CHARACTERIZATION OF FLY ASH FROM FULL-SCALE DEMONSTRATION OF SORBENT INJECTION FOR MERCURY CONTROL ON COAL-FIRED POWER PLANTS

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ABSTRACT

With impending regulation of mercury from coal-fired power plants, control efforts have focused on the most mature retrofit technologies. Powdered activated carbon (PAC) injection has been deemed the most mature technology, but has until recently only been demonstrated in bench- and pilot-scale experiments. Under a DOE NETL cooperative agreement, large-scale, continuous injection of PAC was accomplished for periods of several weeks at four utility power plants. Leaching analyses were performed using two widely accepted methods in order to assess the stability of the ash byproduct in landfill situations. Results are reported here for three of the four plants, which represent different coal rank and composition, different particulate control devices, and different operating conditions; however, the same powdered activated carbon was used at all plants. Little or no detectable Hg leached by the TCLP or SGLP procedures for any of the ash samples. The amounts of mercury leached from these samples were about 100 times lower than the primary drinking water standard. At one plant, where ash was tested for mercury leaching with and without injection of PAC, PAC injection did not seem to have increased the amount of mercury leached from the ash.

INTRODUCTION

In December 2000, EPA announced their intent to regulate mercury emissions from nation's coal-fired power plants. Legislation is currently being drafted, with indications that the final regulations may require removal efficiencies as low as 68% or as high as 90% from existing sources. Estimates for the cost of meeting mercury regulations at the level of 90% removal efficiency range from $2 to $5 billion per year. With mercury regulations imminent, mercury control technologies need to be proven at full scale to document performance and costs.

The Department of Energy's National Energy Technology Laboratory (NETL) is the primary funding agency on an industry cost-shared test program to obtain the necessary information

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to assess the costs of controlling mercury from coal-fired utility plants that do not have scrubbers for SO_2 control.

The most mature retrofit technology available today is the injection of sorbents such as powdered activated carbon (PAC) into flue gas upstream of particulate control devices (PCDs). The gas-phase mercury in the flue gas is adsorbed (either chemically or physically) on the sorbent. This can take place in-flight or once the sorbent has deposited on the bags of a fabric filter. Preliminary evidence suggests that sorbent deposited in ESPs can also remove gaseous mercury to some degree. Existing particulate control equipment collects the mercury-containing sorbent along with the fly ash.

Issues related to the implementation of PAC-injection for mercury control on coal-fired power plants include:

- Cost of sorbents and associated capital equipment.
- Impact on operation of existing particulate control device.
- Impacts on the fly ash, which include loss of byproduct sales due to contamination and potential for leaching of mercury from the ash in either utilization or disposal of ash.

In this paper, report on measurements of the leachability of sorbent-containing fly ash from three full-scale tests of PAC-injection at coal-fired utility boilers.

Ash Utilization From Coal-Fired Power Plants

PAC-injection applied to coal-fired boilers will result in the fly ash being mixed with a certain amount of mercury-containing sorbent. This material will be sent to land disposal or used in specific applications (assuming that the presence of the sorbent is compatible with the application). Since the mercury on the spent sorbent may be present in a different form than on fly ash, it is necessary to consider what might be the most likely routes for release of mercury in sorbent-fly ash mixtures and how sorbent-containing coal utilization byproducts (CUBs) should be tested.

In the US, approximately 67% of all fly ash produced from utility coal combustion is disposed of in landfills or surface impoundments. The remaining 33% is used for a variety of commercial applications as shown in Table 1 (taken from Reference 1).

There are approximately 600 waste disposal sites for CUBs in the US, half are landfills and half are surface impoundments. Note that here CUBs include other streams such as bottom ash and scrubber sludge. A 1999 EPA study estimated that about half of the CUB landfills and a little less than a third of the surface impoundments have some type of liner, the most common type being compacted clay. Volatilization of mercury from landfills was estimated by EPA to be small. To date, there has been no evidence based on laboratory leaching studies for leaching of large amounts of mercury from fly ash under landfill conditions.

Leaching appears to be the most likely pathway for liberation of mercury from fly ash. Volatilization may be important for certain applications of fly ash as filler in concrete applications. Volatilization is, of course, the primary pathway for mercury if fly ash is used as a raw material in cement kilns. However, volatilization will be complete in this case.

