

## TRACE EMISSIONS FROM COAL COMBUSTION: MEASUREMENT AND CONTROL

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### INTRODUCTION

Combustion of coal is a potential source of emissions of many trace elements and organic compounds to the atmosphere. It is important that emissions of potentially toxic air pollutants from sources such as coal combustion are measured and, if necessary, controlled in order to limit any environmental effects. Increasing concern about the effects of trace pollutants in the environment may lead to the introduction of emission standards for some of these species. If such emission standards are adopted they must be supported by commercially available equipment which can measure and monitor the emissions with enough accuracy to ensure compliance.

Efficient coal combustion is not a significant source of emissions of organic compounds and therefore these compounds are not discussed further here. However, since there is increasing concern over emissions of mercury from coal combustion, specific attention will be paid to this particular trace element.

Several reviews have been published by IEA Coal Research on emissions from coal combustion. These include the halogens (Sloss, 1992), trace elements (Clarke and Sloss, 1992), organic compounds (Sloss and Smith, 1993), and mercury (Sloss, 1995). A complementary report has also been published on sampling and analysis of emissions of these compounds from coal-fired power station stacks (Sloss and Gardner, 1994). This paper draws together the conclusions from these reports.

### EMISSIONS OF POTENTIAL AIR TOXICS

Various estimates have been published which attempt to evaluate coal combustion as a source of potential air toxic emissions. Data from Nriagu and Pacyna (1988) indicate the importance of coal as a source of some trace elements on a global scale. For example, coal combustion may be responsible up to 21% of Sb emissions, around 18% of Ni and Se emissions and 15% of Cr emissions. Emissions of Cu, Sn, Tl and Zn from coal combustion are also thought to contribute between 5 and 20% of global emissions of these elements.

Estimates from the early 1980s (Pacyna and others, 1993) indicate that coal combustion may be responsible for up to 25% of total global mercury emissions to the atmosphere. There are a few more recent estimates from some countries in the 1990s, for example, coal's contribution to mercury emissions from human activities is 23% in Finland, 27% in the former FRG, about 10% in the Netherlands, 45% in the UK, and 16% in the USA (Sloss, 1995).

Estimation of global and regional budgets is difficult. Emission factors commonly based on a relatively small amount of actual measured data. The wide variation in the composition of coals, in combustion conditions, and in pollution control equipment need to be taken into account when estimating emission factors. Furthermore, many of the techniques used for the measurement of emissions of trace species, and thus for the estimation of emission factors, are still under development and are known to have serious limitations. Estimates for global and even regional emissions of trace species from most sources can therefore be considered as no more than educated guesses.

### LEGISLATION

Concern over the emissions of potential air toxics from all sources and their possible effects in the environment has led to the introduction of legislative controls in several countries. Legislation specific to the emission of individual trace elements has been specified in Austria, Germany and certain states in Australia (AHC, 1992; Maier, 1990; Nilsson, 1991). This legislation is summarised in Table 1.

The 1990 US Clean Air Act requires the evaluation of emissions of several trace elements with a view to the possible introduction of relevant legislation in the future (Chow and others, 1990). Legislation for power stations is also being considered in Canada and the Netherlands. Although no specific emission standards apply in Sweden, electrical utilities are required to fit best available technologies. These include particulate controls and FGD processes and therefore result in a substantial reduction in the emissions of most trace elements (Clarke and Sloss, 1992).

## MEASUREMENT OF EMISSIONS

Sampling and analysis techniques for the measurement of trace species at the concentrations emitted from coal-fired power plants are still under development. Countries such as Germany, Japan and the UK have published guidelines for sampling and analysis of some trace pollutants. In the USA, the methods are specified by law within the Code of Federal Regulations. However, many of these methods are known to have inherent problems and are still subject to review.

The majority of sampling techniques are based, initially, on the separation of gases from particles on filters, in cyclones or in cascade impactors. Each of these techniques are known to have problems such as clogging and irreversible adsorption (Masterson and Barnert-Wiemer, 1987).

Gaseous species may be analysed directly by analytical instruments, but such instruments are rarely portable. Samples are more commonly transported to the laboratory for analysis. Some vapour-phase species may be reduced to liquid form simply by condensation in cooled chambers. Other species are captured in a series of impinger bottles containing solutions which selectively solubilise the species of interest. Activated carbon can be used to capture volatile trace metals such as mercury. Although solid sorbents have the advantage of allowing volatile species to be trapped and transported in a stable form, some have problems with background contamination and decomposition products (Sloss and Gardner, 1994).

The development of sampling and analysis techniques for mercury is proving to be a particularly challenging problem. The speciation of mercury, as oxidised forms such as mercury chloride, or in the elemental form, determines its behaviour in pollution control equipment and in the environment. However, mercury emissions cannot be speciated with the standard methods currently available for sampling emissions of trace metals. New techniques based on sorbents such as activated carbon appear to be the most promising methods (Sloss and Gardner, 1995; Sloss, 1995).

