process such as

cement clinker production has the ability to release all four metals from fly ash when exposed to the high temperatures found in production. Laboratory simulation of the asphalt and wallboard production processes showed a significant release of mercury during heating, but the temperatures were too low to volatilize the arsenic, Se, or Pb. Whereas, the Hg loss for wallboard production suggest non-Hg metals being retained in wallboard with a potential Hg loss of 9 to 48%. However, the actual mass emission rates must be considered when determining potential concern to human health and the environment.

Chapter 1

Introduction

More wide-spread implementation of multi-pollutant controls is occurring at U.S. coal-fired power plants. Research is underway by the U.S. Environmental Protection Agency (EPA) to document changes that may occur to coal combustion residues (CCRs) as a result of implementation of mercury and multi-pollutant control technology at coal-fired power plants. The Air Pollution Prevention and Control Division (APPCD) of EPA's Office of Research and Development (ORD) is conducting research to evaluate cross media transfers of mercury and other constituents of potential concern (COPCs) resulting from the management of CCRs resulting from wider use of state-of-the art air pollution control technology. This research was cited as a priority in EPA's Mercury Roadmap to ensure that one environmental problem is not being traded for another. (2006b) The objective is to understand the fate of mercury (Hg) and other COPCs in air pollution control residues and support EPA's broader goal of ensuring that emissions being controlled in the flue gas at power plants are not later being released to other environmental media. The focus of this report is on the use of CCRs in high-temperature processes that are encountered during the production of cement clinker, asphalt, and wallboard.

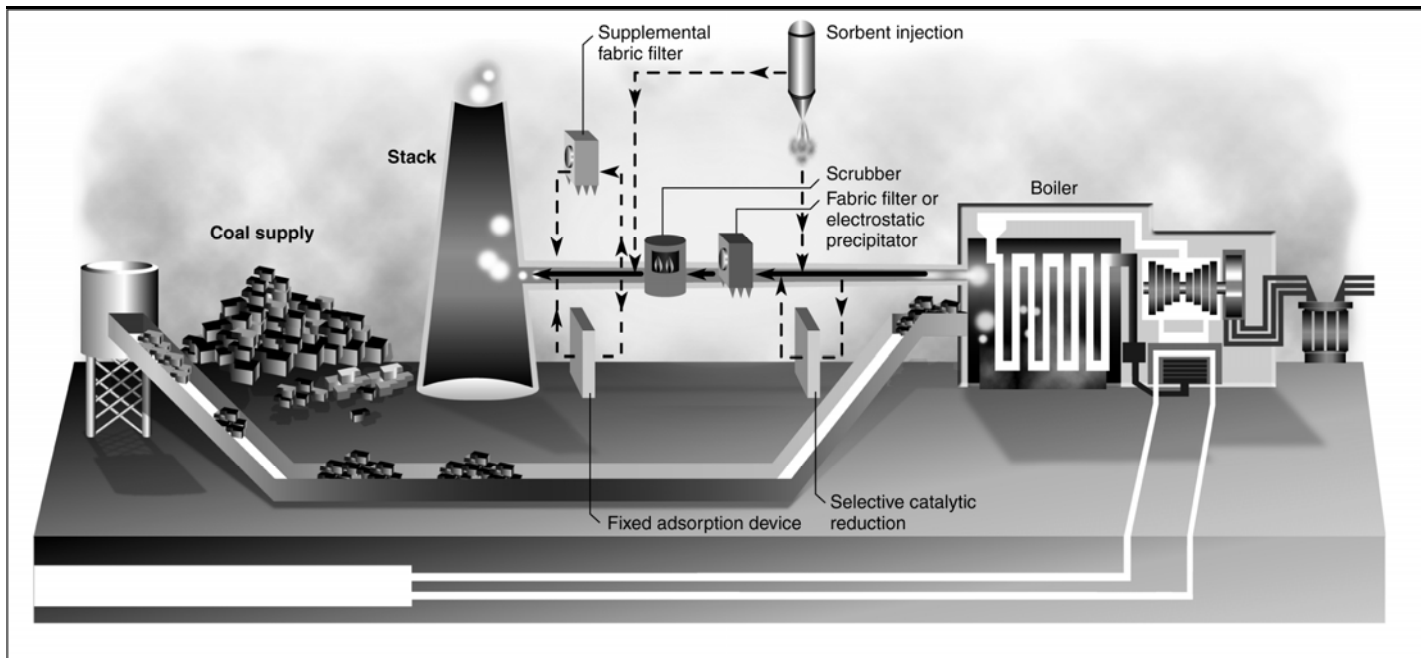
1.1 Coal Combustion Residues from Multi-Pollutant Control Technology

Coal-fired power plants are the largest remaining source of anthropogenic mercury emissions in the U.S. Power plants are also a major source of nitrogen and sulfur oxides, particulate matter, and carbon dioxide. New environmental regulations in the U.S. will result in lower mercury air emissions. However, the mercury and other pollutants are transferred from the flue gas to fly ash and other air pollution control residues. The Clean Air Mercury Rule (CAMR) would have required the electric utility sector to remove at least 70% of the mercury released from power plant stack emissions by 2018. CAMR was vacated by the United States Court of Appeals for the District of Columbia Circuit in 2008. EPA is currently developing regulations under Section 112 of the Clean Air Act to reduce hazardous air pollutants (including mercury) from coal-fired power plants. Twenty states have implemented their own mercury regulations already, according to the National Association of Clean Air Agencies. (Senior et al., 2009) Other EPA regulations² will necessitate the addition of new air pollution control devices for NO_x and SO₂ at some power plants. This can also affect the fate of mercury and other COPCs.

Figure 1 illustrates the types of air pollution control that coal-fired power plants are installing to reduce air emissions of concern. These control technologies include the addition of flue-gas desulfurization (FGD) systems to control sulfur dioxide, post-combustion NO_x control [selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR)], and activated carbon injection to enhance mercury capture. These controls are typically added to particulate control devices which include the use of electric static precipitators (ESPs). Fabric filters are also in use for particulate control. The specific type and combination of control technology as well as the coal type being burned can impact the physical and

²On March 10, 2005, EPA announced the Clean Air Interstate Rule (CAIR) (FR 25612, May 2005) which is expected to increase the use of wet scrubbers and selective catalytic reduction (SCR) units to help reduce sulfur dioxide and nitrogen oxides emissions from coal-fired power plants. On July 11, 2008, United States Court of Appeals for the District of Columbia Circuit remanded CAIR back to EPA for further review and clarification. Thus the rule remains in effect; however, EPA is in the process of developing a replacement rule that will address the Court's concerns.

chemical characteristics of the CCRs. Use of air pollution control technologies will shift Hg and other pollutants from the stack gas to fly ash, FGD gypsum, and other air pollution control residues.



Source: GAO analysis of Electric Power Research Institute data.

Figure 1-1. Illustration of the types of air pollution control that can be used at a coal-fired power plant (U.S. Government Accountability Office, 2009)

Annual statistics of CCR production and utilization is provided through the American Coal Ash Association. (www.aaa-usa.org) As of 2008, 136 million tons of CCRs were produced with ~61 million tons (or 45%) being used in commercial, engineering, and agricultural applications (ACAA, 2009). CCRs result from unburned carbon and inorganic materials in coals that do not burn, such as oxides of silicon, aluminum, iron, and calcium. Fly ash, representing 53% of CCRs, is the unburned material from coal combustion that is light enough to be entrained in the flue gas stream, carried out of the process, and collected as a dry material in the air pollution control equipment. Bottom ash is the unburned material that is too heavy to be entrained in the flue gas stream and drops out in the furnace. Boiler slag, unburned carbon or inorganic material in coal that does not burn, falls to the bottom of the furnace and melts. Bottom ash and boiler slag are not affected by air pollution control technology and, therefore, these materials are not being evaluated as part of this study.

Both fly ash and FGD residues have been identified as CCRs with the potential to have increased mercury and/or other pollutant concentrations from the implementation of new air pollution technologies (EPA, 2002; Srivastava et al., 2006; Thorneloe et al., 2008). The chemical and physical properties may also change as a result of sorbents and other additives being used to improve air pollution control. The samples used in this study have been evaluated for their chemical and physical composition and the potential for leaching of mercury and other COPCs. Companion reports are available providing additional data on the characterization of these samples. (EPA 2006b, 2008b, 2009)

Table 1-1 provides the quantity of fly ash and FGD gypsum generated in 2008, the amount used in commercial applications, and the primary applications (ACAA, 2009). Three commercial applications of

CCRs that involve exposure to high-temperature include production of cement clinker, asphalt, and wallboard. As shown in Table 1-1, fly ash and FGD gypsum are used in the production of cement clinker. According to the ACAA, 3.2 million tons of fly ash and 0.4 million tons of FGD gypsum are used in the production of cement clinker. For wallboard production, only FGD gypsum (and not fly ash) is used which avoids the need for mining natural gypsum. Of the 17.8 million tons of FGD gypsum produced in 2008, 8.5 million tons (or 48%) were used in the production of wallboard. Because of the wider use of wet scrubbers in response to CAIR regulations, this amount is expected to increase with a higher volume of FGD gypsum³ being generated. Much less volume of CCRs is used in the production of asphalt. Review of the ACAA statistics indicate that only fly ash is used as mineral filler in the production of asphalt with a quantity of 17 thousand tons (ACAA, 2008). Therefore, of the three high-temperature processes, about 12 million tons of CCRs were used in the production of cement clinker, asphalt, and wallboard with asphalt representing less than 1% of this quantity.

Table 1-1. Fly ash and FGD gypsum production and use in the U.S.^a

CCR Type	Produced (million tons)	Used in Commercial Applications (million tons)	Percent Used	Primary Applications
Fly Ash	72.4	30.1	42%	Concrete & grout, structural fill, waste stabilization/solidification, cement clinker
FGD Gypsum	17.8	10.6	60%	Wallboard, cement clinker, concrete

^aData from industry survey by ACAA, 2009

Tracking the fate of Hg and other metals removed from the flue gas at a coal-fired power plant, requires an understanding of the air pollution control in use. Mercury can be found in the gaseous elemental (Hg^0), gaseous oxidized (Hg^{2+}), and particulate bound (Hg_p) forms. Air pollution control devices designed to capture SO_2 and particulate matter (PM) can also remove Hg from flue gases in two ways: removal of Hg_p in particulate control devices and removal of Hg^{2+} in FGD scrubbers. Thus, the Hg removed from the flue gas may be found in fly ash and in the scrubber solids and liquid effluent. (Senior et al., 2009)

The Hg that is removed in the FGD scrubber can partition to the solid or liquid streams. Figure 1-2 illustrates the measured partitioning of Hg in FGD outlet streams at five pulverized-coal fired power plants. (Withum, 2006) The plants fired bituminous coals and had cold-side ESPs for particulate control. Each of these plants had a selective catalytic reduction (SCR) system for NO_x control and a wet FGD using calcium-containing slurry to control SO_2 . Gaseous Hg removal by the FGDs ranged from 77% to 95%, and the Hg was found to be in the scrubber solids. (Senior et al., 2009)

³ If natural or inhibited oxidation occurs, then calcium sulfite and not calcium sulfate (i.e., gypsum) is produced.

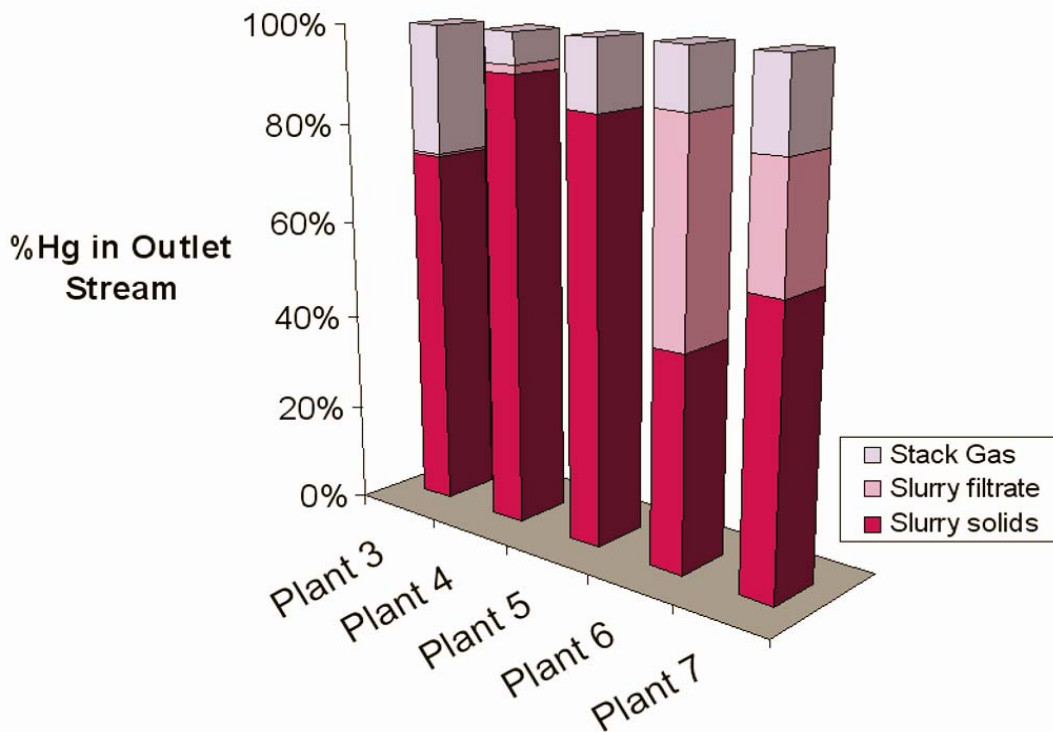


Fig. 1-2 Distribution of mercury in FGD scrubber outflows at five bituminous coal-fired power plants with SCR and FGD. (Senior et al., 2009; Withum, 2006)

Mercury appears to be concentrated in fine particles of scrubber solids that are predominantly iron oxyhydroxides, and is not strongly associated with the solid calcium sulfate in the scrubber. (Senior et al., 2009; Kaires et al., 2006; Schroeder, 2007). In some wet FGD systems, the fine solids are recycled back to the scrubber after dewatering of the byproduct solid, while in others, they are disposed of, as was the case for two FGDs noted in an EPRI study. (Richardson et al., 2003) Table 2 shows the distribution of mercury in the scrubber outlet streams for three limestone scrubbers in the EPRI study. For the two forced-oxidation scrubbers sampled, most of the Hg leaving the scrubber did so in the gypsum fines or fines liquor after the dewatering process. In forced oxidation scrubbers, this means that Hg can ultimately be in the gypsum fines as well as in the FGD byproduct. Therefore, it is important to understand how the FGD gypsum fines are managed in tracking the fate of Hg and other metals in the use of FGD gypsum in wall board production or other applications.

Table 1-2. Distribution of mercury among scrubber outlet streams. (Richardson et al., 2007)

Plant – Scrubber Type	FGD Byproduct^a	Gypsum Fines^b	Gypsum Fines Liquor^c	Stack Gas
1 – Forced Oxidation	18.9%	7.8%	58.9%	14.4%
	7.3%	5.2%	65.6%	20.8%
2 – Forced Oxidation	48.1%	48.1%	0.0%	3.7%
3 – Inhibited Oxidation	65.7%			35.4%

^aCalcium sulfate hemihydrate or gypsum produced by the FGD system.

^bSolid phase from hydroclone overflow stream sent to disposal.

^cLiquid phase from hydroclone overflow stream sent to disposal.

1.1.1 CCR Use in Cement Clinker

The making of cement involves the heating of various feedstocks in a cement kiln to make “clinker.” This clinker is ground with gypsum and transported to ready-mix concrete manufacturers. Various components are needed for feedstock including lime (CaO), iron oxide (Fe₂O₃), silica (SiO₂) or alumina (Al₂O₃). Fly ash can replace a portion of these, representing a maximum of about 5% (by weight) of the typical raw mix to the kiln. Other inputs typically include limestone (90%), iron ore (3%), and sand (2%). Fly ash contains high amounts of calcium, iron, silicon, and aluminum, replacing or augmenting raw feed stocks used in cement production. Cement kiln residence time is typically one to three hours, and temperatures reach over 1427 °C (2600 °F) (EPA, 2002). Because of the high temperatures, virtually all mercury will be volatilized when CCRs are used as feedstock to cement kilns.

Because of the concern for Hg and other hazardous air pollutants, EPA has proposed (74 FR 21136m May 6, 2009) regulations to reduce Hg emissions from cement kilns, which may result in use of air pollution control technology similar to that used at coal-fired power plants (e.g. wet scrubbers and sorbents for enhanced Hg capture). The addition of air pollution control at cement kilns should not affect the ability to use fly ash or FGD gypsum in the production of clinker. However, to avoid installation of air pollution control, kiln inputs (such as fly ash) containing Hg may be avoided which could impact usage of some CCRs.

1.1.2 CCR Use as Aggregate in Asphalt

Hot mix asphalt is a combination of 95% aggregate (e.g., stone, sand, or gravel) bound together by asphalt cement, a product of crude oil. Fly ash can make up approximately 5% of the total aggregate weight, replacing natural fillers such as hydrated lime or stone dust (EPA, 2002). Asphalt manufacturing consists of a very short residence time mixing process (about one minute), a long residence time storage process (several hours), and then application. The storage process occurs at temperatures of about 5 °C higher than the mixing process. Asphalt is delivered to the paving machine at approximately the same temperature as it is stored. Therefore, the most important step (in terms of thermal desorption) is the

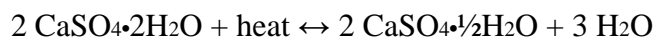
storage step. Storage temperatures typically range from 127-143 °C for binder grade PG46-28 and 157-168 °C for binder grade PG82-22.).

1.1.3 FGD Gypsum Use in Wallboard

In 2007, FGD gypsum (e.g., gypsum produced from use of wet scrubbers) accounted for 35% of the total domestic gypsum production (9.2 million tons of FGD gypsum used versus 26.4 million tons of domestic gypsum supply (ACAA, 2008; USGS, 2008). Almost 85% of the gypsum consumed in the U.S. (approximately 24 million tons) in 2008 was used in the manufacture of wallboard and plaster products with U.S. wallboard plant capacity at 27 billion square feet per year (USGS, 2009). As more coal combustion facilities add scrubbers, the production (and use) of FGD gypsum is projected to grow.