When considering leaching of mercury from CUBs, whether it takes place in landfills or in concrete, it is difficult to specify one single condition (in terms of pH and temperature) that will apply in every case. There are many different leaching solutions that have been tested with fly ash. Since conditions may vary from one landfill to another, and since the inorganic portion of the fly ash may be acidic or basic, it is hard to specify a single test that can be applied to all future end-uses or disposal options for CUBs. In this work, we used a variety of different leaching procedures to characterize the stability of sorbent-containing fly ash in the environment.

Table 1. Fate of Fly Ash from Coal Combustion in the United States in 1999.[1]

Fate	Millions of tons	%	Potential release mechanisms
Land disposal	42.210	67.0%	Leaching, windblown dust
Concrete/grout	10.000	15.9%	Leaching, volatilization (application-specific)
Structural fills	3.200	5.1%	Unlikely
Waste stabilization	1.900	3.0%	Unlikely
Mining applications	1.500	2.4%	Leaching
Raw feed for cement kiln	1.300	2.1%	Volatilization in the kiln, with recovery in fines
Road base/subbase	1.200	1.9%	Not expected to be significant
Flowable fill	0.850	1.3%	Unlikely
Other	0.840	1.3%	
Total	63.000		

Description Of Field Demonstration Program

Under a DOE/NETL cooperative agreement, ADA Environmental Solutions is working in partnership with PG&E National Energy Group (NEG), WE Energies, a subsidiary of Wisconsin Energy Corp., Alabama Power, a subsidiary of Southern Company, and EPRI on a field test program of sorbent injection upstream of existing particulate control devices for mercury control. Other organizations participating in the program include Ontario Power Generation, First Energy, TVA, Arch Coal, Kennecott Energy, Hamon Research-Cottrell, EnviroCare and Norit Americas.

The four sites, shown in Table 2, burn coal and have particulate control devices only (no scrubbers); this is representative of three-quarters of the coal-fired electric utility boilers in the US. At each site, sorbent injection for mercury control was implemented on full-scale particulate control devices to obtain performance and operational data. Combustion byproduct samples were collected concurrently to determine the impact of sorbents on waste disposal and byproduct reuse practices. The tests were conducted in three distinct phases:

- Baseline testing;

- Parametric testing; and
- Long-term testing (two weeks).

Baseline measurements were conducted before the sorbent injection equipment was installed. During this phase, mercury concentrations in the flue gas were measured with a Semi-continuous Emissions Monitor (S-CEM) and by the Ontario Hydro method. During this period, operating data and coal and ash data were also collected.

Table 2. Test sites for dry sorbent injection.

Test Site	Coal	Particulate Control Device
PG&E NEG Salem Harbor	Low sulfur bituminous	Cold-Side ESP
PG&E NEG Brayton Point	Low sulfur bituminous	Cold-Side ESP
Wisconsin Electric Pleasant Prairie	Powder River Basin (PRB) sub-bituminous	Cold-Side ESP
Alabama Power E.C. Gaston	Low sulfur bituminous	Hot-Side ESP, plus COHPAC Fabric Filter

A series of parametric tests were then conducted to determine the optimum sorbent and operating conditions that would be required for several levels of mercury control. The maximum injection rate was set based on the preliminary injection performance data that have been developed from consideration of slip-stream testing, modeling exercises, the practical limitations of the particulate control device (PCD), and sorbent costs.

Based on results from these tests, a two-week test under optimized conditions (i.e., the long-term test) was conducted to assess the long-term impacts to the PCD, byproduct management practices and auxiliary equipment operation. During the long-term test, mercury removal efficiencies were measured by the S-CEMs and verified by Ontario Hydro method measurements. (Note that while these tests are referred to in this paper as "long term," this does not imply that such tests will be indicative of the performance of sorbent injection over periods of many weeks or months.)

At each site, a standard powdered activated carbon was tested in all cases as a benchmark sorbent; this is FGD carbon, a lignite-derived sorbent supplied by Norit Americas.

Testing at all the sites has been completed. Results from the E.C. Gaston plant and the Pleasant Prairie plant have been reported elsewhere[2-4] and will only be mentioned here in summary. Analyses have been completed for the long-term samples at Brayton Point, and will be reported here. Analyses of the long-term samples from Salem Harbor are still in progress.