Sampling and analysis techniques are not at the stage where they are accurate enough to produce a single value which would be considered representative. From what is already known of the behaviour of potential air toxics in coal-fired systems, their emissions are never constant, they vary with coal type, combustion conditions, pollution control systems and even depend on the concentration of other pollutants within the flue gas with which they may react.

Continuous emissions monitors produce virtually real-time data, avoiding transport and handling errors, and providing true representation of potential air toxic concentrations over time. However, continuous emissions monitors are not currently available for air toxics. Several systems, such as those based on FTIR, are under development (Sloss and Gardner, 1994).

## EFFECTS OF EMISSION CONTROL TECHNOLOGIES

Currently there are no widely available control technologies designed specifically for the removal of trace elements from coal-fired power stations. However, technologies for the removal of particulates, such as electrostatic precipitators (ESP) and fabric filters, and control technologies for SO<sub>x</sub> and NO<sub>x</sub>, may affect emissions of potential air toxics.

Particulate control systems capture any pollutants which are associated with the particles retained. The capture of individual air toxics thus depends upon their volatility. Most trace elements are not especially volatile and are captured efficiently by particulate controls, for example only 2% of Cd in the flue gas passes ESP uncaptured. However, B and Se are slightly more volatile and between 20 and 30% of these elements may pass uncaptured. Unless lime or a similar sorbent has been used in the boiler, virtually all the halogen gases pass through particulate controls (Clarke and Sloss, 1992; Sloss, 1992).

The capture of mercury by particulate control devices depends upon its speciation. Mercury in the particulate form (<5%) is captured efficiently. Oxidised mercury may also be associated with fly ash or can adsorb onto particles already associated with baghouses. Average mercury capture efficiencies in ESP and baghouses are around 35-40%. Since mercury speciation is temperature dependant, the capture of mercury in particulate control devices can be optimised by keeping temperatures as low as possible (<150°C) to increase the proportion of mercury in the oxidised form (Sloss, 1995).

Wet and dry flue gas desulphurisation (FGD) systems, required in many countries to remove SO<sub>x</sub>, incidentally remove some amounts of potential air toxics. For example, Figure 1 shows the average removal of volatile elements in wet-lime FGD systems in the Netherlands (Clarke and Sloss, 1992). Some FGD systems remove around 50% of the remaining B and Se in the flue gas. Reductions of over 90% for all the halogens have been achieved in such systems (Clarke and Sloss, 1992; Sloss, 1992).

Wet and dry FGD systems have wide ranges of efficiency for mercury capture from 20% up to 90%. Mercury capture in FGD depends upon its speciation. Up to 95% of oxidised mercury can be removed in spray dry scrubbers whereas elemental mercury passes through uncaptured. Capture of mercury in FGD systems can be maximised by increasing the proportion of oxidised mercury in the flue gas (Sloss, 1995).

Combustion modifications for NO<sub>x</sub> control may lead to increased concentrations of unburned carbon in flue gases. It is not clear to what extent this unburnt carbon may affect the distribution and behaviour of potential air toxics. NO<sub>x</sub> control systems do not appear to reduce or increase trace or minor element emissions. However, high dust SCR systems can oxidise up to 95% of the mercury in flue gas, enhancing the capture of mercury in FGD systems downstream (Sloss, 1995).

### SPECIFIC CONTROL OF POTENTIAL AIR TOXICS

There is currently no requirement for the specific removal or abatement of potential air toxics from the flue gas of coal-fired power stations. However, in the future, legislation on air toxics emissions is likely to become more stringent. Some specific technologies for the capture of potential air toxics are already under development and some are commercially available for use on waste incineration units. Concentrations of the more harmful air toxics, such as mercury, may be several orders of magnitude higher in flue gas emissions from waste incinerators than from coal-fired power plants. Work has already been started in several countries to reduce emissions of air toxics from waste incinerators. Some of the technologies used in waste incinerators may be applicable, with modification, to coal-fired units (Clarke and Sloss, 1992).

Sorbents which are available for the removal of heavy metals, such as mercury, from flue gases, include those based on activated carbon, zeolites, siliceous materials, alumina, and calcium compounds. Up to 100% of oxidised mercury and 60% of elemental mercury in flue gas may be captured with activated carbon. Sulphur impregnated activated carbons can capture over 90% of total mercury emissions and iodine impregnated activated carbons are reported to capture up to 100%. Figure 2 shows mercury removal by different types of activated carbon injected upstream of a spray dry scrubber and a baghouse. The use of some sorbents in coal-fired power stations may be limited due to low operating temperatures, harmful secondary effects and the high cost of some sorbents (Mojtahedi and Mroueh, 1989).

### CONCLUSIONS

Coal combustion is an important source of some trace elements to the environment.

Existing legislation for the control of particulate emissions effectively controls emissions of the majority of trace elements. Flue gas desulphurisation technologies may efficiently capture many of the remaining vapour phase pollutants. Over 90% of the halogens and 40-50% of the B and Se may be captured by this means.