FGD gypsum is typically dewatered at the utility plant before shipment to a wallboard manufacturing facility (EPA, 2002). The mercury in the FGD sludge has been reported to be associated with the fines (i.e., fine solid particles) and not the FGD liquors (DOE; 2005; Schroeder and Kairies, 2005). There are several ways FGD solids can be prepared for use at a wallboard manufacturing plant. If the FGD sludge does not meet the wallboard manufacturer's specifications (as-is), then the fine solid particles are typically removed. This removal process is often completed with hydrocyclones and the fines are either disposed or sold for other uses (DOE, 2005). Other facilities have to "blow down gypsum fines" as a part of the chlorine purge, limiting chlorine buildup in the FGD liquor (DOE, 2005). As wall deposits buildup, the scrubber efficiency will be reduced until scrubber water rich in solids or salts is wasted or "blown down" and replaced with low solids water. Since Hg is associated with the fine particles of the FGD sludge (DOE, 2005), both of these processes result in a gypsum product which typically contains less mercury than the wet FGD sludge itself. If the FGD sludge is used as-is, the mercury content is typically greater than those processes that remove the fines.

The first process in making wall board is to dry the gypsum so that it contains no free moisture – only chemically bound waters of hydration. This material is referred to as "land plaster". The next step is to calcine the land plaster to form calcium sulfate hemi hydrate (i.e., stucco or plaster of Paris) according to the following reaction:



The stucco is mixed with water and additives to form slurry that is extruded between two sheets of paper to form wallboard. The final step is to dry the wallboard prior to processing and stacking it as final product. The drying step is not likely a release point for mercury since the wallboard is between two sheets of paper at this point and typically does not reach temperatures of more than 100 °C. Meischen (2004) conducted a study on laboratory-produced FGD containing Hg and concluded that Hg volatilization would not be likely where only the edges of the wallboard were exposed. Mercury release diminished as the weight of the wallboard increased.

Any potential loss in Hg is considered more likely to occur during the calcining step. The highest temperature that FGD gypsum is exposed to is 128°C. However, possible losses could also occur in the gypsum dryer and the finished wallboard dryer. However, the maximum temperature to which the gypsum is exposed in the dryers is less than during calcining (77 to 110°C). (Sanderson et al., 2008)

The drying step is not likely a release point for mercury since the wallboard is between two sheets of paper at this point and typically does not reach temperatures of more than 100 °C. Meischen (2004) conducted a study on laboratory-produced FGD containing mercury and concluded that mercury

volatilization would not be likely where only the edges of the wallboard were exposed. Mercury release diminished as the weight of the wallboard increased.

Sanderson et al., 2008, provide data evaluating the fate of Hg in FGD gypsum across wallboard production plants. This work was conducted by U.S. Gypsum through funding by DOE and the Electric Power Research Institute (EPRI). Table 1-3 provides a summary of the results from measurements of the Hg content in FGD gypsum and across the gypsum dryer, calciner, and wallboard dryer. The results show a wide-range of Hg losses ranging from 2 to 55% loss of mercury in the feedstock and using Ontario Hydro method at the process stacks. Most of the loss was found to occur at the gypsum calciner when the total Hg loss was greater than 10%. There was less of a difference across the gypsum dryer, calciner, and wall board dryer when the mercury loss was below 10%. (Sanderson et al., 2008)

The authors caution drawing conclusions from this research because only seven sets of wallboard plant measurements were made and it is difficult to identify what factors impact mercury loss percentages. One finding is that the operation of the wet scrubber can affect the fate of Hg. The effectiveness of the scrubbing solution in removal of COPCs depends on the concentration of the scrubbing chemical which is continuously being depleted during the process. COPCs transferred to the liquid phase are removed from the scrubber by continuous or periodic overflow of blow down. For those facilities using higher blow down rates of chlorides and fine solid particles at wet FGD systems led to higher percentage of Hg loss at the wallboard plant. However, higher purge rates also led to FGD gypsum with lower Hg concentrations. The authors conclude that improved understanding the physical and chemical association of the Hg in gypsum might clarify the conditions that lead to the higher Hg loss.

The US Gypsum study did not include analysis of metals other than mercury. Therefore, wallboard simulation study was included as part of this research. However, testing of full scale production facilities is considered preferable over conducting smaller-scale laboratory simulations. US Gypsum provide two samples from their earlier testing to use in this study.

1.2 Objective

With the increasing metals content of CCRs as a result of changes in air pollution control at coal-fired power plants, there is interest in evaluating the fate of mercury and other metals. The objective of this research is to conduct laboratory simulations of three high temperatures processes that use CCRs in the production of cement clinker, asphalt and wallboard to determine the likelihood of metals being volatilized during the production process. The metals that were analyzed for this study include Hg, arsenic (As), selenium, and lead (Pb). The study support EPA's broader goal of ensuring that emissions being controlled in the flue gas at power plants are not later being released to other environmental media

Table 1-3. Sanderson et al., 2008 study to evaluate of Hg loss across wallboard production facilities

Test #	1	2	3	4	5	6	7
Test Date (2 day test)	July 2004	Dec 2004	Sept 2004	Feb 2005	March 2006	Sept 2006	Aug 2007
Power Plant	A	A	B	C	E	E	F
Coal Type	High-Sulfur Bituminous	High-Sulfur Bituminous	High-Sulfur Bituminous	Texas Lignite	High-Sulfur Bituminous	High-Sulfur Bituminous	Powder River Basin
SCR in use	Yes	By-passed	Yes	No	By-passed	Yes	Yes
FGD Fines Blow Down ^a	Low rate	Low rate	High rate	None	High rate	High rate	Variable ^b
Wallboard plant	1	1	2	3	4	4 ^c	5
Hg content, FGD gypsum ($\mu\text{g/g}$) ^d	0.96 \pm 0.03	1.10 \pm 0.04	0.21 \pm 0.02	0.53 \pm 0.01	0.20 \pm 0.04	0.13 \pm 0.0	1.06 \pm 0.06
Moisture content, wt%	11.9	11.1	11.3	12.6	10.9	6.3	7.2
Hg Loss at Wallboard ^d - % of inlet Hg to each process step							
-Across Dryer Mill (%)	1.1 \pm 0.9	0.3 \pm 0.1	1.0 \pm 0.3	0.8 \pm 0.1	1.8 \pm 0.4	4.1 \pm 1.9	0.6 \pm 0.4
-Across Kettle Calciner (%)	2.3 \pm 1.0	2.6 \pm 0.0	41 \pm 2	0.8 ^e	50 \pm 6	45 \pm 1	15 \pm 2
-Across Board Dryer Kiln (%)	1.9 \pm 0.6	5.5 \pm 2.4	14 \pm 6	0.3 ^e	1.4 \pm 1.2	5.8 \pm 5.6	3.2 \pm 1.0 ^e
Overall Loss	5.1 \pm 1.7	8.3 \pm 2.0	46 \pm 16	1.8 ^e	51 \pm 5	55 \pm 6	18 \pm 2 ^e
Hg Loss Based on Raw Gypsum & Wallboard Product Hg Conc ^d , %	2.0 \pm 5.0	16 \pm 8	66 \pm 2	8.7 ^e	40 \pm 21	32 \pm 2	32 \pm 3
Hg Loss from Process Stacks, g/hr	4.1 \pm 1.7	2.7 \pm 0.1	8.2 \pm 0.5	0.26 ^e	2.0 \pm 0.2	1.4 \pm 0.2	4.2 \pm 0.6 ^e
Hg Loss Rate, lb/MM ft ² of wallboard	0.1	0.1	0.2	0.01 ^e	0.2	0.1	0.4 ^e
Hg Loss Rate, g/ton of dry FGD gypsum	0.05	0.08	0.09	0.01 ^e	0.09	0.06	0.17 ^e

^aMore qualitative than quantitative as reported by Sanderson et al, 2008.

^bWastewater treatment plant for FGD system uses filter press for removing fine particles from hydrocyclone overflow liquor, so fine and chlorides can be "blown down" independently.

^cDuring this test, soluble tri-sodium salt (or TMT) was used to precipitate dissolved Hg (by chemically binding to heavy metals via sulfur groups which can be separated from the FGD liquor by filtration).

^dMean value for three runs \pm 95% confidence interval of mean, unless noted otherwise; loss percentages across dryer mill, kettle calciner, and board dryer kiln are based on feed material to each step, so percentages cannot be summed to the wallboard product overall loss percentage show.

^eMean value for two runs

Chapter 2 Materials and Methods

2.1 CCR Materials for Evaluation

Twenty-one CCR samples were used to evaluate the thermal stability of mercury and other metals during the production of cement clinker, asphalt, and wallboard. This work has been conducted in stages with initial work using samples collected as part of a DOE-funded program to evaluate sorbent technology for enhanced mercury capture. Samples were also obtained through CCR characterization study evaluating changes in CCR composition and constituent release by leaching that may occur to fly ash and FGD gypsum in response to changes in air pollution control technology at coal-fired power plants (EPA 2006, 2008b, 2009). Because samples were obtained on a voluntary basis and represent a minor fraction (<1%) of U.S. boilers, these results are not considered to provide a statistically representative sample. Regardless, care was taken to obtain samples that are considered typical of the CCRs resulting from improvements in air pollution control.

The samples analyzed include:

1. Fly ash from three different facilities evaluated by ADA-Environmental Solutions (ADA) under contract for the Department of Energy's (DOE) National Energy Technology Laboratory (NETL). Powdered activated carbon was injected upstream of particulate control to improve the capture efficiency of mercury. Samples were collected from Brayton Point, Pleasant Prairie, and Salem Harbor with and without the use of activated carbon injection (ACI) for a total of six samples as shown in Table 2-4.⁴
2. Fly ash from two facilities with and without the use of post-NO_x combustion control [Facility A using selective non-catalytic reduction (SNCR) and facility B using selective catalytic reduction (SCR). Fly ash from two additional facilities (Facility E and M) both with SCR in use. This represents a total of five samples as shown in Table 2-5; and
3. FGD gypsum kettle feedstock obtained from U.S. Gypsum (two samples) as part of the research documented in Sanderson et al., 2008. Only a small sample size was provided which did not allow detail characterization as done for the other CCRs.

⁴ These samples were collected during early test programs to evaluate use of ACI for enhancing mercury capture. Samples were obtained prior to and after ACI in use. Industry has found that less carbon is needed to obtain the same level of mercury capture obtained during the early test programs. Therefore more recent samples are suspected to contain less carbon than that used in this evaluation. However, this is not suspected to impact the thermal evaluation.

4. FGD gypsum material obtained directly from eight power plants with wet scrubbers in use (eight samples).

The fly ash samples from the NETL field evaluation program represent the first time that sorbent was used to enhance mercury capture over a test program of several weeks. All three of the facilities in the NETL program (Brayton Point, Salem Harbor and Pleasant Prairie) have particulate control devices and do not use scrubbers (at the time the samples were collected). The same commercial sorbent, Norit Americas Flue Gas Desulfurization (FGD) Carbon, was used for each test. This sorbent has a surface area of 600 m²/g and a mass-mean diameter of 18 μm. The ACI was injected at a rate of 10 lb/Macf during the sorbent testing phase of these tests.

All of the facilities mentioned above are further described in subsequent sections. Tables 2-1 and 2-3 provide the elemental characteristics of the coal combusted at Brayton point, Pleasant Prairie, and Facilities A, B, and E. Table 2-2 provides the elemental analysis [by x-ray fluorescence (XRF) spectroscopy] of the fly ashes from the ADA samples and Facility A, B, E, and M. Except for the samples from U.S. Gypsum (the sample size was too small), for each of the CCRs used in this study, more detailed information is available on the air pollution control configurations, coal burned, and the CCR composition and leaching characteristics. (EPA 2006, 2008b, 2009).

2.1.1 Brayton Point

Brayton Point Station, located in Somerset, Massachusetts, is operated by PG&E National Energy Group. Unit 1 of this facility was selected for evaluation. Emissions from this facility are controlled through the use of low-sulfur coal and cold-side ESP which is typical of coal-fired power plants in the eastern U.S. The unit has a tangentially fired boiler rated at 245 MW, fires low-sulfur coal, and uses a cold-side ESP for particulate control (Senior et al., 2003a).

The primary particulate control equipment consists of two cold-side ESPs in series, with an EPRICON flue gas conditioning system provides SO₃ for fly ash resistivity control and is used on an as-needed basis. The first ESP in this particular configuration was designed and manufactured by Koppers with a weighted wire design and a specific collection area of 0.512 m²/ am³/min (156 ft²/1000 acfm). The second ESP in the series configuration was designed and manufactured by Research-Cottrell with a rigid electrode design and a specific collection area of 1.3 m²/ am³/min (403 ft²/1000 acfm). The precipitator inlet gas temperature is nominally 138 °C (280 °F) at full load (Senior et al., 2003b). The facility uses ACI to increase mercury capture. The ACI control system injects the carbon between the ESPs to capture the mercury with the fly ash. The baseline and post-control ashes used for this study were collected as composite samples from the third row of ash hoppers of the second ESP. The baseline ash was collected on June 6, 2002. The post-control fly ash was collected on July 21, 2002. Both fly ashes were stored in five-gallon buckets in the onsite ADA-ES trailer at ambient temperatures. The buckets were filled to approximately three-fourths capacity.

Elemental composition by XRF and additional characteristics of the fly ashes from baseline and enhanced mercury control testing are provided in Table 2-2. Results for total content analyses for mercury, arsenic, Pb, and Se are provided in Table 2-4.

2.1.2 Salem Harbor

PG&E National Energy Group owns and operates Salem Harbor Station located in Salem, Massachusetts. There are four fossil fuel fired units at the facility designated as Units 1, 2, 3, and 4. Units 1-3 fire a low sulfur, bituminous coal and use oil for startup. Unit 1 was selected for the control technology evaluation because of its combination of firing low-sulfur bituminous coal with urea-based selective non-catalytic reduction (SNCR) for nitrogen oxide reduction, a cold-side ESP, and high loss-on ignition (LOI). This configuration provided an opportunity to quantify the impact of SNCR on mercury removal and sorbent effectiveness. In addition, test results from prior mercury tests have indicated 87 to 94% mercury removal efficiency on this unit. Unit 1 is a B&W single-wall-fired unit with twelve DB Riley CCV-90 burners and is rated at 88 gross MW (Senior et al., 2003b).

Table 2-1. Characteristics of air pollution control and for samples obtained from Brayton Point, Pleasant Prairie, Salem Harbor, and Facilities A, B, and E

Parameter Measured	Brayton Point	Pleasant Prairie	Salem Harbor	Facility A	Facility B	Facility E
Coal Type	Low sulfur bituminous	Powder River Basin (PRB) sub-bituminous	Low sulfur bituminous	Medium sulfur bituminous	High sulfur bituminous	Low sulfur bituminous
Sulfur, wt%	0.7	0.3	0.67	1.05	3.34	0.83
Ash, wt %	10.8	5.1	6.48	10.29	12.4	9.3
Moisture, wt:	4.7	30.7	9.05	6.0	6.1	4.06
HHV, Btu/lb	12,780	8,385	12,420	12,790	12,000	12,852
Hg, µg/g	0.044	0.109	0.0617	0.086	0.08	0.06
Cl, µg/g	1475	8.1	64.3	166	615	4500
As, µg/g	5.68	NT	2.4	NT	NT	4.0
Pb, µg/g	8.9	NT	3.8	NT	NT	6.0
Se, µg/g	3	NT	4.8	NT	NT	3.0
Particulate Control Device	Two Cold-Side ESPs in Series	Cold-Side ESP	Cold-Side ESP	Fabric Filter	Cold-Side ESP	Cold-Side ESP
Sorbent Injection Point	Between Two ESPs	Before ESP	Before ESP	NA	NA	NA
Sampling Location	Ash Hopper Row C	ESP Hopper 1 and 2 Composite	ESP Hopper A	Pug Mill	Ash Hopper	Ash Hopper

NT = Not tested, NA = Not applicable, HHV = Higher Heating Value (Heat of Combustion)

The particulate control equipment consists of a two-chamber, cold-side ESP (chambers designated 1-1 and 1-2), which provides two separate gas flow paths from the outlet of the tubular air heaters to the induced draft (ID) fan inlets. This Environmental Elements ESP has a rigid electrode design and a specific collection area of 1.56 m²/ am³/min (474 ft²/1000 acfm). The precipitator inlet gas temperature is nominally 124 °C (255 °F) at full load. Typical LOI of the Unit 1 ash is about 25%. This ash is landfilled (Senior et al., 2003b).

The baseline and post-control ashes used for this study were collected as grab samples from the first ash hopper (hopper A) of row 1-1 of the ESP. The baseline ash was collected on June 6, 2002. The post-control fly ash was collected on July 7, 2002. Both fly ashes were stored in five gallon buckets in the onsite ADA-ES trailer at ambient temperatures. The buckets were filled to approximately three-fourths capacity. Elemental composition by XRF and additional characteristics of the fly ashes from baseline and enhanced mercury control testing are provided in Table 2-2. Results for total content analyses for mercury, arsenic, Pb, and Se are provided in Table 2-4.

2.1.3 Pleasant Prairie

Wisconsin Electric Power Company, a subsidiary of Wisconsin Energy, owns and operates Pleasant Prairie Power Plant located near Kenosha, Wisconsin. The plant has two 600 MW balanced-draft coal-fired boilers designated units 1 and 2. Unit 2 was selected for inclusion in the NETL program because it burns a variety of Powder River Basin low sulfur, sub-bituminous coals. (Starns et al., 2002).

The primary particulate control equipment consists of cold-side ESPs of weighted wire design with a Wahlco gas conditioning system that provides SO₃ for fly ash resistivity control. The precipitators were designed and built by Research-Cottrell. The design flue gas flow was 61,164 am³/min (2,610,000 acfm). The precipitator inlet gas temperature is nominally 138 °C (280 °F) at full load (Starns et al., 2002).