PG&E National Energy Group operates Brayton Point Station located in Somerset, Massachusetts. There are four fossil fuel fired units at the facility designated as Units 1, 2, 3, and 4. In 1982, three of the four units, (Units 1, 2, and 3) were converted from oil back to coal. The units fire a low sulfur, bituminous coal. Unit 1, which was the test unit, has a tangentially fired boiler rated at 245 net MW.

The primary particulate control equipment consists of two cold-side ESP's in series, with an EPRICON flue gas conditioning system that provides SO_3 for fly ash resistivity control. The EPRICON system is not used continuously, but on an as-needed basis. The first ESP (Old ESP) in this particular configuration was designed and manufactured by Koppers. The Koppers ESP has a weighted wire design and a specific collection area (SCA) of 156 ft^2/1000 acfm. The second ESP (New ESP) in the series configuration was designed and manufactured by Research-Cottrell. The second ESP has a rigid electrode design and an SCA of 403 ft^2/1000 acfm. Total SCA for the unit is 559 ft^2/1000 acfm. The precipitator inlet gas temperature is nominally about 280°F at full load.

The first precipitator consists of four parallel chambers each with 28 gas passages 24' long at 10" centers. Each chamber is further divided into three collecting surface fields. The first ESP has a total of 12 T/R sets.

The second precipitator consists of two parallel chambers. Each chamber is subdivided into 38 gas passages 54' long at 12" centers. The chambers are then divided into six collecting surface fields. The second ESP contains a total of 24 T/R sets.

Hopper ash is combined between both precipitators in the dry ash-pull system. The ash is processed by an on-site Separation Technology Inc. (STI) carbon separation system, to reduce the carbon content. This processed ash is sold as base for concrete and is considered a valuable product for the Brayton Point Station. The remainder of the higher carbon ash is a disposable waste. One precipitator's ash can be isolated from the balance of the unit; however this is a labor intensive procedure.

Brayton Point Unit 1 was chosen for this evaluation because of its combination of firing low-sulfur bituminous coal with a cold-side ESP. This combination covers a wide range of coal-fired power plants operating in the eastern part of the U.S. Brayton Point has unique conditions that are important to this program. They include:

1. PG&E NEG is currently evaluating mercury control options to meet new state compliance regulations in 2006. Sorbent injection is one of the viable options for mercury control.

2. The new ESP (Research-Cottrell) chamber can be treated in isolation, and long duct runs provide good residence times to maximize performance of sorbent injection.

3. Brayton Point has a unique configuration of two ESP's in series. During the test program, sorbent was injected upstream of the second ESP where >90% of the flyash was already removed, and thus it should be easier to document the impact of sorbent injection on ESP performance.

EXPERIMENTAL

Sample Descriptions

The long-term Performance Evaluation for PG&E NEG Brayton Point Station Unit 1 under the DOE/NETL Mercury Demonstration was completed in July, 2002. A commercial sorbent (Norit Americas FGD Carbon) was used for the test. This sorbent had a surface area of 600 m^2/g and a mass-mean diameter of 18 microns. Sorbent for mercury control was injected into the ductwork in between the two electrostatic precipitators. Two injection concentrations were tested for five days each at 10 lb/MMacf and 20 lb/MMacf. Unit 1 flyash was sent to a separate silo for disposal. With coordination from plant personnel, LOI levels in the ash collected from Unit 1 were monitored daily. Sorbent was injected 24 hours/day with no interruptions. Feed rate calibration checks were made with feeder signals and silo weight measurements, both of which indicated that carbon injection was relatively steady at both injection rates. The sorbent injection system was placed under load-following capabilities, in which sorbent feed rate was automatically calculated and adjusted with changes in Unit 1 load conditions.

Fly ash samples were collected daily from both ESPs front and back hoppers. One-liter containers were collected daily and 5-gallon samples collected on designated days during each test condition. One-liter coal samples were collected daily from all four coal feeders. Standard analyses were performed on the coal samples. Ash was analyzed for mercury, LOI and chlorine.

A complete set of Ontario-Hydro sample runs were conducted by TRC Environmental Corporation for both of the injection concentrations. Apogee Scientific sampled with their extractive monitors at four different locations on one-half of Unit 1 gas flow. Data were collected continuously during all test periods. In particular, data were taken simultaneously with each of the Ontario Hydro sample runs. Preliminary results from the S-CEMs indicate at least 90% mercury removal at both injection concentrations during the operating conditions at that time.