The speciation of mercury determines the emissions and effects of mercury from coal combustion. Particulate control devices may capture up to 40% of mercury emissions, and FGD systems commonly up to 70%. These efficiencies may be enhanced by maximising the proportion of mercury present in the flue gas in the oxidised state. More research is required in order to understand mercury speciation and to use this information to determine the most appropriate control strategies.

Emission standards are becoming more stringent and, in the future, it is likely that emission limits for air toxics will be introduced more widely for sources such as coal-fired power plants. However, emission standards are worthless if the emission concentrations they specify cannot be measured accurately and on a regular basis by operators and regulatory authorities.

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**Table 1 National legislation for air toxic emissions from coal-fired power plants**

COUNTRY	AIR TOXIC	LIMIT (mg/m <sup>3</sup> )
Australia	As, Cd, Hg, Ni, Pb, Sb, V	Varies between States and Territories
Austria	Cr, Pb, Zn As, Co, Ni Cd and Hg	2.0 (total of all three) 0.5 (total of all three) 0.05 (total separately)
Germany	<b>Inorganic dust</b>	
Category I	Cd, Hg, Tl	0.2 (total of all three)
Category II	As, Co, Ni, Se, Te	1.0 (total of all three)
Category III	Cr, Cu, Mn, Pb, Pd, Pt, Sb, Sn, V	5.0 (total of all three)
<b>Organic substances</b>		
Category I		20 (total)
Category II		100 (total)
Category III		150 (total)
<b>Carcinogenic substances</b>		
Category I	(including BaP)	0.1 (total)
Category II	As, Co etc	1.0 (total)
Category III	hydrazine etc	5.0 (total)
<b>Planned legislation</b>	<b>Canada, the Netherlands, the USA</b>	

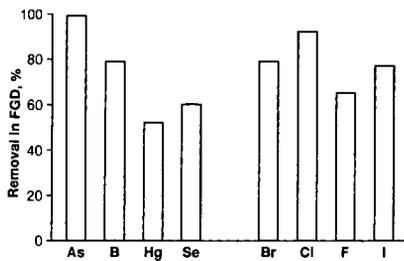


Figure 1 Average removal of volatile elements in wet-lime FGD systems in the Netherlands

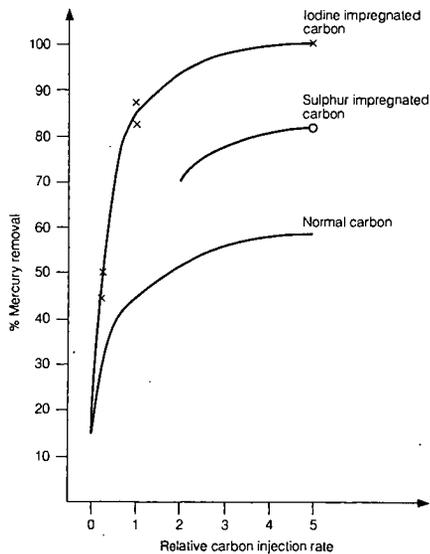


Figure 2 Influence of active carbon type on mercury removal

# TRACE METAL CONTENT OF COAL AND ASH AS DETERMINED USING SCANNING ELECTRON MICROSCOPY WITH WAVELENGTH-DISPERSIVE SPECTROMETRY

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## ABSTRACT

Scanning electron microscopy with wavelength-dispersive spectrometry has been used to measure trace metals in coal and ash. Hg, As, Ni, and Se have been detected in individual pyrite grains in Illinois #6 coal at levels up to 2680 ppm, 410 ppm, 320 ppm, and 880 ppm, respectively. These elements were present in fewer than half the grains analyzed. Cr has been detected at up to 950 ppm in half of clay mineral grains analyzed in Illinois #6 coal. The same trace metals were detected in pyrite and clay grains from Pittsburgh #8 coal.

Ash samples show a similarly heterogeneous distribution of trace metals. Hg has been detected at up to 700 ppm in 24% of aluminosilicate particles analyzed in ash from Absaloka coal, a subbituminous Montana fuel.

These data confirm that coal cleaning processes which remove pyrite are likely to be suitable for trace metal emissions control. In addition, back-end control devices which target specific types of ash particles may be helpful for control of air toxics emissions.

## INTRODUCTION

Scanning electron microscopy (SEM) is one of the analytical tools available for determining the abundance of trace metals in coal and ash samples. This information is important in predicting and evaluating the behavior of these substances in combustion processes, a topic which is of increased importance in recent years as stricter regulation of trace metal emissions from coal-fired power plants is under consideration. Although scanning electron microscopy is not routinely applied to detection of trace quantities of metals, the use of a wavelength-dispersive spectrometer attachment makes such analyses possible.