Precipitator #2 is comprised of four electrostatic precipitators that are arranged piggyback style and designated 2-1, 2-2, 2-3, and 2-4. Each of the four precipitators is two chambers wide and four mechanical fields deep with eight electrical fields in the direction of gas flow. The specific collection area is 1.54 m²/ am³/min (468 ft²/1000 acfm) (Starns et al., 2002).

Hopper ash is combined from all four precipitators in the dry ash-pull system. The ash is sold as a “Class C” fly ash to be used as a base for concrete (Senior et al., 2004). The baseline ash was collected as a composite sample from ash hoppers 7-1 and 7-2 of ESP 2-4. The post-control ash was collected as a grab sample from ash hopper 7-2 of ESP 2-4. The baseline ash was collected on September 11, 2001. The post-control fly ash was collected on November 13, 2001. Elemental composition by XRF and additional characteristics of the fly ashes from baseline and enhanced mercury control testing are provided in Table 2-2. Results for total content analyses for mercury, arsenic, Pb, and Se are provided in Table 2-4.

2.1.4 Facility A⁵

The test site was a 440-MW coal-fired power plant with a reverse-air fabric filter followed by a wet flue gas desulfurization system. The unit burns ~1 percent sulfur eastern bituminous coal. The unit operated at nominally full load for the duration of the test program. A schematic diagram of the power plant is shown in Appendix A. The unit is equipped with a pulverized-coal boiler and in-furnace selective non-catalytic reduction (SNCR); urea was injected into the boiler during the course of operations within the duration of

⁵ EPA was requested not to disclose the identity of the other sites. Therefore, the remaining sites are coded as letters.

the initial part of this test program. However, urea was not injected into the boiler for the final comparison test ("SNCR off"). Gas exiting the furnace is split between two flues equipped with comparable control equipment. Particulate is removed with a reverse-air fabric filter. Flue gas is then scrubbed through a multiple tower wet FGD unit; FGD is a limestone forced-oxidation design. The two flues are joined prior to exhausting to a common stack. The annular stack rises 93.9 meters (308 feet) above the top of the incoming flue. The stack is operated in a saturated condition with no reheat. The fly ash and FGD waste are combined and then dewatered before landfill disposal. Elemental composition by XRF and additional characteristics of the fly ashes from baseline and enhanced mercury control testing are provided in Table 2-3. Results for total content analyses for mercury, arsenic, Pb, and Se are provided in Table 2-5.

2.1.5 Facility B

The test site was a 640 MW coal fired power plant with cold side ESP followed by a wet flue gas desulfurization system with inhibited Mag-lime ($\text{CaO} + \text{MgO}$). The unit burns medium- to high-sulfur eastern bituminous coal. The plant is equipped with a pulverized coal boiler and an in-furnace selective catalytic reduction (SCR) system composed of vanadium pentoxide (V_2O_5), tungsten trioxide (WO_3), and titanium dioxide (TiO_2) mixture. One set of samples was collected during a season of elevated ambient ozone while ammonia was injected into the catalyst box at a concentration of 320 ppm ("SCR on") to control NO_x . A second set of samples was collected during the winter when ammonia was not being injected ("SCR off"). Particulate is removed with a cold-side ESP. Flue gas is then scrubbed through a wet FGD unit; the FGD unit is an inhibited Mag-lime design. The fly ash and FGD waste are combined and then dewatered before landfill disposal in a clay-lined site. Elemental composition by XRF and additional characteristics of the fly ashes from baseline and enhanced mercury control testing are provided in Table 2-3. Results for total content analyses for mercury, arsenic, Pb, and Se are provided in Table 2-5.

2.1.6 Facility E

The test site was a 390 MW coal fired boiler with cold side ESP. The unit burns low-sulfur eastern bituminous coals. The unit is equipped with a pulverized coal boiler and selective catalytic reduction (SCR) system using a titanium dioxide/tungsten trioxide/silicon dioxide/vanadium pentoxide catalyst. Particulate is removed with a cold-side ESP. The fly ash is transported by a dry handling system to a silo where it is combined with fly ash from three additional boilers and wetted with water prior to being transported to a clay-lined landfill. Elemental composition by XRF and additional characteristics of the fly ash are provided in Table 2-3. Results of total content analyses for mercury, arsenic, Pb, and Se are provided in Table 2-5.

2.1.7 Facility M

This test site was a 1,000 + megawatt (MW) power plant. The plant burns high-sulfur bituminous coal in a dry-bottom pulverized coal boiler. Electrostatic precipitators (ESPs) are used on all units for particulate control, and wet FGD systems are used to reduce SO_2 emissions on two units. The wet FGD systems utilize limestone slurry and an inhibited oxidation process. The FGD sludge, consisting primarily of calcium sulfite, is pumped from the absorber to a thickener. Liquid overflow from the thickener is recycled back into the FGD system, and the thickened sludge is pumped to a series of drum vacuum filter for further dewatering. Water removed by the drum vacuum filters is recycled back into the FGD system, and the filter cake is taken by conveyor belt to a pug mill, where it is mixed with dry fly ash and dry quicklime for stabilization. The resulting stabilized FGD solids are taken by conveyor to a temporary outdoor stockpile, and then transported by truck either to a utilization site or to an on-site landfill. The active portion of the landfill is lined and leachate is collected. An older inactive portion of the landfill is clay-lined but does not have leachate collection.

2.1.8 Facility N

Facility N is a wall fired 715 MW coal-fired power plant with cold side ESP followed by a wet FGD system using wet limestone in a forced oxidation process. The unit burns medium to high sulfur eastern bituminous coals with approximately 3% sulfur. The gypsum is washed, dried and then sold to the wallboard industry.

One 5 gallon bucket of un-washed gypsum (NAU) and one 5 gallon bucket of washed gypsum (NAW) were collected from this site. Facility N was sampled on June 1, 2006. The samples were collected by RMB Consulting & Research, Inc. (Raleigh, NC) personnel. The washed gypsum sample (NAW) was used in the laboratory wallboard simulation.

2.1.9 Facility O

Facility O is a tangentially fired 500 MW coal-fired plant with cold side ESP followed by a wet FGD system with wet limestone forced oxidation. The unit is equipped with a pulverized coal boiler and ammonia based SCR. This unit burns high sulfur eastern bituminous coals. Slurry from the absorber goes to a primary hydrocyclone for initial dewatering. The gypsum (hydrocyclone underflow) is dried on a vacuum belt and washed to remove chlorides, before use in wallboard.

Two samples were collected from the FGD gypsum drying facility by compositing samples collected on June 10, 11, and 12, 2006 when the SCR was operating. On each day, two gallon pails of unwashed gypsum and washed/dried gypsum were collected. The unwashed gypsum was collected from the vacuum belt prior to the chloride spray wash. The washed/dried gypsum was collected from the end of the vacuum belt. The three daily samples were sent to Arcadis for compositing to form sample OAU (unwashed gypsum) and sample OAW (washed gypsum). All samples were collected by plant personnel. The washed gypsum sample (OAW) was used in the laboratory wallboard simulation.

2.1.10 Facility S

This test site is a 600 megawatt (MW) per unit power plant. The plant burns eastern high sulfur bituminous coal in a dry-bottom pulverizer boiler. Cold-side electrostatic precipitators (ESPs) are used on all units for particulate control, and wet FGD systems are used to reduce SO₂ emissions on two units. The wet FGD systems utilize limestone slurry sorbents and an forced oxidation process

Samples of washed (SAW) and unwashed (SAU) gypsum were collected at this site in July, 2007. One five-gallon bucket of each was collected by plant personnel. The washed gypsum sample (SAW) was used in the laboratory wallboard simulation.

2.1.11 Facility T

This power plant test site has three boilers producing a total of a 2,000+ megawatts (MW). The plant burns medium sulfur eastern bituminous coal in a dry-bottom pulverizer boiler. Units 1 and 2 have coal cleaning equipment to reduce ash and SO_x emissions. All three of these units have low NO_x burners and selective catalytic reduction systems for NO_x control. Ammonia was injected upstream of the SCR

catalysts. Cold-side electrostatic precipitators (ESPs) are used on all three units for particulate control. A wet FGD systems using limestone in a forced oxidation mode are used to reduce SO₂ emissions on Unit 3.

Four samples were collected by plant personnel on September 17, 2007: one 5 gallon bucket of fly ash from Unit 2 (TFA), one 5 gallon bucket of un-washed gypsum from Unit 3 (TAU), one 5 gallon bucket of washed gypsum from Unit 3 (TAW), and one 5 gallon bucket of FGD waste water treatment plant filter cake from Unit 3 (TFC). The washed gypsum sample (TAW) was used in the laboratory wallboard simulation.

2.1.12 Facility W

This site is operated by American Electric Power (AEP) and has two 800 MW coal-fired boilers for a plant total of 1,600 MW. The plant burns eastern bituminous coal in a dry-bottom pulverizer boiler. Cold-side electrostatic precipitators (ESPs) are used on both units for particulate control, and wet FGD systems are used to reduce SO₂ emissions on two units. The wet FGD systems utilize limestone slurry sorbents and a forced oxidation process. SO₂ concentrations of the inlet FGD are approximately 1990 ppm with removal efficiencies of 98%. The plant has a Trona injection system for SO₃ control, but this system was not operating at the time of sampling.

Samples were collected as follows: dry FGD gypsum after water wash (WAW), moist FGD gypsum before the water wash (WAU), wastewater treatment system filter cake (WFC), and dry fly ash (WFA). Five gallon buckets of each of the samples were collected by plant personnel on 11/20/08. Samples were delivered to ARCADIS on 11/28/07. The washed gypsum sample (WAW) was used in the laboratory wallboard simulation.

2.1.13 Facility X

Wisconsin Electric Power Company, a subsidiary of Wisconsin Energy, owns and operates Pleasant Prairie Power Plant located near Kenosha, Wisconsin. The plant has two 600 MW balanced-draft coal-fired boilers designated units 1 and 2. Unit 2 was selected for inclusion in the NETL program because it burns a variety of Powder River Basin low sulfur, sub-bituminous coals. In addition, this facility has the ability to isolate one ESP chamber (1/4 of the unit) (Starns et al., 2002).

The primary pollution control equipment consists of SCR, cold-side ESPs, and a wet-FGD system. NO_x is controlled in the SCR by injecting ammonia in the presence of a catalyst. The forced oxidation FGD system uses wet-limestone as a sorbent for SO₂ control. This site also contains an additional mercury oxidation catalyst.

Samples were collected as follows: dry FGD gypsum after water wash (XAW), moist FGD gypsum before the water wash (XAU), FGD wastewater treatment system filter cake (XFC), and dry fly ash (XFA). Five gallon buckets of each of the samples were collected by plant personnel and delivered to ARCADIS on 6/16/08. The washed gypsum sample (XAW) was used in the laboratory wallboard simulation.

2.1.14 Facility Aa

This test site has four boilers producing a total of 2,424 megawatt (MW) of power. The plant burns eastern-bituminous coal in a dry-bottom pulverizer boiler. Cold-side electrostatic precipitators (ESPs) are used on three units and hot-side ESP on one unit for particulate control. Unit 1 at this plant was burning

medium sulfur coal and the SCR was operating. Unit 2 burns medium sulfur coal and has an SCR, but this unit was not operating during the time of sampling. Unit 3 was burning high sulfur coal and the SCR was operating. Unit 4 was burning low sulfur coal; the SCR was operating, and uses a hot-side ESP to control particulate. A dry handling system is used to collect the fly ash from the ESPs.

Units 3 and 4 were connected to a single FGD system. The wet FGD systems utilize limestone slurry sorbents and a forced oxidation process. Samples of the washed (AaAW) and un-washed (AaAU) FGD gypsum were collected. Fly ash was collected from units 1 (AaFA), 3 (AaAB), and 4 (AaFC). Unit 2 was not operating at the time of sampling. The washed gypsum sample (AaAW) was used in the laboratory wallboard simulation.

2.1.15 Facility Da

This test site has two supercritical boilers producing 2,240 megawatts (MW) of power. The plant burns eastern-bituminous coal in a dry-bottom pulverizer boiler. The primary pollution control equipment consists of low NO_x burners, SCR, cold-side ESPs, and a wet-FGD system. NO_x is controlled in the SCR by injecting ammonia in the presence of a catalyst. The forced oxidation FGD system uses wet-limestone as a sorbent for SO₂ control. A dry handling system is used to collect the fly ash from the ESPs.

One five gallon bucket each of fly ash (DaFA), washed gypsum (DaAW), and FGD waste water treatment plant filter cake (DaFC) were collected by plant personnel. Samples were received by ARCADIS on 12/12/2008. The washed gypsum sample (DaAW) was used in the laboratory wallboard simulation.

Table 2-2. ADA fly ashes: elemental composition (by X-ray Fluorescence) and other characteristics

Element	Reference Fly Ash	Pleasant Prairie		Brayton Point		Salem Harbor	
		Baseline	w/ACI	Baseline	w/ACI	Baseline	w/ACI
	Average %	Average %	Average %	Average %	Average %	Average %	
Al	14.7	10.0	10.2	13.4	12.4	9.52	7.62
As	0.010	BML	BML	BML	BML	BML	BML
Ba	0.110	0.695	0.647	0.010	0.095	0.091	0.099
Br	BML	BML	BML	0.005	0.065	BML	BML
Ca	0.860	18.4	16.6	6.08	2.03	1.30	0.803
Cl	0.026	BML	0.045	0.030	0.440	0.101	0.203
Cr	0.017	0.016	0.013	0.022	0.018	0.011	0.012
Cu	0.018	0.022	0.022	0.022	0.020	0.007	0.008
Fe	5.11	4.31	4.28	4.650	2.50	4.87	3.63
I	BML	BML	BML	BML	0.014	BML	BML
K	2.46	0.371	0.455	1.85	1.50	1.250	0.977
Mg	0.637	2.81	2.46	0.800	0.641	0.785	0.420
Mn	0.015	0.057	0.020	0.041	0.020	0.045	0.021
Na	0.346	1.66	1.31	0.511	0.242	0.270	0.293
Ni	0.011	0.006	0.006	0.015	0.016	0.009	0.009
Pb	0.008	BML	BML	BML	0.010	0.005	BML
Px1	0.087	0.560	0.508	0.161	0.042	0.086	0.057
Se	BML	BML	BML	0.005	0.020	0.005	0.005
Si	26.4	16.6	16.2	23.1	23.2	21.9	23.5
Sr	0.089	0.369	0.341	0.124	0.083	0.042	0.032
Sx2	0.174	0.635	0.971	0.351	0.582	0.335	0.761
Ti	0.897	0.964	0.943	1.015	0.100	0.453	0.407
V	0.031	0.030	0.033	0.043	0.032	0.029	0.030
Zn	0.023	0.009	0.010	0.021	0.011	0.013	0.013
Zr	0.050	0.035	0.035	0.031	0.031	0.019	0.019
Total Carbon (%)	0.76	0.25	3.6	2.3	13	7.8	11
Surface Area (m ² /g)	1.36	1.8	23	6.5	92	28	36
LOI (wt %)	0.85	0.60	3.5	5.5	12	21	25

Notes: BML=below method limit (As<0.009%, Cl<0.006%, I<0.006%, Pb<0.003%, Se<0.003%); ¹P_x = phosphorus in oxidized form such as phosphate; ²S_x = sulfur in oxidized form such as sulfate

Table 2-3. Facility A (SNCR, facility B (SCR), facility E (SCR) and facility M CCRs: elemental composition (by X-ray Fluorescence) and other characteristics

Element	Fly Ash Facility A		Fly Ash Facility B		Fly Ash Facility E	FGD Fly Ash Mix Facility M
	With SNCR %	Without SNCR %	With SCR %	Without SCR %	With SCR %	With SCR %
Al	11.4	12.8	10.8	11.0	15.7	6.44
As	0.013	0.014	0.014	BML	0.010	BML
Ba	0.096	0.124	0.128	0.122	0.116	0.021
Br	0.009	0.008	BML	BML	BML	BML
Ca	3.53	3.60	3.40	3.11	1.21	32.3
Cl	0.542	0.610	0.044	0.030	0.010	0.096
Co	0.007	0.006	0.005	BML	0.014	0.004
Cr	0.018	0.017	0.024	0.022	0.020	0.009
Cu	0.019	0.018	0.005	0.006	0.023	0.013
Fe	4.68	5.20	10.782	11.1	4.17	7.63
Ga	0.005	0.005	0.004	BML	0.011	0.003
Ge	BML	BML	0.003	BML	0.003	0.006
K	1.67	2.10	1.960	1.87	2.50	0.972
La	0.012	BML	BML	BML	0.011	0.009
Mg	0.835	0.931	0.869	0.774	0.714	0.797
Mn	0.030	0.052	0.025	0.024	0.021	0.018
Mo	BML	BML	BML	BML	BML	0.005
Na	0.375	0.362	0.724	0.663	0.350	0.884
Nb	BML	0.004	0.003	BML	0.004	BML
Ni	0.012	0.010	0.007	0.005	0.021	0.044
Pb	0.007	0.007	0.004	BML	0.013	0.007
Px1	0.122	0.137	0.235	0.170	0.060	0.056
Rb	0.011	0.013	0.013	0.011	0.016	0.006
Sc	0.003	0.002	0.002	0.002	0.003	0.008
Se	0.003	0.003	BML	BML	BML	BML
Si	19.5	23.1	21.2	21.2	25.2	11.6
Sr	0.092	0.116	0.111	0.099	0.100	0.038
Sx2	0.364	0.394	0.711	0.512	0.162	37.7
Ti	0.767	0.931	0.596	0.570	1.03	0.399
V	0.033	0.029	0.019	0.019	0.041	0.024
Y	0.009	0.009	0.003	0.005	0.012	0.003
Zn	0.013	0.013	0.014	0.013	0.022	0.021
Zr	0.026	0.031	0.021	0.020	0.030	0.016
Total Carbon (%)	9.15	3.69	5.74	2.37	1.12	0.75
Surface Area (m ² /g)	13.9	2.57	5.30	6.20	4.48	7.36
LOI (wt %)	17.6	5.30	10.8	11.0	5.62	4.01

Notes: BML=below method limit (As<0.009%, Cl<0.006%, I<0.006%, Pb<0.003%, Se<0.003%); ¹Px = phosphorus in oxidized form such as phosphate; ²Sx = sulfur in oxidized form such as sulfate

Table 2-4. ADA fly ashes: total content of mercury, arsenic, lead and selenium¹

Sample ID	Mercury (ng/g)	Arsenic (µg/g)	Lead (µg/g)	Selenium (µg/g)
Brayton Point Baseline	651 ± 6.8	80.5 ± 1.9	117 ± 4.9	51.4 ± 1.7
Brayton Point (w/ACI)	1530 ± 1.1	27.9 ± 2.1	82.9 ± 2.3	152 ± 6.2
Pleasant Prairie Baseline	158 ± 0.2	21.3 ± 0.3	41.5 ± 0.8	BML
Pleasant Prairie (w/ACI)	1180 ± 1.2	24.0 ± 0.8	47.0 ± 0.3	BML
Salem Harbor Baseline	528 ± 5.2	25.9 ± 0.04	24.9 ± 1.4	41.9 ± 0.06
Salem Harbor (w/ACI)	412 ± 13	26.0 ± 0.03	24.0 ± 0.02	44.0 ± 0.04

¹All analyses according to EPA Method 3052. Mercury analysis performed by ARCADIS, arsenic, Pb, and Se analysis performed by STL Savannah. All samples tested in duplicate.