During the sorbent injection testing, coal feeder samples were taken. Table 3 gives selected properties of the coals burned during the sorbent injection testing described here and in Reference 4.

At Brayton Point, ash samples were taken from both the first (Old) ESP and the second (New) ESP. There were not large differences between the samples from the two ESPs. Ash from the New ESP had somewhat higher Hg, Cl and LOI, but this did not represent a consistent difference between the Old and New ESPs.

Table 3. Fuel characteristics during long-term sorbent injection tests

	Brayton	Gaston	Pleasant Prairie
Rank	Bituminous	Bituminous	PRB
Sulfur, wt%	0.68	1.24	0.32
Ash, wt%	10.76	14.78	5.10
Moisture, wt%	4.65	6.85	30.69
HHV, Btu/lb	12,780	11,902	8,385
Hg, µg/g	0.065	0.136	0.109
Cl, µg/g	1475.4	169.0	8.1

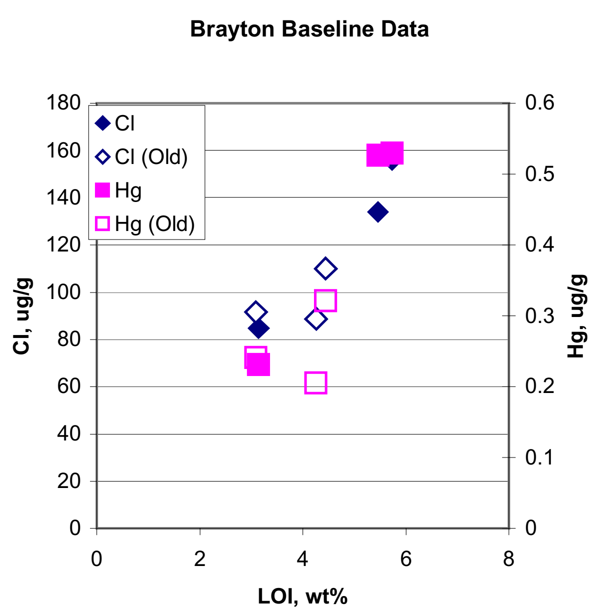

Figure 1. Hg and Cl in ash as a function of LOI for Brayton baseline (no sorbent) tests.

The amount of LOI in the ash appears to correlate with the mercury or chlorine contents of the ash for the New ESP ash; the correlation does not appear as strong for the Old ESP ash (Figure 1), but it is difficult to draw conclusions from so few samples. Unburned carbon in the ash may adsorb both mercury and chlorine, although this does not say anything about the nature of the adsorbed species or whether chlorine affects mercury adsorption on the ash.

Since PAC was injected after the Old ESP in the long-term sorbent injection tests, there should not be any impact of PAC on the ash properties of the Old ESP samples. Neither the LOI nor the mercury content of the Old ESP ash differ significantly between the baseline and long term samples.

The New ESP ash samples from the long-term tests contain activated carbon. As shown in Figure 2, there is a predictable increase in mercury with LOI. The chlorine content of the ash also increases with increasing LOI (that is, with PAC injection).

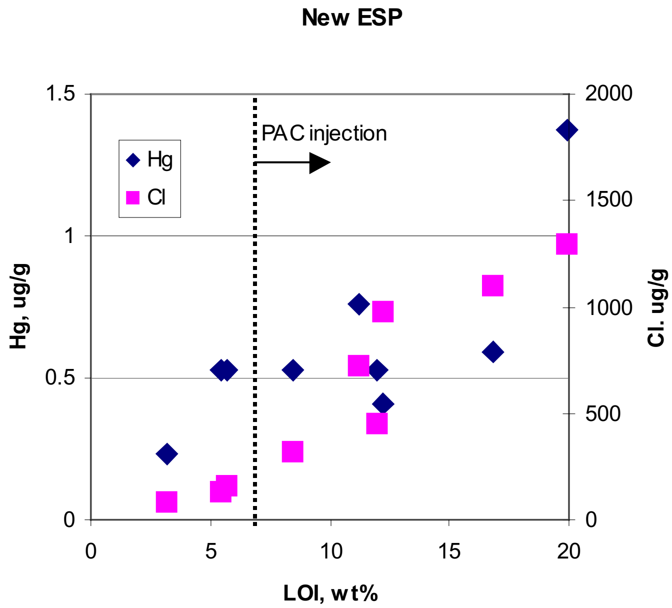

Figure 2. Mercury and chlorine as a function of LOI for New ESP ash samples (with and without sorbent injection).