Scanning electron microscope techniques differ from traditional trace metal analysis techniques in that SEM provides information with high spatial resolution, compared with the bulk compositions obtained through atomic absorption and other widely-used methods. High-spatial-resolution data concerning trace metal distribution in coal and ash is important for two reasons. First, ash behavior in fossil fuel combustion systems is best understood in terms of the behavior of individual particles. Knowledge of the bulk composition of an ash deposit frequently is not sufficient in determining what caused that deposit to have its particular physical characteristics such as size, friability, crystallinity, and density. Information concerning the chemical and mineralogical composition of individual ash particles can provide insight into how particles interact and transform to produce a deposit. Methods for obtaining this information using SEM with energy-dispersive x-ray spectrometry (EDS) have become widely available (1-3). The SEM-EDS technique provides data for major elements only, with detection limits of approximately 0.1 wt%. In order to obtain similar information concerning trace elements, SEM with wavelength-dispersive spectrometry (SEM-WDS) must be used. The SEM-WDS technique has detection limits of approximately 100 ppm (0.01 wt%) for most metals. Although it is time-consuming, the SEM-WDS method is valuable because it provides a means for acquiring single-particle trace element data for coal and ash particles, information that is essential in understanding how best to control the emission of trace elements from combustion sources. Trace metal emissions from coal-fired power plants may be subject to increased regulation; thus knowledge of how best to control them is vital.

A second reason for investigating the distribution of trace metals at high spatial resolution is that this information is helpful in understanding potential health effects of these substances. Trace metals can occur as coatings on airborne particles, and frequently are found in particles in the respirable size range (4,5); in these instances, the toxicity of the trace metals is greater than if those elements were distributed evenly throughout a particle, or were present in larger, non-respirable particles. For the purposes of assessing potential health impacts of trace metal emissions, it is important to know whether these elements are distributed homogeneously throughout an ash sample, or whether their distribution varies on an individual-particle basis.

## METHODS

Samples were mounted in epoxy, cross-sectioned, polished, and coated with carbon to improve conductivity. Analyses were conducted on a JEOL 35C scanning electron microscope equipped with two JEOL wavelength-dispersive spectrometers with xenon-filled proportional counters, and a Noran Instruments energy-dispersive spectrometer. The analytical capabilities of the microscope are controlled by a Noran Instruments Voyager 2 computer system, which can coordinate simultaneous EDS and WDS.

The microscope was operated at an accelerating voltage of 25 kV with a beam current of 8 nA. Wavelength-dispersive spectral peaks were counted for 100 s; the total energy-dispersive live time per spectrum was 3 s. Certified standards were used for calibration. The data were subjected to ZAF corrections following collection.

Individual coal mineral grains and ash particles as small as 5  $\mu\text{m}$  in diameter were analyzed. Under the more commonly used SEM-EDS analysis conditions, it is possible to analyze volumes as little as 1  $\mu\text{m}$  in diameter, but the more intensely energetic conditions required of SEM-WDS make it impossible to analyze these smaller quantities without exciting the surrounding area (6).

## RESULTS AND DISCUSSION

Coal and ash samples were analyzed for trace metal content using SEM-WDS. EDS was also used to determine the major element composition of each coal mineral grain or ash particle.

**Ash Analyses.** A sample of Absaloka ash was inspected for Hg content using SEM-WDS. Iodated activated carbon sorbent had been added to this Montana subbituminous coal. Ash particles analyzed ranged from 5 to 20  $\mu\text{m}$  in diameter. As shown in Table 1, Hg was detected in six particles (21% of the total analyzed), in amounts ranging from 100 to 700 ppm (0.01 to 0.07 wt%). These Hg-bearing particles are mostly Ca- and Al-bearing silicates, with some S present.

Results for the 22 non-Hg-bearing particles analyzed in the same ash sample are shown in Table 2. The major element composition of these particles is similar to that of the Hg-bearing particles listed in Table 1, suggesting that the occurrence of Hg in these ash particles is not related to any compositional parameter.

Another sample of Absaloka ash, produced from coal to which a non-iodated activated carbon sorbent had been added, did not have any detectable Hg in individual particles. The ash particles in this sample were predominantly Ca- and Al-bearing silicates, as in the sample produced using iodated carbon sorbent, but with little S present.

**Coal Analyses.** In a sample of Illinois #6 bituminous coal, individual mineral grains were selected for trace metal analysis. Table 3 shows results for pyrite grains in Illinois #6 coal. Hg, As, Ni, and Se are present in individual grains at levels up to 2680 ppm, 410 ppm, 320 ppm, and 880 ppm, respectively. These trace metals were present in fewer than half of the pyrite grains analyzed. Clay mineral grains from the Illinois #6 coal sample were examined for Cr content; this element was detected at up to 950 ppm in half of the grains analyzed. These results show the heterogeneous distribution of these trace metals in coal mineral grains.

Similar results are evident for Pittsburgh #8 bituminous coal. Table 4 shows the distribution of trace metals in pyrite grains. As and Hg values for individual grains range up to close to 3000 ppm; Cd was detected in amounts less than 100 ppm only; Ni ranges up to approximately 1300 ppm; and Se values are as high as almost 2000 ppm. In clay mineral grains from Pittsburgh #8 coal, Cr ranges up to 377 ppm in 27 individual grains, including six grains with Cr not detected. The average value for Cr in the Pittsburgh #8 clay mineral grains is 75 ppm.