BML = below method limit (4.0 µg/g)

ACI = Activated Carbon injection (sorbent for enhancing mercury capture)

Table 2-5. Facility A (SNCR, facility B (SCR), facility E (SCR) and facility M (SCR) CCRs : total content of mercury, arsenic, lead and selenium

All analyses were conducted according to EPA Method 3052. Mercury analysis performed by ARCADIS, arsenic, Pb, and Se analysis performed by STL Savannah.

Sample ID	Mercury (ng/g)	Arsenic (µg/g)	Lead (µg/g)	Selenium (µg/g)
Facility A Fly Ash (SNCR on)	602 ± 5.2	70.8 ± 1.4	80.5 ± 2.1	25.6 ± 0.2
Facility A Fly Ash (SNCR off)	380 ± 7.0	88.2 ± 0.3	68.6 ± 0.3	21.9 ± 0.6
Facility B Fly Ash (SCR on)	88.3 ± 27.4	82.3 ± 12.6	47.4 ± 8.1	2.5 ± 0.4
Facility B Fly Ash (SCR off)	114 ± 9.6	90.0 ± 3.4	36.0 ± 0.1	2.9 ± 0.0
Facility E Fly Ash (SCR on)	396 ± 57.4	50.1 ± 0.1	34.1 ± 0.1	24.0 ± 2.9
Facility M Fly Ash (SCR on)	121 ± 0.2	106 ± 6.8	5.2 ± 0.4	91.0 ± 6.5

Note: All samples tested in duplicate.

2.1.16 FGD Gypsum Sample from U.S. Gypsum

As discussed in Section 1.1.3, U.S. Gypsum (USG) performed an evaluation of mercury release from FGD gypsum use in the production of wallboard. This evaluation was completed at five wallboard manufacturing plants (Marshall et al., April 2005). The USG study was limited to mercury and did not evaluate other metals. Therefore, samples of the FGD gypsum from the USG study were obtained for a simulation test in the U.S. EPA laboratory. The first USG sample, corresponding to Task #1 of the USG/DOE study, obtained for this study was from a power plant that burned high-sulfur bituminous coal, used limestone as the FGD reagent, had *in situ* forced oxidation, online SCR, and did not practice fines blow down (no fines removed) (Marshall et al., April 2008). The sub-sample consisted of the FGD gypsum fed to the kettle calciner (the most likely point of release as discussed in Section 1.1.3). For

further details on the characteristics of this sample see Marshall et al., April 2005. The second USG sample obtained for this study was from the same plant during recent testing performed by DOE. This plant was sampled during a time period during which the SCR was bypassed. Results for total content analyses for mercury, arsenic, Pb, and Se are provided in Table 2-6.

Table 2-6. USG FGD gypsum samples: total content of mercury, arsenic, lead and selenium¹

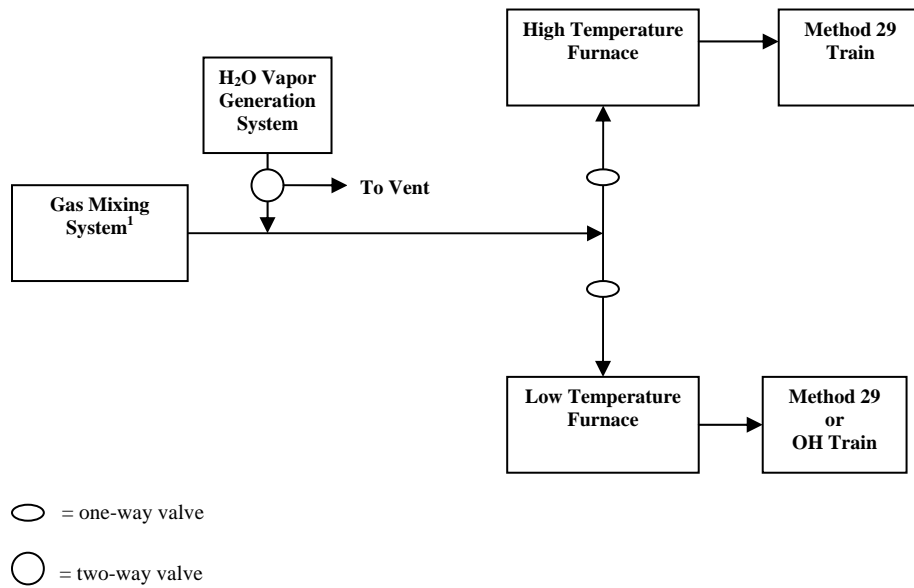
Sample ID	Mercury (ng/g)	Arsenic (µg/g)	Lead (µg/g)	Selenium (µg/g)
USG Sample #1 (Corresponds to DOE Task #1)	674 ± 0.4	5.88 ± 0.4	2.31 ± 0.03	5.4 ± 0.7
USG Sample #2 (Corresponds to DOE Task #2)	468 ± 21	5.74 ± 0.26	2.08 ± 0.09	5.26 ± 0.98

¹All analyses according to EPA Method 3052. Mercury analysis performed by ARCADIS, arsenic, Pb, and Se analysis performed by STL Savannah. All samples tested in duplicate.

2.2 Thermal Stability Protocols

A fixed-bed reactor design was used to simulate the thermal processes of concern in this study. Figure 2-1 provides a schematic of the general setup for simulating asphalt manufacturing, wallboard manufacturing, and cement clinker manufacturing. For all simulations, samples consisting of various mixes and matrices were loaded into shallow-bed containers and placed in the reactor. The fixed-bed reactor used for the asphalt and wallboard simulation assays consisted of a horizontal quartz tube in a thermally controlled furnace. The low temperature furnace was manufactured by Lindberg/Blue M (Model 55035) and had a reactor size of 12” by 1” and a maximum temperature of 1200 °C (Figure 2-2). In the case of the high temperature cement clinker manufacturing (1450 °C), a high temperature furnace was utilized. This high temperature furnace was manufactured by Lindberg/Blue M (Model STF54233C) and had a reactor size of 12” by 2” and a maximum temperature of 1500 °C (Figure 2-3).

In each simulation the tests were performed in duplicate. Samples were exposed to a flow rate of 400 cc/min of inlet flue gas consisting of 14% CO₂, 3% O₂, 5.6% H₂O and 100 ppm NO_x, except for the wallboard simulation of the kettle calciner, in which the inlet gas consisted of N₂. Kettle calciners are indirectly fired and therefore the sample is not exposed to flue gases. The time in the fixed-bed reactor for each simulation was one hour. The samples placed in the fixed-bed reactor, as well as the temperatures in the processes varied for each simulation. For mercury, the effluent of the reactor was sampled using a mini-impinger Ontario Hydro train (ASTM, 2002). For sampling the other metals, a Method 29 (EPA, 1996b) mini-impinger train was utilized. Table 2-7 outlines the differentiations in the various simulations. Some simulations involved the addition of sand, limestone (CaCO₃) or iron powder. All added materials were certified reagent grade from Fisher Scientific.



¹The same gas mix was used for the simulation of cement clinker and asphalt production (a flow rate of 400 cc/min of inlet flue gas consisting of 14% CO₂, 3% O₂, 5.6% H₂O and 100 ppm NO_x). The wall board similar used inlet gas of N₂ since kettle calciners are indirectly fired and therefore the sample is not exposed to flue gas)

Figure 2-1. Schematic of the setup for simulating the production of cement clinker, asphalt, and wallboard



Figure 2-2. Asphalt and wallboard simulation quartz reactor and furnace with sample



Figure 2-3. High temperature cement simulation furnace with Method 29 mini-impinger train

Although the percentage of fly ash in asphalt is typically 5%, a mix containing 50% fly ash was tested for the ADA fly ashes. During the initial phase of these studies a 50% mix was used as a conservative approach to optimize the chances of detecting any volatilized mercury. The fly ashes from Facilities A, B and E were tested using a mix containing 10% fly ash.

Table 2-7. Description of asphalt, wallboard and cement clinker simulations to test for metal thermal stability

Simulation	Sample	Inlet Gas	Temperature
Asphalt (ADA-ES samples) – Hg	5 g of fly ash and 5 g of quartz sand	Flue gases	170 °C
Asphalt (Facilities A and B samples) – Hg	1 g of fly ash and 9 g of quartz sand	Flue gases	170 °C
Asphalt – As, Se, Pb	1 g of fly ash and 9 g of quartz sand	Flue gases	170 °C
Wallboard	10 g of FGD gypsum kettle feed	Nitrogen	160 °C
Cement clinker (high temp)	1 g of fly ash, 8.55 g CaCO ₃ , 0.3 g iron powder and 0.2 g sand	Flue gases	1450 °C

Notes: all samples were tested in duplicate, exposed to gases/temperatures for one hour.

2.3 Analytical Methods

2.3.1 Mercury (CVAA Method 7471A, Method 3052, Method 7473, Method 30B)

Gas phase mercury emissions from the simulation studies for the production of cement clinker, asphalt, and USG gypsum testing were analyzed according to ASTM Method D6784-02, Ontario Hydro (OH), with the following modifications. Due to spacing constraints, mini-impingers were used for sampling instead of the large impingers described in the OH method. The method states that flow will be pulled through the impingers using negative pressure; however, for these experiments the flow had to be pushed through the impingers using positive pressure in order to not change the flow through the reactor. The method also requires a dry gas meter to continuously measure flow, but instead a Gilian Gilibrator 2 (Sensidyne, Inc.) bubble flow meter was used and measurements were recorded every five minutes throughout the entire sampling period. A silica gel trap was not used in this study, so the measurements obtained were wet gas flow rates. Because the flue gas was not particle-laden, the filter apparatus setup prior to the impingers (i.e., Method 5 filter) was not required. Analysis of the samples was performed as outlined in Method D6784-02, Ontario Hydro.

Sample preparation for the cement clinker, asphalt, and USG gypsum solids was carried out by HF/HNO₃ microwave digestion according to Method 3052 (EPA, 1996a). Mercury analysis of each digest was carried out by Cold Vapor Atomic Absorption Spectrometry (CVAA) according to EPA SW-846 Method 7470A “Mercury in Liquid Waste (Manual Cold Vapor Technique)”, (EPA, 1998a). A Perkin Elmer FIMS 100 Flow Injection Mercury System was used for the analyses. The instrument was calibrated with known standards ranging from 0.025 to 1 µg/L Hg. The method detection limit for Hg in aqueous samples is 0.01 µg/L.

Gas phase Hg sampling for the repeated gypsum testing was performed using an EPA Method 30B (EPA 2008a) system. This technique used an iodated activated carbon tube to capture the Hg in the gas stream. A Lumex RA-915+ Zeeman effect atomic adsorption Hg analyzer with a RA-91C combustion furnace attachment to analyze the carbon tubes. The Hg analyzer was calibrated with known standards ranging from 50 to 1000 ng of Hg. The method detection limit for Hg in the carbon tube is 0.2 ng. Blank samples measured by the analyzer resulted in an average of 0.5 ng detectable concentration by the software.

Thermal Hg analysis was conducted of the FGD solids that were retested. This analysis used a modified Method 7473 “Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry” (EPA, 1998b). The instrument used was a Lumex RA-915+ Zeeman effect atomic adsorption Hg analyzer with a RA-91C combustion furnace attachment for solids analysis. The instrument was calibrated with known standards ranging from 50 to 1000 ng of Hg. The method detection limit for Hg in solids is 0.145 ng/g. Blank samples measured by the analyzer resulted in a 0.0 ng/g.

2.3.2 Arsenic, Selenium and Lead (ICP-MS, Method 3052, Method 6020)

Inductively coupled plasma-mass spectroscopy (ICP-MS) analysis for other elements of interest were carried out by Oxford and STL laboratories.

Liquid samples were analyzed by ICP-MS as recovered from the Method 29 trains. Solid samples were digested by EPA Method 3052 prior to ICP-MS analysis.

2.3.2.1 Severn Trent Laboratories, Inc. (STL)

STL (Savannah, Georgia) was selected to carry out the solid digest ICP-MS analyses for this project. Analysis for As, Se, and Pb was performed on an Agilent ICP-MS with octopole reaction system (ORS). Mixed calibration standards were prepared for each metal at five levels ranging from 0.5 µg/L to 100 µg/L.

2.3.2.2 Oxford Laboratories

Oxford Laboratories (Wilmington, North Carolina) was selected to carry out the ICP-MS analyses for this project on the Method 29 impinger samples. Analysis for As, Se, and Pb was performed on an Agilent ICP-MS with octopole reaction system (ORS). Mixed calibration standards were prepared for each metal at five levels ranging from 0.5 µg/L to 100 µg/L.

Chapter 3 Results and Discussions

3.1 Cement Simulations

Cement simulation tests for As, Se, and Pb desorption were performed in duplicate on the ADA fly ashes without the use of ACI. Because of its inherently high volatility, Hg was assumed to volatilize at the 1450°C and therefore recovery was not analyzed in the samples. Table 3-1 and Figure 3-1 present the results of these tests. Therefore the focus was on the other metals (i.e., As, Se, and Pb).

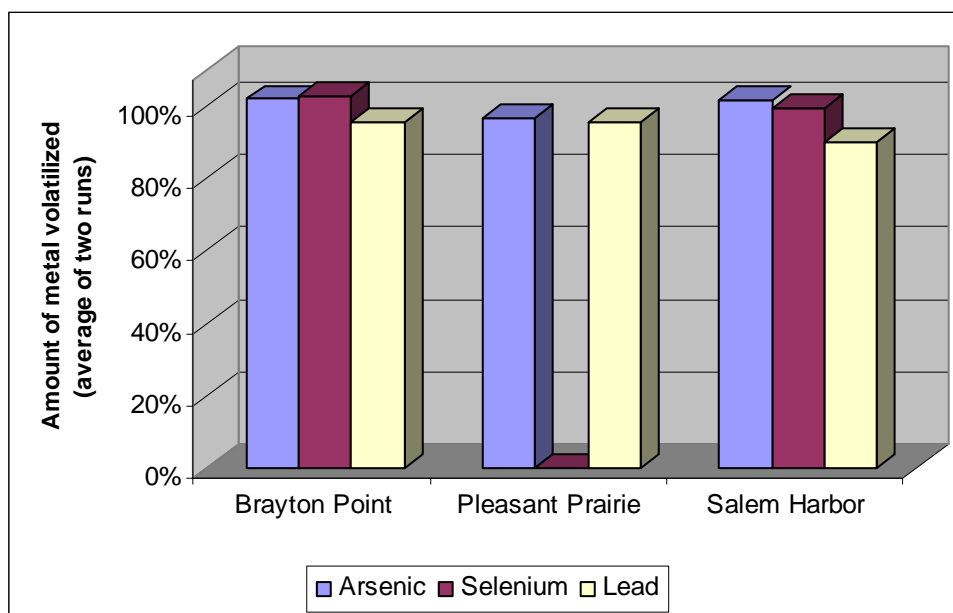
The tests show excellent reproducibility and indicate that virtually all of the metals tested were volatilized when exposed to a temperature of 1450°C.

Table 3-1. Results of cement simulations for arsenic, selenium, and lead (all values in µg/g unless noted)

Metal	Run	Brayton Point (µg/g)		Pleasant Prairie (µg/g)		Salem Harbor (µg/g)	
Arsenic	As received	80.5 ± 1.9		21.3 ± 0.3		25.9 ± 0.04	
	Run 1	82.6	103%	20.6	96.8%	27.5	106%
	Run 2	81.8	102%	20.6	96.6%	25.2	97.5%
Selenium	As received	51.4 ± 1.7		BML		41.9 ± 0.8	
	Run 1	53.6	104%	BML	NA	39.8	94.9%
	Run 2	52.6	102%	BML	NA	43.6	104%
Lead	As received	117 ± 4.9		41.5 ± 0.8		24.9 ± 1.4	
	Run 1	118.6	101%	40.6	97.9%	21.5	86.3%
	Run 2	106.0	90.4%	38.8	93.5%	23.4	94.1%

BML – Below method limit (4.0 µg/g)

NA = not applicable



Note: Se was not tested for Pleasant Prairie fly ash; the amount in the baseline fly ash was below minimum detection levels.