Leaching Protocol

Many standard leaching procedures exist. The procedure used most often is the toxicity characteristic leaching procedure (TCLP). The method was designed to simulate leaching in an unlined, sanitary landfill, based on a co-disposal scenario of 95% municipal waste and 5% industrial waste. The method is an agitated extraction test using leaching fluid that is a function of the alkalinity of the phase of the waste. Typically an acetic acid solution having a pH of 2.88 is used. Details of the procedure can be found in Reference 5.

The synthetic ground water leaching procedure (SGLP) was developed at the University of North Dakota Energy and Environmental Research Center (EERC) and was designed to simulate the leaching of CUBs under important environmental conditions. It was initially used to characterize highly alkaline CUBs, primarily fly ash produced from the combustion of low rank coals. The procedure was modeled after the TCLP, but allowing for disposal conditions other than those of a sanitary landfill. Deionized water is used as the leaching solution instead of the acidic solutions used in the TCLP. The SGLP was designed primarily for use with materials such as low-rank coal ash that undergo hydration reactions upon contact with water. Test conditions are end-over-end agitation, a 20:1 liquid to solid ratio and a thirteen-hour equilibration time. Details of the procedure can be found in Reference 6.

RESULTS AND DISCUSSION

Leaching Results

Samples from Brayton Point, Gaston and Pleasant Prairie were leached at EERC using the standard TCLP procedure and also the synthetic groundwater leaching procedure (SGLP). Detectable amounts of mercury were leached from most of the Brayton Point samples, in the range of 0.01 to 0.07 µg/L (or ppbw). For the previously reported results from Gaston and Pleasant Praire, the amounts of Hg in the leachate were below the detection limit of 0.01 µg/L, with one exception.

Note that the primary drinking water standard specifies 2 ppbw for Hg via TCLP analysis. Thus, the amounts of mercury leached from these samples are about 100 times lower than the primary drinking water standard.

At Brayton Point, where ash was tested for mercury leaching with and without injection of PAC, there is no clear difference between the Old ESP and New ESP, nor between the baseline and long-term New ESP samples. Thus, PAC injection does not seem to have increased the amount of mercury leached from the ash.

Table 4. Leaching results

		Injection Rate	**Hg in**	**(µg/L)**
Plant	**Location**	**lb/MMacf**	**TCLP**	**SGLP**
Brayton	New ESP	0	< 0.010	0.01
Brayton	Old ESP*	0	0.02	0.05
Brayton	New ESP	10	0.07	0.03
Brayton	Old ESP*	10	0.03	0.01
Brayton	New ESP*	20	< 0.010	0.01
Brayton	Old ESP	20	0.02	0.02
Gaston	COHPAC B-Side	1.5	0.01	<0.01
Gaston	COHPAC B-Side	1.5		<0.01
Gaston	COHPAC B-Side	1.5	<0.01	<0.01
Prairie	ESP Hopper Composite	10	<0.01	<0.01
Prairie	ESP Hopper Composite	10	<0.01	<0.01
Prairie	ESP Hopper Composite	10	<0.01	

*Note: Sorbent injected downstream of the Old ESP

CONCLUSIONS

The three coal-fired power plants represented in this study had very different coal compositions and operating conditions, although the same powdered activated carbon was used at all three sites. The Brayton and Gaston samples (the product of a bituminous coal) had high LOI and mercury contents because most of the ash was removed upstream of the sorbent injection location. Thus these samples had a relatively high proportion of sorbent. The Pleasant Prairie sample (the product of a sub-bituminous coal) had a low LOI and mercury content. Sorbent was injected upstream of an ESP and was combined with the full ash stream. The LOI and mercury content were much lower than the other samples.

Little or no detectable Hg was leached by the TCLP or SGLP procedures for any of the ash samples. The amounts of mercury leached from these samples were about 100 times lower than the primary drinking water standard. At Brayton Point, where ash was tested for mercury leaching with and without injection of PAC, PAC injection did not seem to have increased the amount of mercury leached from the ash.

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