## CONCLUSIONS

This study has shown the varied distribution of trace metals in coal and ash samples. The relative abundance of Hg and other trace metals in pyrite grains suggests the effectiveness of coal-cleaning processes in helping to reduce toxic emissions from power plants. Further investigation of the distribution of trace elements in ash particles of different compositions may lead to the development of emissions control devices tailored for removal of specific metals.

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Table 1. Composition of Hg-Bearing Particles in Absaloka Ash  
(With Iodated Activated Carbon Sorbent Added)

Particle number	Normalized composition (wt%, C- and O-free basis)									
	Hg	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
1	0.04	0.0	11.0	25.4	10.1	1.8	0.0	49.0	1.7	1.1
2	0.02	0.0	0.0	10.7	12.0	0.0	0.5	1.0	0.0	76.2
3	0.01	0.0	7.4	14.7	25.6	0.0	0.0	52.4	0.0	0.0
4	0.03	0.0	4.2	26.7	28.1	4.3	0.0	36.7	0.0	0.0
5	0.03	0.0	10.5	17.0	12.5	6.5	0.0	52.0	0.8	0.7
6	0.07	0.0	6.1	11.9	37.8	0.0	0.0	44.1	0.0	0.0
Avg.	0.03	0.0	6.5	17.7	21.0	2.1	0.1	39.2	0.4	13.0

Table 2. Composition of Non-Hg-Bearing Particles in Absaloka Ash  
(With Iodated Activated Carbon Sorbent Added)

Particle number	Normalized composition (wt%, C- and O-free basis)								
	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
1	0.0	0.0	10.6	26.7	0.0	0.0	62.7	0.0	0.0
2	0.0	0.0	20.4	41.9	0.0	0.0	37.8	0.0	0.0
3	0.0	10.5	9.4	19.3	0.0	0.0	58.5	1.1	1.2
4	2.2	3.4	19.0	42.6	0.4	0.7	29.5	1.3	0.9
5	0.0	6.8	12.4	27.7	1.8	0.0	49.6	1.8	0.0
6	0.0	5.7	20.7	21.8	2.6	0.0	46.0	0.7	2.5
7	1.7	1.6	27.6	42.2	0.0	1.8	23.1	1.0	1.0
8	4.0	2.9	18.7	40.7	0.0	0.8	21.4	0.0	11.4
9	0.0	4.3	13.5	15.0	0.0	0.0	64.9	1.6	0.8
10	0.0	1.2	22.3	31.6	8.2	2.6	29.4	0.0	4.7
11	0.0	6.2	20.6	12.1	10.6	0.0	50.4	0.0	0.0
12	0.0	4.2	18.9	37.9	0.0	0.0	35.5	1.7	1.9
13	0.0	0.0	33.9	57.2	0.0	1.6	5.9	1.5	0.0
14	0.0	0.0	31.9	59.8	0.0	1.4	4.7	1.0	1.2
15	0.0	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0
16	0.0	7.5	27.8	18.3	0.0	0.0	43.3	1.6	1.5
17	0.0	6.2	14.9	29.5	2.3	1.2	41.5	2.6	1.8
18	0.0	6.9	14.8	17.3	4.5	0.0	54.4	0.0	2.1
19	0.0	10.1	18.2	17.2	6.4	0.0	48.1	0.0	0.0
20	4.4	2.9	21.7	43.1	2.2	1.3	22.0	2.4	0.0
21	0.0	9.7	11.1	10.3	7.6	0.0	61.4	0.0	0.0
22	0.0	11.7	14.7	10.1	0.0	0.0	63.6	0.0	0.0
Avg.	0.6	4.6	18.3	32.8	2.1	0.5	38.8	0.8	1.4

Table 3. Trace Element Content of Pyrite Grains in Illinois #6 Coal

Element	Values in ppm	
	Mean	Range
As	310	210-410
Cd	ND	---
Hg	2680*	2680*
Ni	210	140-320
Se	760	530-880

ND = not detected

\* Hg values are for a single pyrite grain

Table 4. Trace Element Content of Pyrite Grains in Pittsburgh #8 Coal

Particle number	Values in ppm				
	As	Cd	Hg	Ni	Se
1	273	ND	2660	459	ND
2	ND	ND	103	797	ND
3	ND	ND	ND	1330	1810
4	2030	77	1240	149	730
5	123	ND	1870	285	13
6	532	ND	974	ND	1220
7	2900	13	ND	ND	1280
8	ND	ND	ND	90	1950
9	575	ND	1040	ND	1120
10	146	ND	ND	ND	1650

ND = not detected

# LABORATORY LEACHING BEHAVIOR OF ENVIRONMENTALLY SENSITIVE TRACE ELEMENTS FROM FLY ASH AND BOTTOM ASH SAMPLES

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Keywords: Fly ash, Bottom ash, Trace elements

## INTRODUCTION

The distribution of trace elements in coal combustion residues such as fly ash and bottom ash have received considerable attention.<sup>1,2</sup> Several studies of fly ash have concentrated on relationships of trace elements to fly ash particle size<sup>3,4,5</sup>. Studies related to etching<sup>6</sup>, mineralogical transformation during combustion<sup>7</sup> and leaching have also been reported. Dudas<sup>8</sup> conducted long-term leachability studies. Grisafe et al.<sup>9</sup> examined leachability of fly ash as a source of Se contamination. Fernandez-Turiel et al.<sup>10</sup> have looked at the mobility of heavy metals from coal fly ash. The objectives of these studies were primarily to understand potential problems associated with the storage or disposal. To meet these objectives, the solvents used in these studies were chosen to emulate conditions in nature.