Figure 3-1. Results of cement simulations for arsenic, selenium, and lead

3.2 Asphalt Simulations

3.2.1 Asphalt Simulation Tests for Mercury Thermal Stability on ADA Fly Ashes

Results for duplicate asphalt simulation tests using the ADA fly ashes are presented in Table 3-2. In all cases, the majority of the Hg was retained in the solid after simulation, with minimal measured volatilization of Hg (<10% in all cases). Generally, the addition of carbon increased the tendency for Hg to be retained in the solids at the temperature tested. Total Hg volatilized from samples with activated carbon injection was <1% for all samples tested. Figure 3-2 shows the results of these experiments that have been normalized by adjusting the mass balance to 100%. Mass balances were approximately 90% for all tests except for the Pleasant Prairie Baseline tests (~67%). No reason for the lack of closure for Hg for this sample was found, though it is noted that the as-prepared sample had the lowest initial Hg value of these fly ashes.

For confirmatory purposes, measurements of volatilized Hg were taken from Method 29 total metals analyses for comparison to the Ontario Hydro values for the Brayton Point fly ashes. Table 3-3 shows the comparison. The Method 29 runs agree well with the total Hg values obtained from the Ontario Hydro tests, indicating minimal volatilization of Hg.

Table 3-2. Asphalt simulation test results for mercury on ADA fly ashes

		As Prepared ng/g)	After Simulation (Solid) ng/g	Hg ²⁺ _{gas} ng/g	Hg ⁰ _{gas} ng/g	Total Percent Volatilized Hg	Mass Balance
Brayton Point Baseline	Run 1	650.6 ± 6.8	526	31.7	8.0	6.1%	86.9%
	Run 2		606	5.3	1.8	1.1%	94.7%
Brayton Point ACI	Run 1	1529.6 ± 1.1	1,340	BML	BML	0.0%	87.3%
	Run 2		1,420	BML	BML	0.0%	93.2%
Pleasant Prairie Baseline	Run 1	157.7 ± 0.2	105	BML	1.9	1.2%	67.8%
	Run 2		95.5	BML	7.3	4.7%	65.2%
Pleasant Prairie ACI	Run 1	1180.1 ± 1.2	1,110	1.3	2.3	0.3%	94.6%
	Run 2		1,100	2.2	3.3	0.5%	93.9%
Salem Harbor Baseline	Run 1	528.5 ± 5.2	488	0.1	BML	0.0%	92.4%
	Run 2		486	BML	BML	0.0%	91.9%
Salem Harbor ACI	Run 1	411.5 ± 12.6	388	BML	0.5	0.1%	94.4%
	Run 2		387	BML	BML	0.0%	94.0%

BML=below method limit (Hg<0.05 ng/g)

3.2.2 Asphalt Simulation Tests for Non-Mercury Metals Thermal Stability on ADA Fly Ashes

Since significant amounts of Hg were not significantly released from the ADA fly ash samples (and Hg is the most volatile of the metals being investigated), only one of the three ADA facility sites was chosen to evaluate the release of other metals. The Brayton Point facility samples were chosen because they contained the highest amount of As and Se. Asphalt simulation tests for As, Se, and Pb volatilization were performed on the Brayton Point fly ashes. Table 3-4 summarizes the results. The tests showed no non-Hg metals in the gas phase, indicating that all the As, Se, and Pb were retained in the solid. While the mass balances between the solids after simulation and the as-prepared sample prior to testing are not ideal (varying between 50 and 150%), they generally agree and support that the metals are retained in the solids for the asphalt simulation.

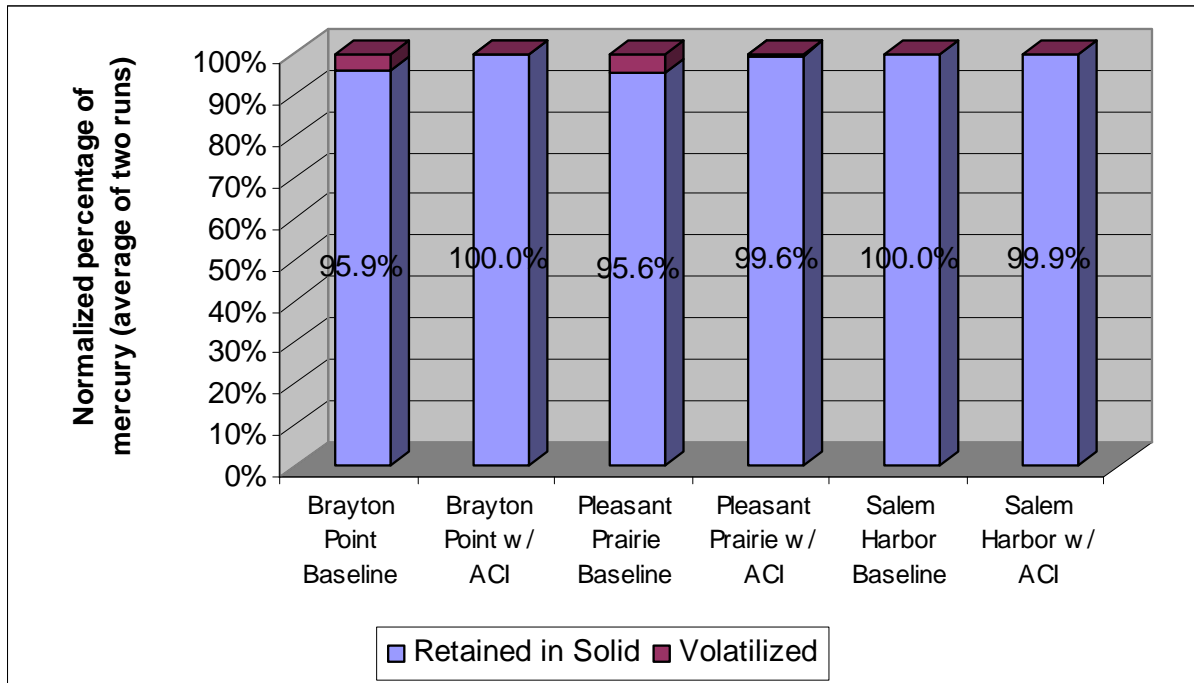


Figure 3-2. Asphalt simulation test results for mercury by Ontario Hydro Method on ADA fly ashes

Table 3-3. Comparison of mercury by Method 29 and Ontario Hydro for Brayton Point fly ashes

Sample	Run	As Prepared ng/g	Gas-Phase Mercury ng/g	Percent Volatilized	Method 29 Average	OH Average
Brayton Point Baseline	Run 1	651 ± 6.8	72.0	11.1%	7.3% ± 5.3%	3.6% ± 3.5%
	Run 2		23.0	3.5%		
Brayton Point w/ACI	Run 1	1530 ± 1.1	20.0	1.3%	1.4% ± 0.1%	0.0% ± 0%
	Run 2		23.0	1.5%		

Table 3-4. Results for asphalt simulations of Brayton Point fly ashes for arsenic, selenium, and lead

Metal	Run	As Received µg/g	As Prepared µg/g	After Simulation (solid) µg/g	Volatilized Metal (gas phase) µg/g	Mass Balance
Arsenic	Baseline Test 1	80.5 ± 1.9	90.5 ± 6.6	85.5 ± 2.0	BML	94.5%
	Baseline Test 2			95.5 ± 22	BML	106%
	ACI Test 1	27.9 ± 2.1	41.9 ± 0.15	26.0 ± 0.07	BML	62.1%
	ACI Test 2			50.1 ± 8.6	BML	120%
Selenium	Baseline Test 1	51.4 ± 1.7	47.7 ± 2.6	45.7 ± 8.0	BML	95.8%
	Baseline Test 2			53.7 ± 13	BML	113%
	ACI Test 1	152 ± 6.2	156.7 ± 9.3	83.1 ± 7.3	BML	53.1%
	ACI Test 2			208 ± 47	BML	132%
Lead	Baseline Test 1	117 ± 4.9	245 ± 71	318 ± 25	BML	128%
	Baseline Test 2			279 ± 55	BML	113%
	ACI Test 1	82.9 ± 2.3	194 ± 0.68	227 ± 74	BML	117%
	ACI Test 2			291 ± 14	BML	150%

BML=below method limit (As<4.0 µg/g, Pb<0.6 µg/g, Se<4.0 µg/g)

3.2.3 Asphalt Simulation Tests for Mercury Thermal Stability on Non-ADA Fly Ashes

Asphalt simulations were run using the non-ADA fly ashes. These samples were from utilities not using ACI; rather, the samples were taken from utilities using SNCR (Facility A) and SCR (Facilities B and E) for NO_x control, or none (Facility M). Table 3-5 shows the results of these experiments. Mass balances for all runs were excellent (92.5 to 101%). Figure 3-3 shows the results of these experiments that have been normalized by adjusting the mass balance to 100%. As was the case for the ADA fly ashes, minimal Hg loss upon heating was found for the fly ashes from Facilities A and E. Facility B, however, demonstrated high Hg volatility (~70-90% loss upon heating). Facility M showed moderate amounts of the Hg being volatilized.

As with the Brayton Point fly ash, Method 29 sampling for Hg was conducted to confirm the results obtained using the Ontario Hydro methodology. These comparisons are shown in Table 3-6. While differing slightly from the Ontario Hydro results, the Method 29 experiments confirm that the Facility B samples showed significantly greater loss of Hg on heating than the other fly ashes tested.

Table 3-5. Mercury results by Ontario Hydro Method for non-ADA fly ashes

Sample	Run	As Prepared ng/g	After Simulation (Solid) ng/g	Hg ²⁺ _{gas} ng/g	Hg ⁰ _{gas} ng/g	Total Percent Volatilized Hg	Mass Balance
Facility A SNCR On	Run 1	602	576	5.2	6.0	1.9%	97.5%
	Run 2		583	4.6	5.8	1.7%	98.6%
Facility A SNCR Off	Run 1	380	366	9.8	8.8	4.9%	101%
	Run 2		358	8.5	13.5	5.8%	100%
Facility B SCR On	Run 1	88.3	9.2	36.5	41.3	88.1%	98.5%
	Run 2		9.3	37.6	38.5	86.2%	98.6%
Facility B SCR Off	Run 1	114	27.0	37.5	42.8	70.4%	94.1%
	Run 2		23.1	40.4	42.2	72.4%	92.7%
Facility E SCR On	Run 1	396	365	15.0	14.7	7.5%	99.6%
	Run 2		326	22.6	17.6	10.1%	92.5%
Facility M		121	57.5	NA	NA	26.6%	74.2%

Facility M was sampled by Method 29 under Asphalt Simulation Conditions.

Gas phase total Hg emissions for Facility M were 32.1 ng/g.

NA = not applicable / no gas phase speciation

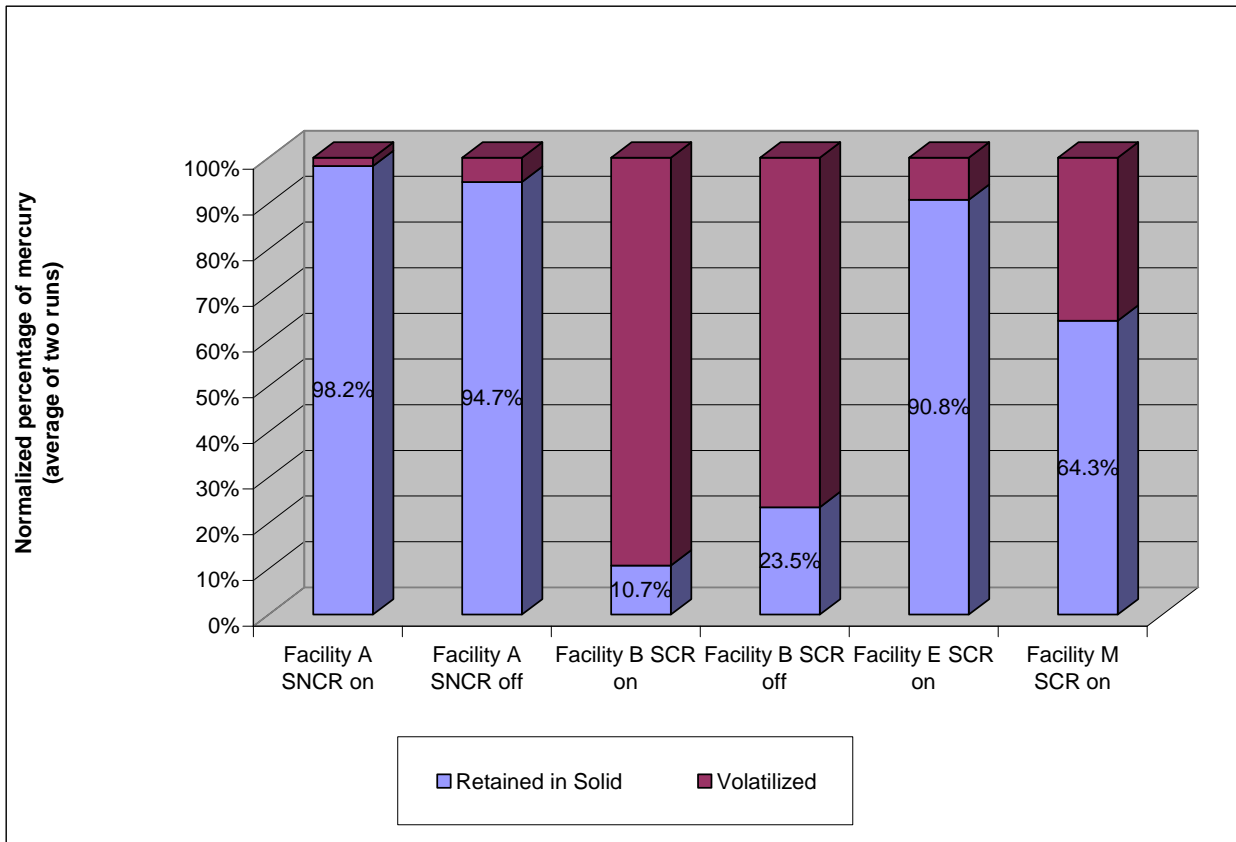


Figure 3-3. Mercury results by Ontario Hydro Method for non-ADA fly ashes

Facility M was sampled by Method 29. Series 1 = Retained in Solid, Series 2 = Gas Phase under Asphalt simulation Conditions.

Table 3-6. Comparison of mercury by Method 29 with Ontario Hydro for facility B fly ashes

		As Prepared, ng/g	Method 29 Gas-Phase Mercury, ng/g	Method 29 Percent Volatilized	Ontario Hydro Gas-Phase Mercury, ng/g	Ontario Hydro Percent Volatilized
Facility B SCR on	Run 1	88.3 ± 27.4	44.2	50.1%	77.8	89.4%
	Run 2		37.8	42.8%	76.1	89.1%
Facility B SCR off	Run 1	114.0 ± 9.6	75.2	65.9%	80.3	74.8%
	Run 2		57.5	50.5%	82.6	78.1%

No clear-cut reason for the higher loss of Hg seen for the Facility B sample can be demonstrated. The SCR design is of the in-furnace variety, contact between fly ash and SCR catalyst occurred even during tests when SCR was not in use. Speculation is that contact between fly ash and SCR catalyst occurred even when no ammonia injected. However, too little information is available to make a more definitive statement. In addition, a similar effect was not found for the sample from Facility E (which is also has SCR in use). Therefore, these results suggest that additional research may be warranted on a wider range of samples to evaluate potential Hg loss from use of CCR in asphalt applications.

3.2.4 Asphalt Simulation Tests for Non-Mercury Metals Thermal Stability on Non-ADA Fly Ashes

Because of the high volatility seen for Hg in the Ontario Hydro analyses for the Facility B fly ash, the Facility B fly ash was selected for testing of volatility of As, Se, and Pb. Results from Method 29 tests are shown in Table 3-7. As was the case for the Brayton Point fly ash, mass balances from the tests show a high degree of variability (41-300%). However, once again no metals were detected in the gas phase, indicating that As, Se, and Pb were retained in the solid after heating. The Pb results likely indicate some degree of contamination of the solid sample prior to analysis. However, As, Se, and Pb were not detected in the gas phase for the Facility B sample.

Table 3-7. Results for Asphalt Simulations of Facility B Fly Ashes for arsenic, selenium, and lead

Metal	Run	As Prepared µg/g	After Simulation (solid) µg/g	Volatilized Metal (gas phase) µg/g	Mass Balance
Arsenic	SCR on Test 1	95.8	85.4	BML	89.1%
	SCR on Test 2	96.0	89.6	BML	93.3%
	SCR off Test 1	75.6	88.2	BML	117%
	SCR off Test 2	75.8	104	BML	137%
Selenium	SCR on Test 1	5.4	5.6	BML	104%
	SCR on Test 2	5.4	5.7	BML	105%
	SCR off Test 1	13.5	6.6	BML	48.8%
	SCR off Test 2	13.5	5.6	BML	41.4%
Lead	SCR on Test 1	236	292	BML	124%
	SCR on Test 2	237	180	BML	76.0%
	SCR off Test 1	81.2	239	BML	295%
	SCR off Test 2	81.4	215	BML	264%

BML=below method limit (As<4.0 µg/g, Pb<0.6 µg/g, Se<4.0 µg/g)

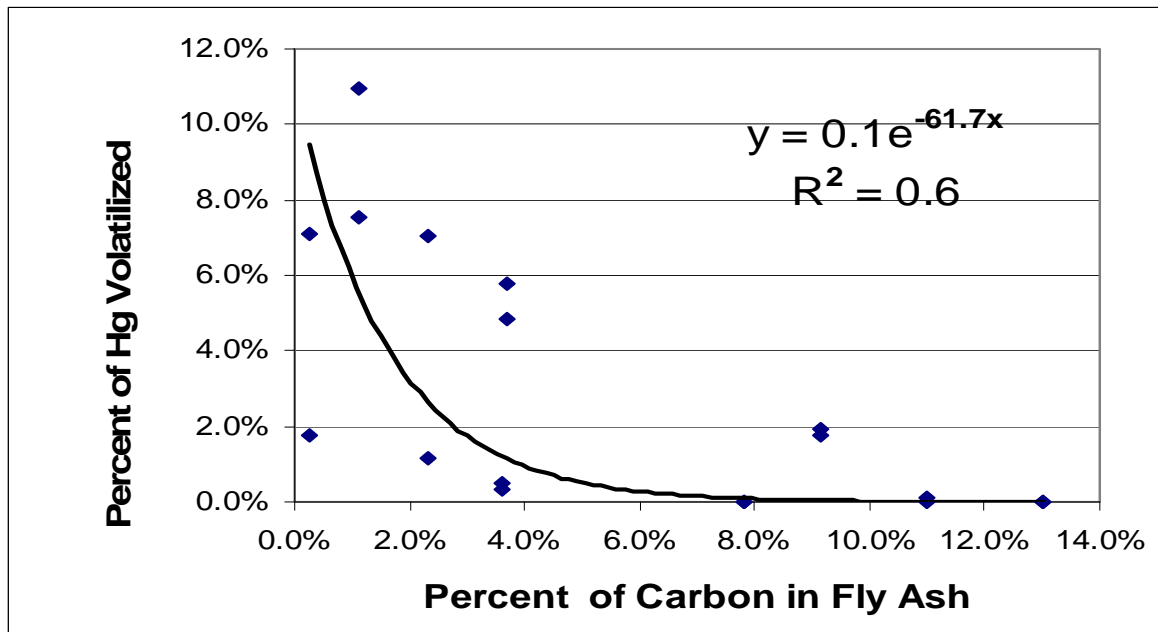
Table 3-8. Results for asphalt simulations of facility M fly ash for mercury, arsenic, selenium, and lead

Metal	Run	As Prepared	After Simulation (solid)	Volatilized Metal (gas phase)	Amount Volatilized	Mass Balance
Arsenic µg/g	SCR on Test 1	101	106	BML	0	105
	SCR on Test 2	110	108	BML	0	97.5%
Selenium µg/g	SCR on Test 1	5.5	6.0	BML	0	111
	SCR on Test 2	4.9	5.5	BML	0	113
Lead µg/g	SCR on Test 1	86.4	91.2	BML	0	106
	SCR on Test 2	95.6	90.6	BML	0	94.8%
Mercury ng/g	SCR on Test 1	121	57.8	31.6	26	74%
	SCR on Test 2	120	57.2	32.5	27	74%

Note: As, Se, and Pb concentrations in µg/g, Hg concentration in ng/g
BML = below method limit (As<4.0 µg/g, Pb<0.6 µg/g, Se<4.0 µg/g)

3.2.5 Correlation of Carbon Content and Mercury Volatilization

In general, Hg volatilization appears to decrease with increasing carbon content. This was the case for 18 of the 22 samples evaluated. The four facilities that did not fit this trend are from the facility that has the in-furnace SCR system. The mercury results were normalized using the ratio of the amount volatilized to the total Hg remaining in the solids plus the amount of mercury volatilized. Figure 3-4 provides these results along with the equation that was derived. The significant figures are not considered more than 1 given the uncertainties. Recommendations for future work include using a larger sample size to evaluate potential Hg loss during asphalt production and to evaluate if the correlation for carbon content and Hg loss is confirmed.



Note – The % Hg volatilized is “normalized” by dividing by the total amount of mercury in the solid and gas phase. Significant figures are not greater than one.

Figure 3-4. Mercury volatilization as a function of carbon content

3.3 Wallboard Simulations

Sanderson et al., (2008) provide the most extensive study to date on the fate of Hg when FGD gypsum is used as feedstock for wallboard production. Testing of full-scale production facilities is considered more reliable than laboratory testing to simulate wallboard production. However, the study did not include other metals. Therefore, laboratory simulation of wallboard production was conducted. Results from Sanderson et al., (2008) indicate that the process where Hg loss is more likely to occur is the kettle calciner. Therefore, laboratory simulation of wallboard production was conducted evaluating Hg and other metals with the focus on trying to simulate potential loss across the kettle calciner. Only FGD gypsum samples were used in this simulation since this is the material used in the production of wallboard (and not fly ash). This research was conducted in two phases. The first phase resulted in unacceptable

mass balance for Hg. The results for the other metals are considered acceptable. Consequently, additional testing was conducting in a second phase using more recent FGD samples. The results from this work are reported along with the results from phase 1. Please note, only the results from non-Hg metals for phase 1 are considered reliable. However, we have not excluded the Hg results from phase 1.

3.3.1 Wallboard Simulation Tests for Mercury Thermal Stability on USG FGD Gypsum

Results for multiple wallboard simulations using the two samples received from U.S. Gypsum are shown in Table 3-9. As noted, the results for the first USG sample had poor mass balance. The amount of Hg remaining in the solids ranged between 90 to 99% which agrees fairly well with the results reported by USG (~98.6%). The results for the second USG sample had a better mass balance than the first sample; however, the mass balances were still less than ideal. The gas-phase results, however, indicate that the samples lost between 75 and 105% of the Hg compared to a USG-reported value of ~2.3%. The gas phase results are not considered reliable as indicated by the poor Hg mass balance results. Therefore, and additional testing was conducted.

Table 3-9. Results of wallboard simulation tests for mercury

		Pre test (solid), ng/g	After Simulation (solid), ng/g	Volatilized Mercury (gas phase), ng/g	Percent Volatilized ^a	Percent Remaining in Solid	Mass Balance
USG-1	Run 1	674.0 ± 0.4	664	518	77%	99%	175%
	Run 2		626	602	89%	93%	182%
	Run 3		627	606	90%	93%	183%
	Run 4		606	705	105%	90%	195%
USG-2	Run 1	467.9 ± 21.3	98.4	478.7	102%	21.0%	123%
	Run 2		81.9	334.9	71.6%	17.5%	89.1%

^aThese results are not considered reliable as indicated by the Hg mass balance. Therefore, additional testing was conducted.

3.3.2 Wallboard Simulation Tests for Non-Mercury Metals Thermal Stability on USG FGD Gypsum

Results for duplicate wallboard simulations using samples received from U.S. Gypsum are shown in Table 3-10. In general, the results for the first USG sample showed that the non-Hg metals including As, Se and Pb did not volatilize from the sample during the wallboard simulation test. While the mass balances between the solids after simulation and the as-prepared sample prior to testing are not ideal (varying between 116 and 128%). However, the results tend to suggest that As and Se are more likely retained in the FGD gypsum and less likely to be volatilized during the kettle calcining process.

Table 3-10. Results of wallboard simulation tests for arsenic, selenium, and lead

Metal	Run	As Prepared	After	Volatilized	Mass
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			µg/g	Simulation (solid) µg/g	Metal (gas phase) µg/g	Balance
Arsenic	USG-1	Run 1	5.88	7.02	BML	119%
		Run 2		7.34	BML	125%
	USG-2	Run 1	5.74	5.89	BML	102%
		Run 2		5.79	BML	100%
Selenium	USG-1	Run 1	5.39	6.27	BML	116%
		Run 2		6.62	BML	123%
	USG-2	Run 1	5.26	5.17	BML	98.2%
		Run 2		5.30	BML	101%
Lead	USG-1	Run 1	2.31	2.95	BML	128%
		Run 2		2.82	BML	122%
	USG-2	Run 1	2.08	2.04	BML	98.2%
		Run 2		1.97	BML	94.7%

BML=below method limit (As<0.4 µg/g, Pb<0.06 µg/g, Se<0.4 µg/g)

3.3.3 Additional Wallboard Simulation Tests for Mercury Thermal Stability on Gypsum Samples

Because of the unacceptable Hg mass balance in the previous wallboard simulation, additional testing was conducted using FGD samples from eight different facilities. Sufficient quantity of the USG FGD gypsum was not available to be used in the repeated wallboard simulation tests. The experimental method was modified to include additional quality assurance. Vapor phase Hg was collected with iodated carbon sorbent tubes using Method 30B, at a constant temperature of 160 °C. Method 7473 was used to analyze the Hg content of the solid gypsum. For each sample, three replicates were conducted. The amount of volatilized Hg was calculated using the Hg trapped on the carbon tubes and the solid gypsum before heating. The amount remaining in solid was calculated using the solid gypsum before and after heating. Table 3-11 shows the averages and standard deviation for each sample. Figure 3-6 shows the amount of Hg retained in solid and Hg volatilized. Appendix C has more detailed results.

This series of tests gave improved mass balance results compared to the earlier testing to loss of Hg across the kettle calciner. The results (Figure 3-5) indicate potential Hg loss of 9 to 48%. The USG results from wallboard manufacturing facilities indicate Hg loss across the kettle calciner (excluding the Texas lignite sample) of 2 to 50% (found in Table 1-3). This is considered confirmation of the previous USG research with emphasis on the degree of variability across samples.

Table 3-11. Results of additional wallboard simulation tests for mercury

Sample ID		Pre-test (solid), ng/g	After Simulation (solid), ng/g	Volatilized Mercury (gas phase), ng/g	Percent Volatilized	Percent Remaining in Solid	Mass Balance
AaAW	Average	538	426	122	23%	79%	102%
	St Dev	20.9	24.3	24.5	5%	5%	4%
DaAW	Average	653	529	134	21%	81%	102%
	St Dev	15.0	6.86	3.86	1%	3%	4%
NAW	Average	466	228	204	44%	49%	93%
	St Dev	9.27	17.8	7.51	2%	3%	3%
OAW	Average	44.3	32.0	15.5	35%	72%	108%
	St Dev	2.12	1.29	0.68	2%	6%	7%
SAW	Average	312	159	151	48%	51%	99%
	St Dev	6.75	27.8	17.3	6%	8%	3%
TAW	Average	765	519	198	26%	68%	94%
	St Dev	58.3	17.5	64.6	8%	6%	4%
WAW	Average	938	865	87.5	9%	92%	101%
	St Dev	18.6	26.1	44.4	5%	3%	5%
XAW	Average	1,030	815	212	21%	79%	100%
	St Dev	6.24	14.0	16.8	2%	2%	2%

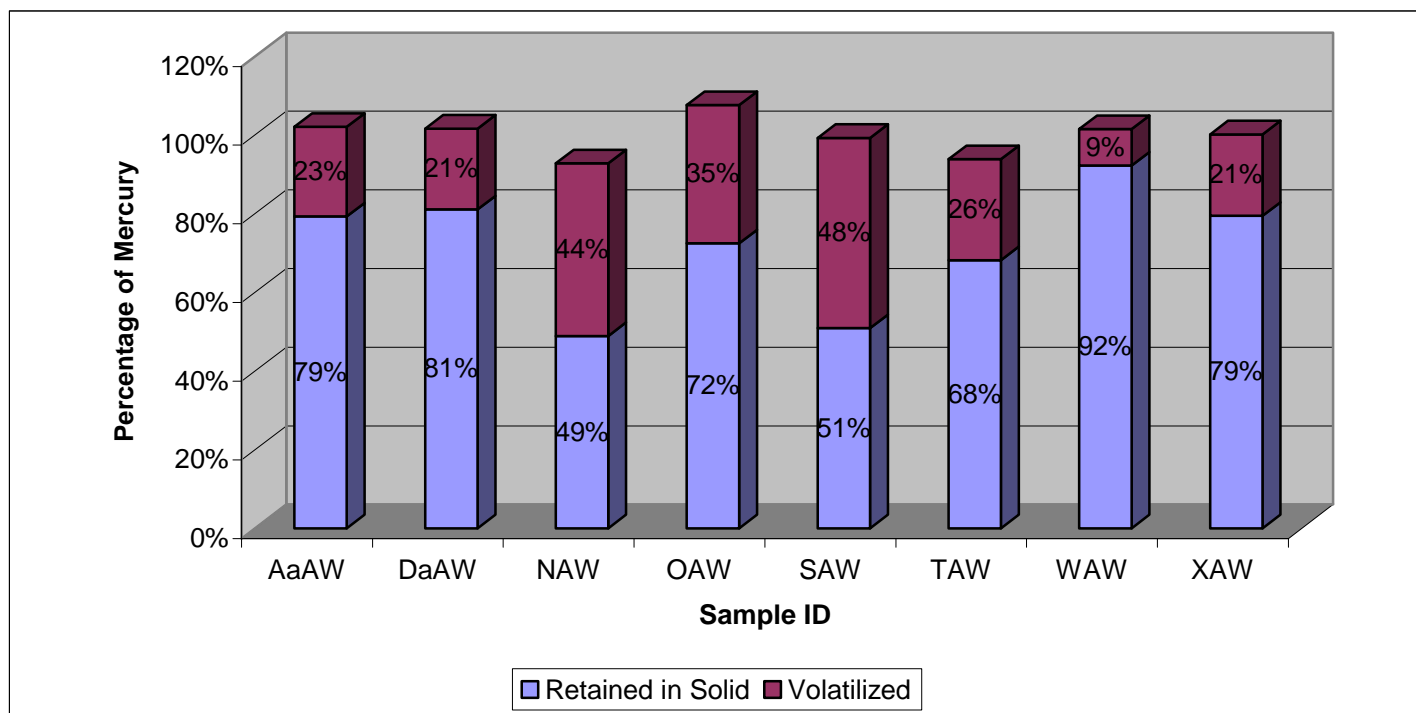


Figure 3-5. Results for additional wallboard simulation tests for mercury

3.3.4 Wallboard Simulation Tests for Mercury Thermal Stability at Various Temperatures

Gypsum sample DaAW was tested at three temperatures (120°C, 140 °C, 160 °C) to compare the amount of volatilized Hg versus temperature during the simulation test. Method 30B and Method 7473 were used. Table 3-12 and Figure 3-7 display a summary of the results and show that the amount of volatilized Hg increases as temperature increases. The linear trend line in Figure 3-7 shows an R-squared value of 0.9269. Detailed results are included in Appendix C. Therefore, the operating temperature of the kettle calciner is important to consider in predicting potential loss at a production facility.

Table 3-12. Results for wallboard simulation tests on sample DaAW at various temperatures

Furnace Temperature, °C		Pre-test (solid), ng/g	After Simulation (solid), ng/g	Volatilized Mercury (gas phase), ng/g	Percent Volatilized	Percent Remaining in Solid	Mass Balance
120	Average	551	532	10.8	2%	97%	99%
	St Dev	8.85	5.13	2.64	0%	1%	2%
140	Average	621	588	42.1	7%	95%	102%
	St Dev	34.7	23.3	1.80	1%	2%	2%
160	Average	653	529	134	21%	81%	102%
	St Dev	15.0	6.86	3.86	1%	3%	4%

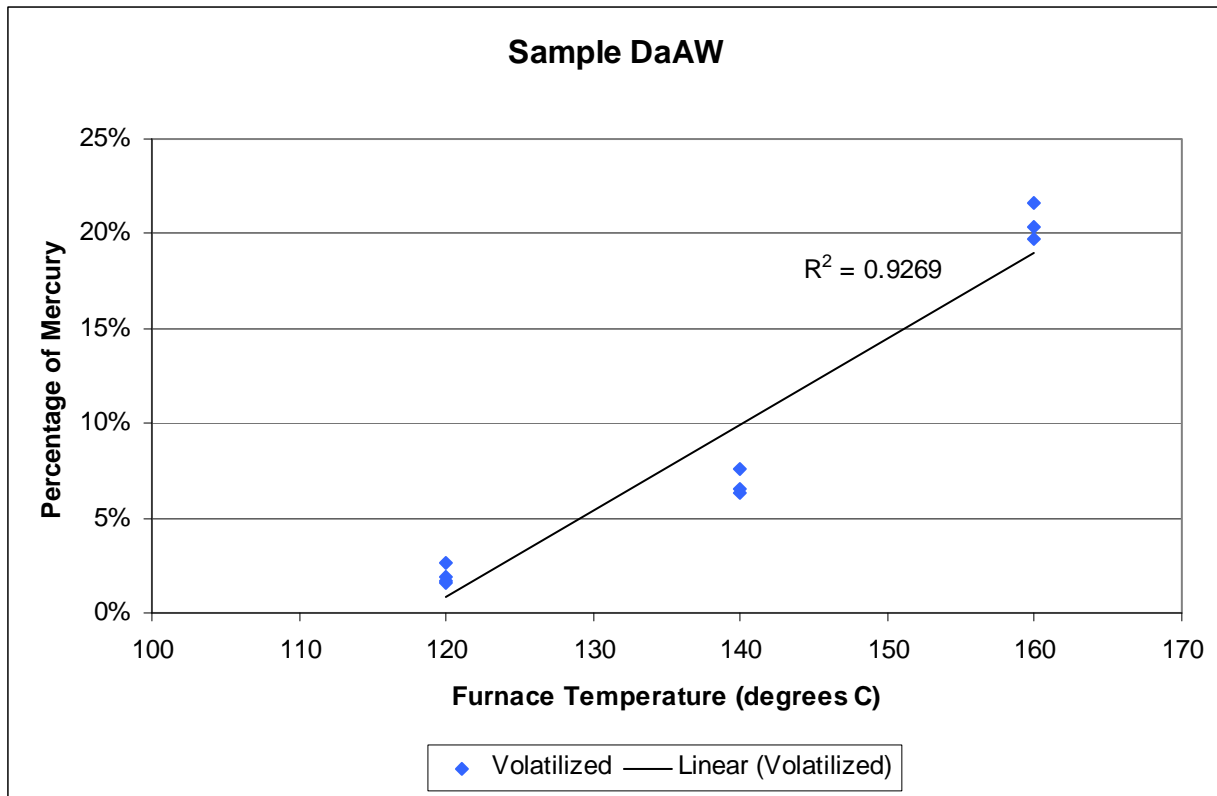


Figure 3-6. Results for wallboard simulation tests at various temperatures

Chapter 4

Conclusions and Future Considerations

Approximately 40% of the 126 million tons of CCRs produced in the U.S. as of 2006 were utilized in agricultural, commercial, and engineering applications. The remainder (i.e., 75 million tons) was managed in either landfills or impoundments. The physical and chemical characteristics of CCRs make them potentially suitable as replacements for materials used in a wide range of products including cement, concrete, road base, and wallboard. Use of CCRs as an alternative to virgin materials helps conserve natural resources and energy, as well as decrease the amount of CCRs being land disposed.