The leaching study presented in this paper differs from previous leaching studies because the primary objective was to obtain information on modes of occurrence of trace elements in the fly ash and bottom ash and provide data which could be compared to previous studies on the leaching behavior on whole coal samples<sup>11</sup>. Although preliminary data for 29 elements in the fly ash and bottom ash are available at this time, only results for environmentally sensitive trace elements and other related elements will be discussed in this paper. These elements include those identified in 1990 Clean Air Act Amendments: Co, Cr, Ni, Sb, and radionuclides (Th and U). Fe was also studied because of its importance to coal cleaning and S removal, and Zn because of its relationship to Cd.

## EXPERIMENTAL

The samples were collected from an electric utility power plant having boilers burning high sulfur (3.3 weight percent total sulfur) and low sulfur (0.9 weight percent total sulfur) coal. Approximately 10 grams from each of two fly ash samples and two corresponding bottom ash samples were subjected to sequential leaching. In this procedure each sample was automatically shaken for 18 hours, centrifuged, and the leachate filtered. The samples were first leached with 1N ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ). A representative 0.5 gram split of each of the leached samples was reserved for analysis by instrumental neutron activation analysis. This procedure was repeated using 2N hydrochloric acid (HCl), concentrated (48 to 51 %) hydrofluoric acid (HF) and 1.5 N nitric acid ( $\text{HNO}_3$ ) and a representative 0.5 gram split was obtained for INAA from the material leached by each solvent.

All resulting splits and representative samples of the original material were irradiated for 8 hours at a neutron flux of about  $2 \times 10^{12}$  neutrons/cm<sup>2</sup>sec<sup>-1</sup> using instrumental neutron activation analysis (INAA) procedures similar to those of Palmer.<sup>12</sup> The data was calculated using the SPECTRA program.<sup>13</sup> The mass of each of the splits used to calculate percent material leached and the concentrations for each of the splits determined by INAA were used to calculate the percent of each element leached by each solvent.

## RESULTS AND DISCUSSION

The proportion of an element leached by a specific solvent is an indicator of the elements' mode of occurrence. In contrast to coal, which is primarily an organic matrix not leachable to a significant extent by most inorganic solvents, the bottom ash and fly ash are mainly silicates which are leachable to a large degree by inorganic solvents, particularly by HF. In addition, because of the high temperature of combustion ( $\sim 1500$  °C) phases present in the coal such as clays, carbonates, and sulfides have also been transformed to silicates and oxides. Table 1 shows the percent of the material leached by each of the solvents used in this study. The total amount of material leached ranged from 78 to 99 percent, with 97 percent or more leached from the fly ashes. Seventy to seventy-nine percent of all samples was leached by HF. Clearly a large percentage of the fly ash and bottom ash are in the silicate phases. Generally less than 5 percent of the fly ash and bottom ash is ammonium acetate soluble (probably water soluble as well). Less than 5 percent of the bottom ash and fly ash is HCl soluble. About 5 to 15 percent of the material was leached by nitric acid. Because sulfides are not likely to be present in the fly ash or the bottom ash (as discussed above) it is not clear which mineral forms were leached by nitric acid. It is possible that species soluble in the nitric acid, unleached by HF, and encased in the silicates during combustion could have been leached only after the destruction of the silicates. It should be noted that the fly ash is generally more soluble in the solvents used in this study than is the bottom ash. This trend may be explained in part by the presence of a larger proportion of unburned carbon in the bottom ash than the fly ash. Preliminary results from CHN analyses and ash determinations showed that up to 18 percent unburned carbon was found in the bottom ash in BA3.

The percentage of some environmentally important elements leached differed from that of the bulk material indicating that their modes of occurrence were clearly different from those of the bulk material. More than 80 percent of the As in the fly ash samples and about 45 percent of the As in one bottom ash sample were leached with HCl. Davidson et al.<sup>3</sup> suggest that As, as well as some other elements, may be volatilized during combustion and recondensed on the surface of the particles as they cool in the stack. Turner<sup>14</sup> and EPRI<sup>15</sup> suggest that As may exist as a metal arsenate, such as  $\text{Ca}_3(\text{AsO}_4)_2$  or  $\text{Ba}_3(\text{AsO}_4)_2$ . These suggestions explain why As was leached to a large degree by HCl. The behavior of As in BA3 is different from the other bottom ash sample and from the fly ash samples. Condensation of volatile species such as As is unlikely to occur in bottom ash samples.