This study evaluated the potential loss of Hg and other metals for the production of cement clinker, asphalt, and wallboard. When this study was originally started, there were no controls for Hg from the production of cement. Subsequent to this research, EPA has proposed (74 FR 21136m May 6, 2009) regulations to reduce mercury emissions from cement kilns, which may result in use of air pollution control technology similar to that used at coal-fired power plants (e.g. wet scrubbers and sorbents for enhanced Hg capture). The addition of air pollution control at cement kilns should not affect the ability to use fly ash or FGD gypsum in the production of clinker. However, to avoid installation of air pollution control, kiln inputs (such as fly ash) containing Hg may be avoided which could impact usage of some CCRs.

The focus of the laboratory simulation of cement clinker production using a high-temperature Lindberg was on non-Hg metals (i.e., As, Se, and Pb). The results indicate that all of the As, Se and Pb are volatilized as a result of the high temperatures (1450 °C) the samples are exposed to during this process. With potential changes in air pollution control at cement plants, there will be less Hg and other metals being emitted. However, these metals will be retained in the cement kiln dust and the air pollution control residues. Ensuring that these metals are not later released based on how the air pollution control residues (FGD gypsum and cement kiln dust) are managed, requires additional research to evaluate the potential leaching of Hg and other metals for the conditions that the residues are managed. Currently there are no federal requirements for lining of landfills used for cement kiln dust disposal. In addition, some sites are using cement kiln dust in engineering and commercial applications.

The asphalt manufacturing simulation results presented indicate that all of the non-Hg metals including As, Se and Pb are retained in the samples after exposure. Mercury showed minimal volatilization from the ADA samples as well as the samples from Facilities A and E. The Facility B results, however, showed significant loss of Hg into the gas-phase as a result of exposure to the asphalt manufacturing conditions. Facility B is the only facility included in this study that has an in-furnace SCR design. This design type necessitates that the fly ash come in contact with the SCR catalyst surface regardless of whether ammonia is being injected or not. Further investigation of fly ashes from facilities with an in-furnace SCR design is probably warranted.

Sanderson et al., (2008) provide the most extensive study to date on the fate of Hg when FGD gypsum is used as feedstock for wallboard production. Testing of full-scale production facilities is considered more reliable than laboratory testing to simulate wallboard production. However, the study did not include other metals. Therefore, laboratory simulation of wallboard production was conducted as part of this

study. Results from Sanderson et al., (2008) indicate that the process where Hg loss is more likely to occur is the kettle calciner. Therefore, laboratory simulation of wallboard production was conducted evaluating Hg and other metals with the focus on trying to simulate potential loss across the kettle calciner. Only FGD gypsum samples were used in this simulation since this is the material used in the production of wallboard (and not fly ash). This research was conducted in two phases. The first phase resulted in unacceptable mass balance for Hg. The results for the other metals are considered acceptable. Consequently, additional testing was conducting in a second phase using more recent FGD samples.

The first phase of testing suggests that As and Se are more likely retained in the FGD gypsum and less likely to be volatilized during the kettle calcining process. The second phase of testing provided improved Hg mass balance results. The results (Figure 3-5) indicate potential Hg loss of 9 to 48%. The USG results from wallboard manufacturing facilities indicate Hg loss across the kettle calciner (excluding the Texas lignite sample) of 2 to 50% (found in Table 1-3). This is considered confirmation of the previous USG research with emphasis on the degree of variability across samples. Additional testing was conducted at three different temperatures that the kettle calciner can be operated. The linear trend line in Figure 3-7 shows an R-squared value of 0.9269. Therefore, the operating temperature of the kettle calciner is important to consider in predicting potential loss at a production facility.

In interpreting the results from this study, please note that the samples are not considered to be a representative sample. Samples were obtained on a voluntary basis and represent a minor fraction (<1%) of U.S. boilers at coal-fired power plants. However, every effort was made to obtain samples that are considered typical of the air pollution control configurations to be more widely used as the result to changes in U.S. EPA and state regulations.

The results from this laboratory study demonstrate the varying degree of volatility for mercury, arsenic, Se and Pb in CCRs depending on the process temperature being used. A high temperature process such as cement clinker production has the ability to release all four metals from fly ash when exposed to the high temperatures found in production. Laboratory simulation of the asphalt and wallboard production processes showed a significant release of mercury during heating, but the temperatures were too low to volatilize the arsenic, Se, or Pb. Whereas, the Hg loss for wallboard production suggest non-Hg metals being retained in wallboard with a potential Hg loss of 9 to 48%. However, the actual mass emission rates must be considered when determining potential concern to human health and the environment.

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Chapter 5 Quality Assurance / Quality Control

5.1 Quality Indicator Goals

Data quality indicator goals for critical measurements in terms of accuracy, precision and completeness are shown in Table 5-1.

Table 5-1. Data Quality Indicator Goals

Measurement	Method	Accuracy	Precision	Completeness
As, Se, and Pb Concentration	ICP/6010B	90 – 110 %	10%	>90%
Hg Concentration	CVAA/7470A	80 – 120 %	10%	>90%

Accuracy was determined by calculating the percent bias from a known standard. Precision was calculated as relative percent difference (RPD) between duplicate values and relative standard deviation (RSD) for parameters that have more than two replicates. Completeness is defined as the percentage of measurements that meet DQI goals of the total number measurements taken. Types of QC samples used in this project included blanks, instrument calibration samples, replicates, and matrix spikes

5.2 Ontario Hydro and Method 29 Mercury Analyses

Accuracy and precision for the Ontario Hydro samples for Hg concentration in the process gas determinations were made using replicates and matrix spike analyses. The Figure 5-1 shows the spike recoveries obtained during the analysis of the recovered fractions. Figure 5-2 shows the spike recoveries for Hg obtained during the Method 29 sampling. The Ontario Hydro samples had a completeness of 98% and the Method 29 samples had a completeness of 94%.

Required QC samples for metals and Hg sampling trains are detailed in EPA Method 29 and the Ontario Hydro Method. QC samples required for CVAA analysis are detailed in 7470A. The Hg analyzer software has been programmed with the acceptance criteria for Method 7470A. All calibrations and samples analysis parameters have passed the QA/QC criteria and may be considered valid samples. The Ontario Hydro samples had a completeness of 98% and the Method 29 samples had a completeness of 94%.

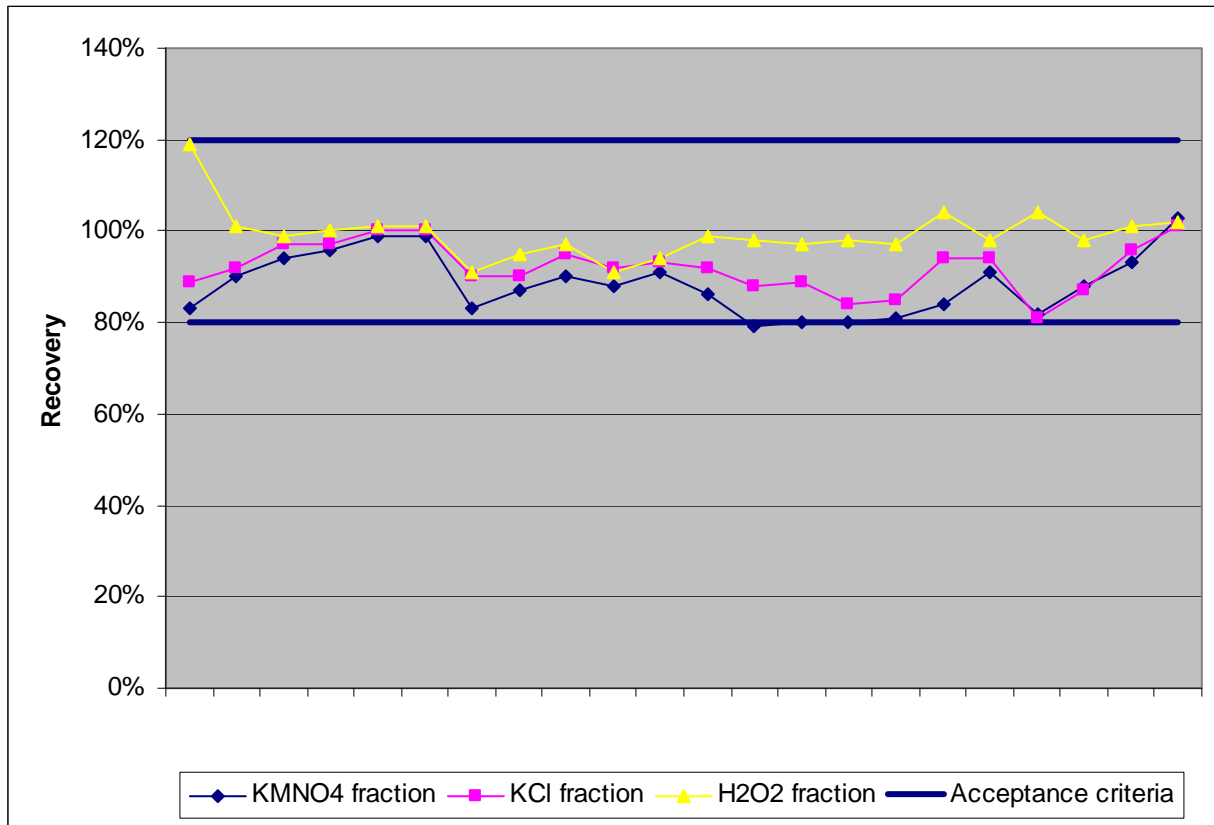


Figure 5-1. Ontario Hydro spike recovery for multiple runs

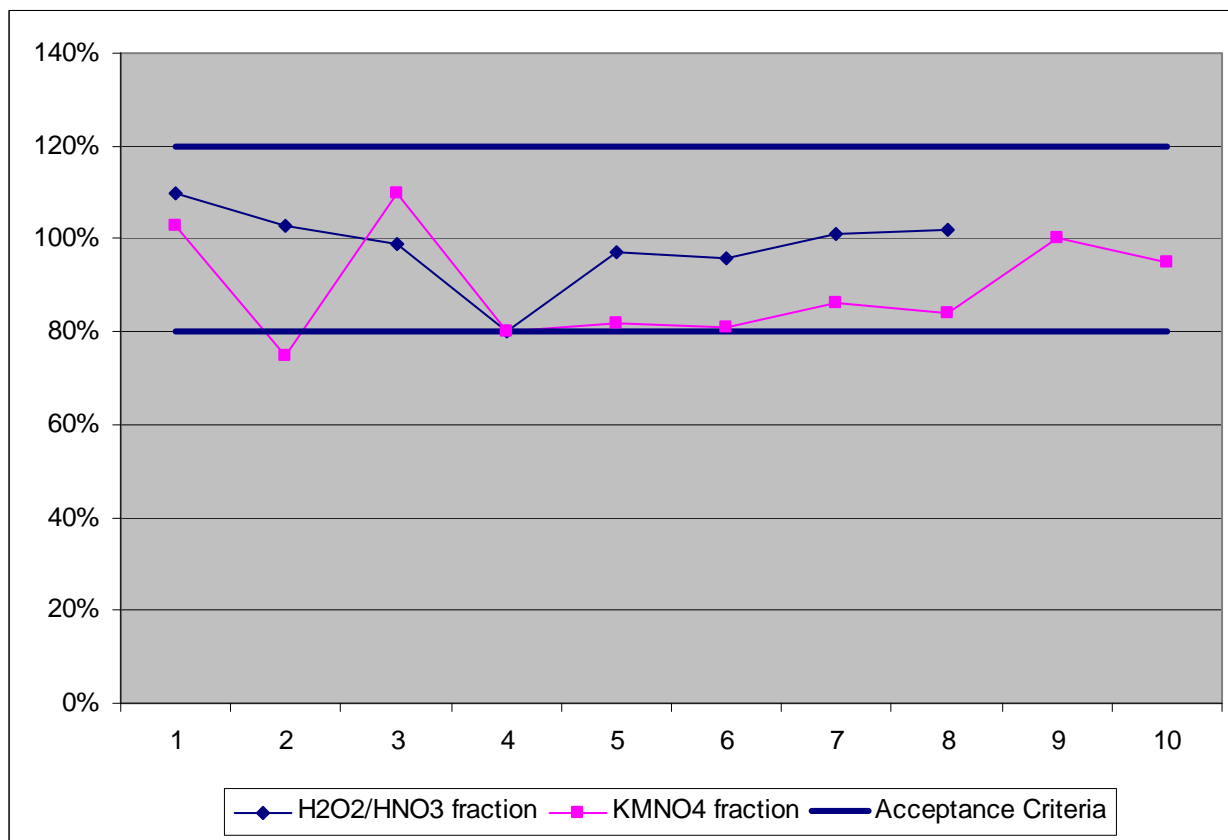


Figure 5-2. Method 29 mercury spike recoveries for multiple runs

5.3 Method 29 Analyses for Arsenic, Lead, and Selenium

QA/QC samples for the determination of As, Pb, and Se included blanks, replicates, and matrix spikes. Table 5-2 presents accuracy of the matrix spike recovery data for the Method 29 cement kiln simulation metals analyses. Table 5-3 presents the accuracy of the matrix spike recovery data for the asphalt simulation testing. Table 5-4 presents the accuracy of the matrix spike recovery data for the gypsum wallboard simulation testing.

Table 5-2. Method 29 Matrix Spike Recoveries for Arsenic, Lead, and Selenium for the Cement Kiln Simulations

Facility Name	As	Se	Pb
Brayton Point BL	111%	104%	108%
Pleasant Prairie BL	104%	102%	109%
Salem Harbor BL	92%	90%	89%

Table 5-3. Method 29 Matrix Spike Recoveries for Arsenic, Lead, and Selenium for the Asphalt Simulations

Facility Name	As	Se	Pb
Brayton Point BL	109%	111%	101%
Brayton Point ACI	109%	103%	111%
Facility B (SCR on)	91%	92%	91%
Facility B (SCR off)	93%	97%	110%
USG-1	106%	107%	108%
USG-2	101%	103%	100%

Table 5-4. Method 29 Matrix Spike Recoveries for Arsenic, Lead, and Selenium for the Gypsum Wallboard Simulations

Facility Name	As	Se	Pb
USG-1	106%	107%	108%
USG-2	101%	103%	100%

Overall completeness for the Method 29 non-Hg metals matrix spike samples was 30 valid out of 33 total matrix spikes or 91%.

Chapter 6 References

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Appendix A DOE NETL Full-Scale Test Site Flow Diagrams

A.1 Brayton Point Unit 1

- Carbon injected upstream of second ESP (Research Cottrell). Only ½ of the unit was treated, or carbon was injected into one of the two new ESPs (Research Cottrell ESPs).
- Hopper ID's also shown. Samples from C-row are from the first row of hoppers in the second ESP.