Significant quantities of Sb (Figure 2) are leached by HCl in the two fly ash samples; although the amounts are not as large as those for As. Results from a comparison of magnetic and non-magnetic fractions<sup>16</sup> show similarities in behavior between Sb and As. The results of this study however, suggest that Sb and As behave differently.

A few elements, such as U and Th, are leached only to a small degree (as little as 20 percent leached by all solvents). This behavior may be due to their association with minerals such as zircon which are inert and are not significantly altered by either combustion or leaching. Once again these elements are significantly more soluble in fly ash (especially FA1) than in the bottom ash, and U is more soluble than Th. The data for U in fly ash suggests that it may exist in several modes of occurrence because there is roughly equal leaching by HCl and HF in both fly ash samples and equal leaching by  $\text{HNO}_3$  in FA1. Figure 3 shows the percentage of these elements leached by each solvent.

Most of the other elements studied show leaching behavior similar to the bulk material. Figure 4 shows the percentage leached for Fe, Ni, Co, and Cr in the bottom ash and the fly ash. In all cases, the majority of these elements are leached by HF, which indicates that they are concentrated in the glassy or crystalline silicates. Most of these elements showed a small amount (<20 percent) of material leached by HCl. Any oxides present are probably locked in the matrix and not exposed until HF destroys the silicates.

Figure 5 shows the percent Zn leached (likely an indicator of Cd behavior). The leaching behavior of Zn is similar to the leaching behavior of the bulk material (Table 1). However, there is a significant fraction of Zn leached by HCl in sample FA3. In addition, about 20 percent Zn was leached by ammonium acetate in sample BA3.

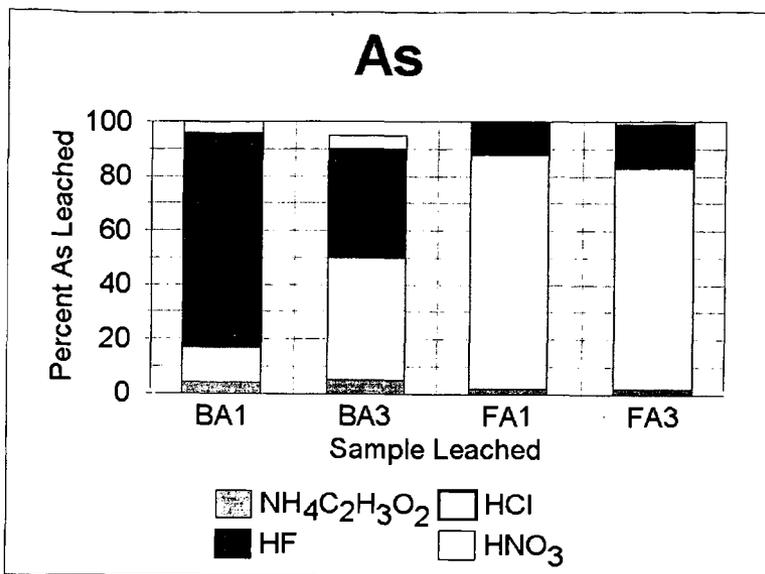
In summary, most, but not all, elements studied behave similarly to the bulk material and are probably associated with the glassy or silicate portions of the fly ash and bottom ash. Because As, U, Th and possibly Sb (in the fly ash) display behavior significantly different than that for the bulk sample, it can be inferred that they are associated with different minerals or chemical forms than the major elements. Other minor differences in the leaching behavior may indicate that small amounts of that element are associated with minor phases in the ash. Some of these minor phases may be material which has not been completely combusted.

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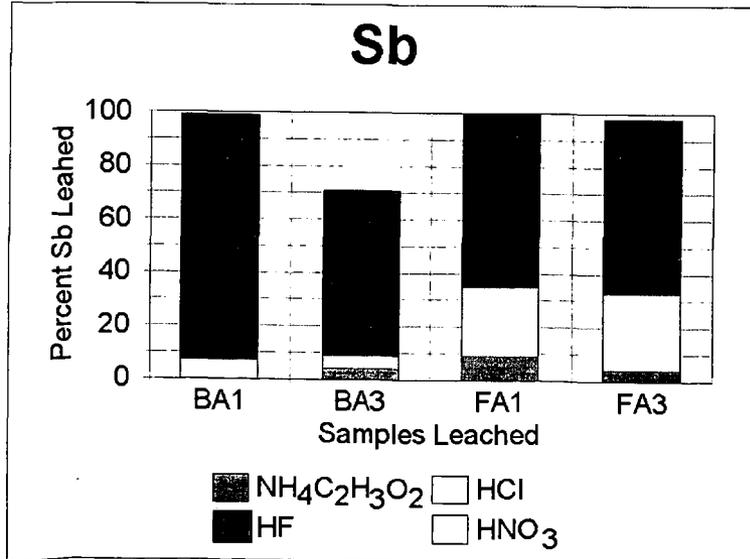
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**Table 1.** Weight percentage of material leached by solvents used in this study.