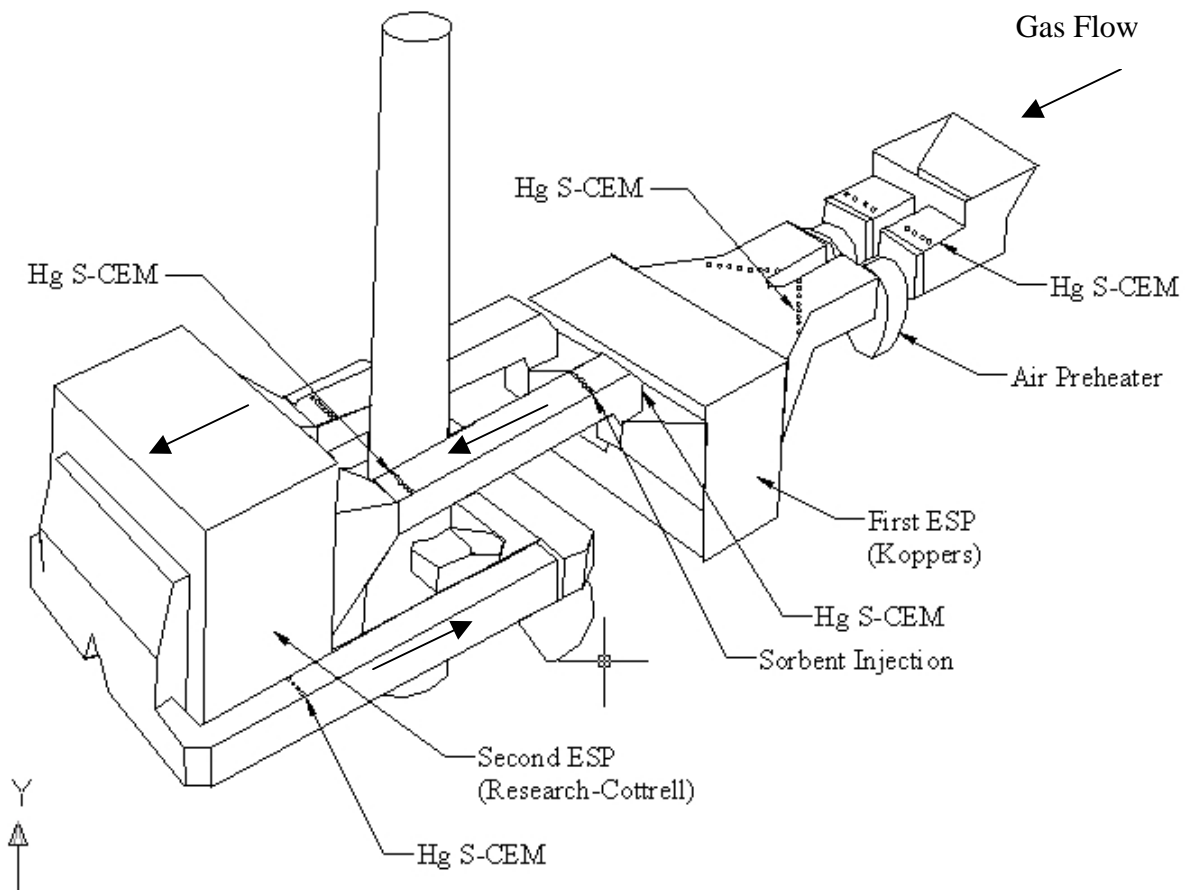


Figure A-1. Brayton Point Unit 1

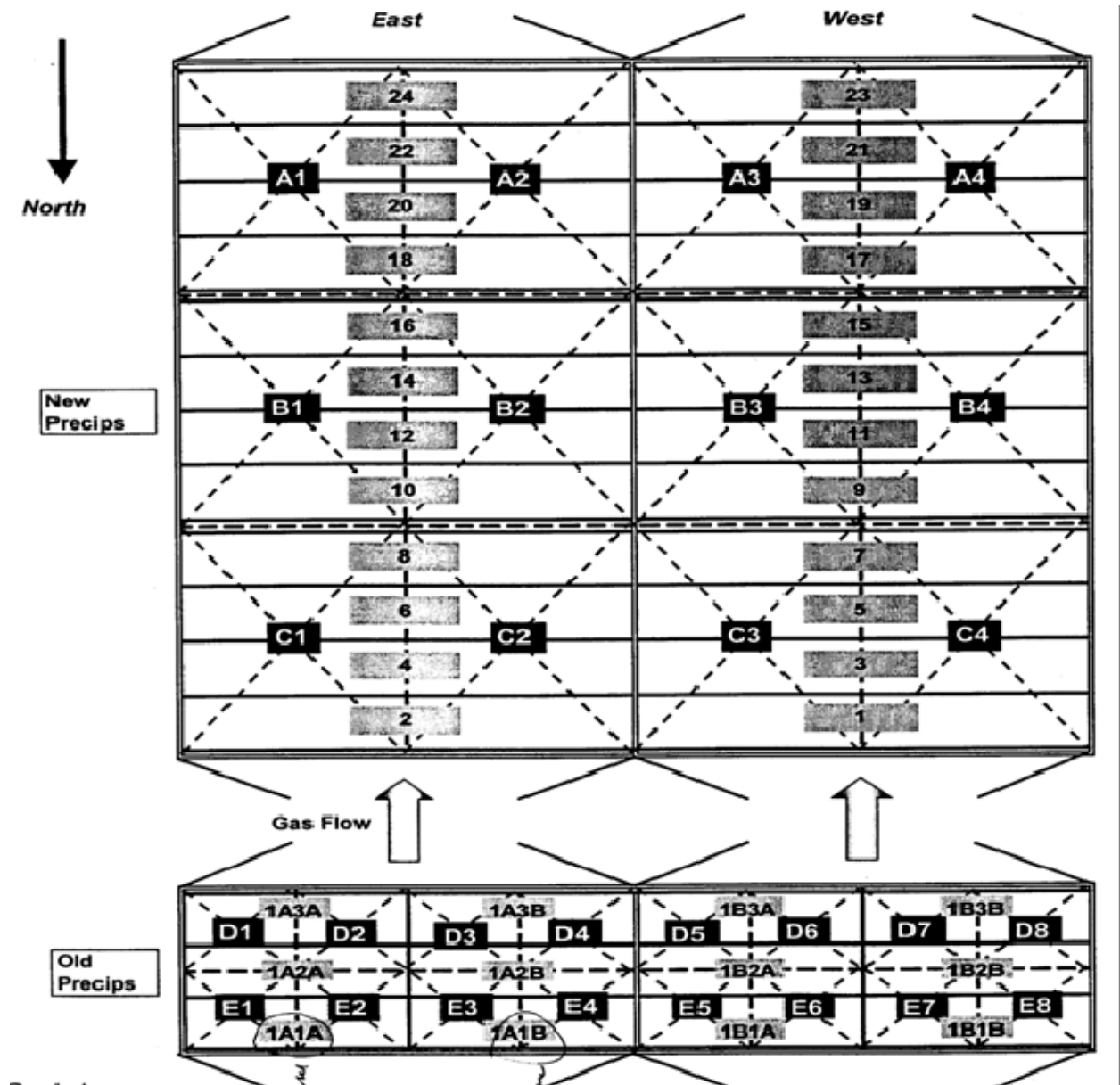


Figure A-2. Brayton Point Unit 1 Hopper Identification

A.2 Pleasant Prairie Unit 2

- Carbon injected upstream of cold-side ESP. Only 1/4 of the unit was treated. Test ESP was ESP 2-4.

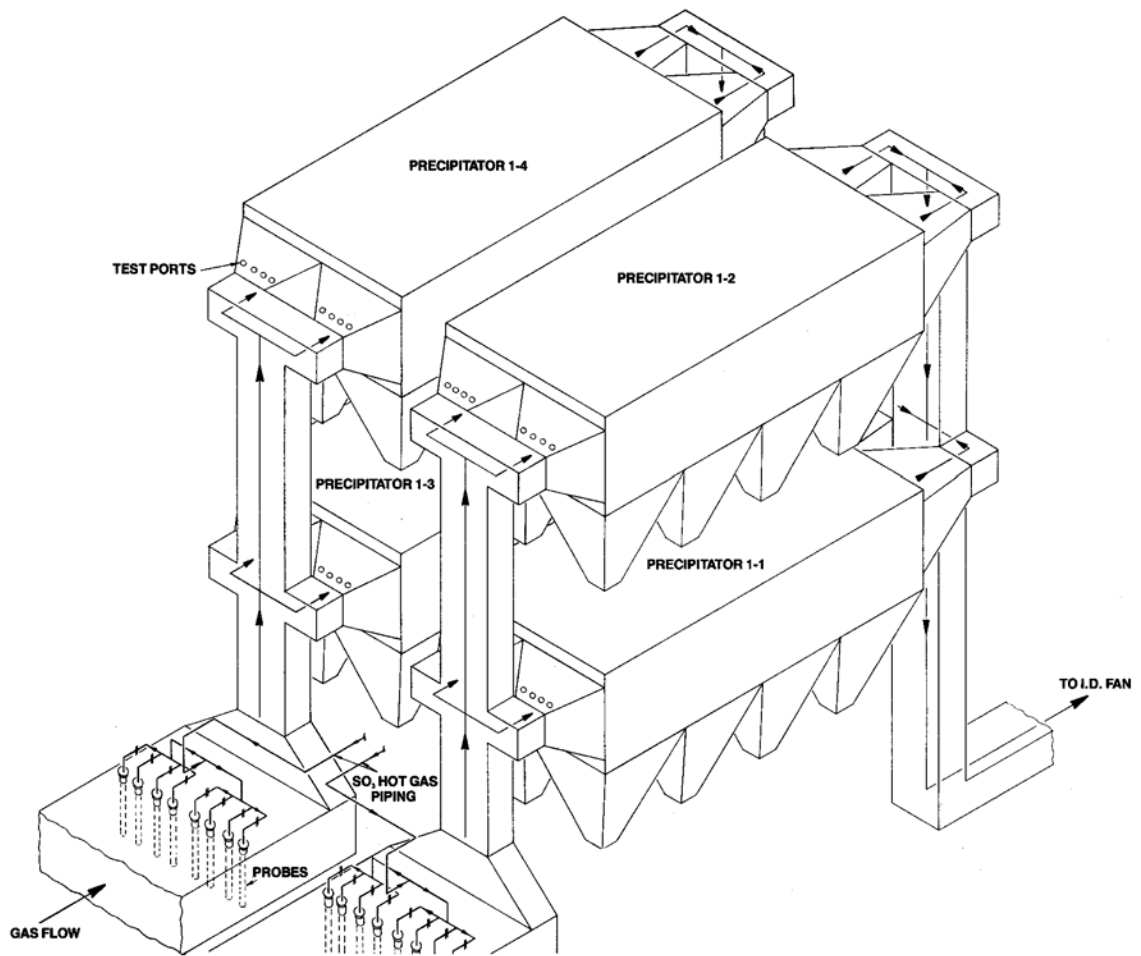


Figure A-3. Pleasant Prairie Unit 2

A.3 Salem Harbor Unit 1

- Carbon injected upstream of cold-side ESP. Row-A hoppers were the front hoppers.

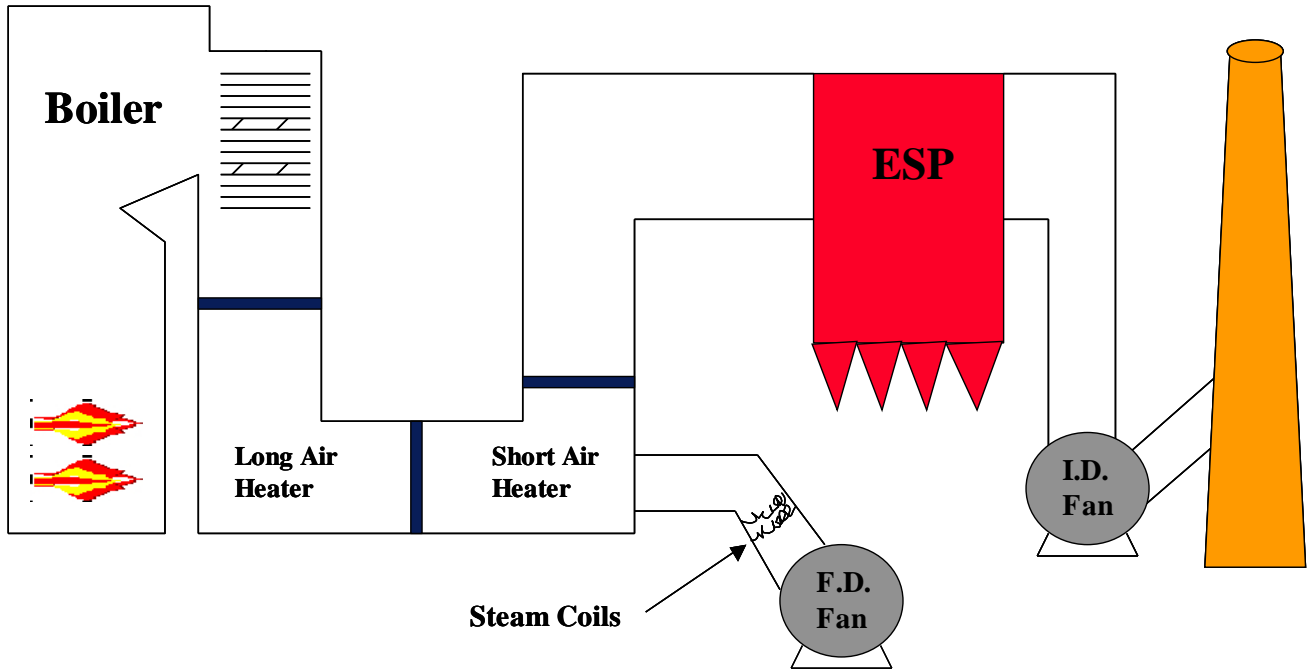


Figure A-4. Salem Harbor Unit 1

Appendix B Non-DOE NETL Full-Scale Test Site Flow Diagrams

B.1 Facility A

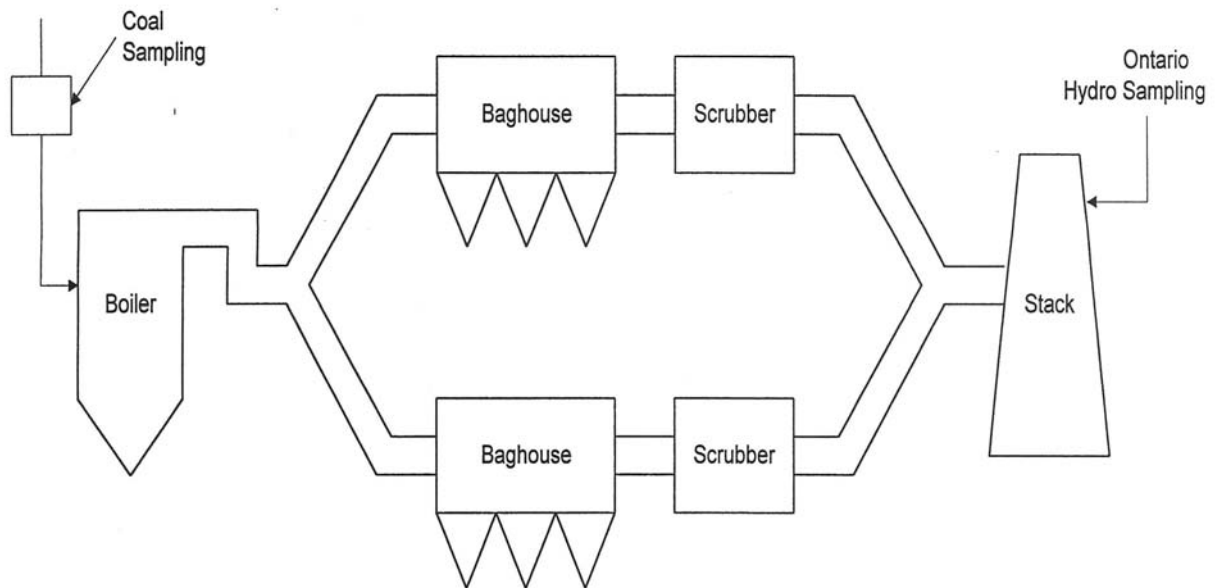


Figure B-1. Facility A

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Appendix C Detailed Results for Additional Wallboard Simulation Tests

Table C-1. Description of Facilities Providing Eight Gypsum Samples.

Sample ID	Coal Rank	NOx Control	Particulate Control	FGD Scrubber Type		Date Received
				Lime Type	Oxidation	
AaAW	Eastern-Bituminous	SCR	ESP	Limestone	Forced	10/14/08
DaAW	Eastern-Bituminous	SCR	ESP	Limestone	Forced	12/12/08
NAW	Bituminous	None	CS-ESP	Limestone	Forced	6/1/06
OAW	Bituminous	SCR	CS-ESP	Limestone	Forced	6/10-6/12/06
SAW	High Sulfur Bituminous	SCR	CS-ESP	Limestone	Forced	7/19/07
TAW	Eastern-Bituminous	SCR	CS-ESP	Lime	Forced	9/18/07
WAW	Eastern-Bituminous	SCR off	ESP	Limestone Trona	Forced	11/28/07
XAW	Sub-Bituminous Powder River Basin	SCR	ESP	Limestone	Forced	6/16/08

SCR = selective catalytic reduction

ESP = electro static precipitator

CS-ESP = cold-side electro static precipitator

Table C-2. Detailed Results for Additional Wallboard Simulation Tests

Sample ID		Pre-test (solid), ng/g	After Simulation (solid), ng/g	Volatilized Mercury (gas phase), ng/g	Percent Volatilized	Percent Remaining in Solid	Mass Balance
AaAW	Run 1	571	428	107	19%	75%	94%
	Run 2	554	467	112	20%	84%	104%
	Run 3	515	440	97.2	19%	85%	104%
	Run 4	522	412	111	21%	79%	100%
	Run 5	536	414	149	28%	77%	105%
	Run 6	531	398	157	30%	75%	105%
	Average	538	426	122	23%	79%	102%
	St Dev	20.9	24.3	24.5	5%	5%	4%
DaAW	Run 1	647	528	132	20%	82%	102%
	Run 2	670	523	132	20%	78%	98%
	Run 3	641	536	139	22%	84%	105%
	Average	653	529	134	21%	81%	102%
	St Dev	15.0	6.86	3.86	1%	3%	4%
NAW	Run 1	473	240	196	41%	51%	92%
	Run 2	455	207	206	45%	46%	91%
	Run 3	469	237	211	45%	51%	96%
	Average	466	228	204	44%	49%	93%
	St Dev	9.27	17.8	7.51	2%	3%	3%
OAW	Run 1	46.7	30.7	15.5	33%	66%	99%
	Run 2	42.8	32.0	16.2	38%	75%	113%
	Run 3	43.3	33.3	14.8	34%	77%	111%
	Average	44.3	32.0	15.5	35%	72%	108%
	St Dev	2.12	1.29	0.68	2%	6%	7%
SAW	Run 1	307	127	167	54%	41%	96%
	Run 2	320	172	153	48%	54%	101%
	Run 3	309	178	133	43%	58%	100%
	Average	312	159	151	48%	51%	99%
	St Dev	6.75	27.8	17.3	6%	8%	3%
TAW	Run 1	831	521	240	29%	63%	92%
	Run 2	723	536	123	17%	74%	91%
	Run 3	739	501	230	31%	68%	99%
	Average	765	519	198	26%	68%	94%
	St Dev	58.3	17.5	64.6	8%	6%	4%
WAW	Run 1	910	843	97.3	11%	93%	103%
	Run 2	929	836	24.0	3%	90%	93%
	Run 3	928	870	33.7	4%	94%	97%
	Run 4	960	866	128	13%	90%	104%
	Run 5	933	890	103	11%	95%	107%
	Run 6	955	906	84.1	9%	95%	104%
	Run 7	954	843	141	15%	88%	103%
	Average	938	865	87	9%	92%	101%

	St Dev	18.6	26.1	44.4	5%	3%	5%
XAW	Run 1	1033	799	222	21%	77%	99%
	Run 2	1023	823	193	19%	80%	99%
	Run 3	1021	823	222	22%	81%	102%
	Average	1026	815	212	21%	79%	100%
	St Dev	6.24	14.0	16.8	2%	2%	2%

Table C-3. Detailed Results for Wallboard Simulation Tests on Sample DaAW at Various Temperatures

Furnace Temperature (°C)		Pre-test (solid), ng/g	After Simulation (solid), ng/g	Volatilized Mercury (gas phase), ng/g	Percent Volatilized	Percent Retained in Solid	Mass Balance
120	Run 1	547	525	8.87	2%	96%	98%
	Run 2	546	531	14.6	3%	97%	100%
	Run 3	546	536	9.08	2%	98%	100%
	Run 4	564	536	10.6	2%	95%	97%
	Average	551	532	10.8	2%	97%	99%
	St Dev	8.85	5.13	2.64	0%	1%	2%
140	Run 1	640	601	40.4	6%	94%	100%
	Run 2	642	603	41.8	7%	94%	100%
	Run 3	581	561	44.0	8%	97%	104%
	Average	621	588	42.1	7%	95%	102%
	St Dev	34.7	23.3	1.80	1%	2%	2%
160	Run 1	647	528	132	20%	82%	102%
	Run 2	670	523	132	20%	78%	98%
	Run 3	641	536	139	22%	84%	105%
	Average	653	529	134	21%	81%	102%
	St Dev	15.0	6.86	3.86	1%	3%	4%