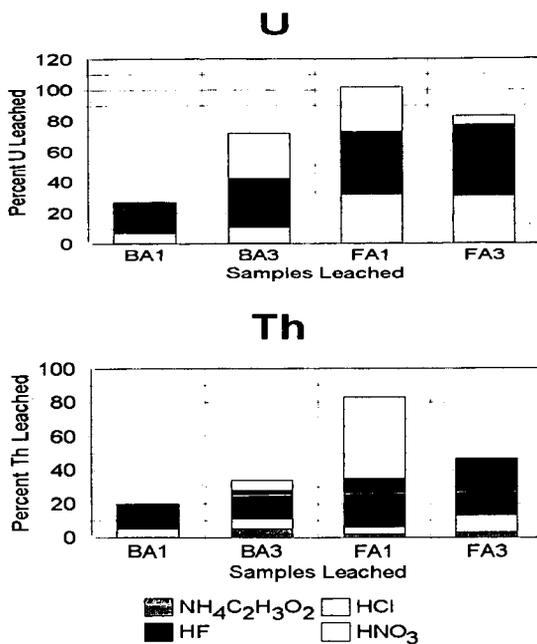
Solvent	BA1	BA3	FA1	FA3
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	1	1	5	3
HCl	2	1	5	3
HF	70	71	78	79
$\text{HNO}_3$	14	5	10	13
Total	86	78	99	97



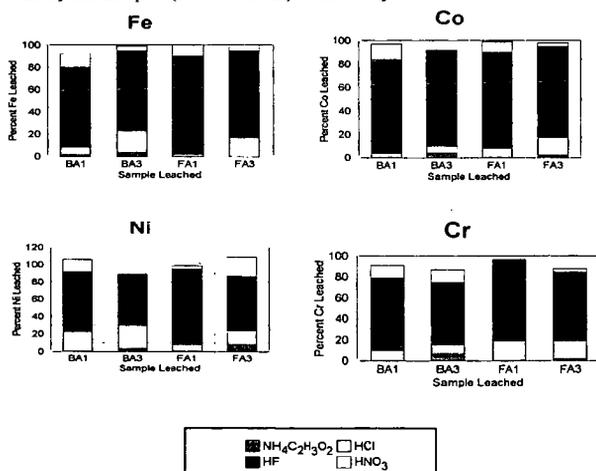
**Figure 1.** Percent As leached in bottom ash samples (BA1 and BA3) and fly ash samples (FA1 and FA3) by solvents used in this study.



**Figure 2.** Percent Sb leached in bottom ash samples (BA1 and BA3) and fly ash samples (FA1 and FA3) by solvents used in this study.



**Figure 3.** Percent U and Th leached in the bottom ash samples (BA1 and BA3) and the fly ash samples (FA1 and FA3) in this study.



**Figure 4** Percent Fe, Co, Ni and Cr leached in the two bottom ash samples and the two fly ash samples by the samples in this study.

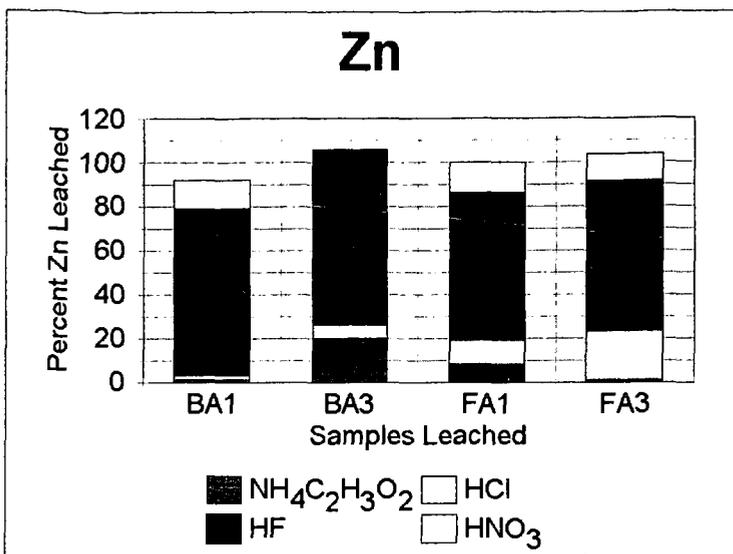


Figure 5. Percent Zn leached in the bottom ash (BA1 and BA3) and fly ash (FA1 and FA3) by solvents used in this study.

# DETERMINATION OF CHROMIUM OXIDATION STATES IN COAL COMBUSTION PRODUCTS BY XAFS SPECTROSCOPY

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**Keywords:** XAFS spectroscopy, chromium speciation, hazardous air pollutants.

## ABSTRACT

Chromium XAFS spectroscopy has been used to determine the relative amounts of Cr(VI) and Cr(III) in ash samples obtained from coal combustion. The method, which is based on the relative heights of the pre-edge peaks for the different Cr oxidation states in XANES spectra, can be used to speciate as little as 50 ppm of chromium in ash. The results indicate that the fraction of Cr(VI) oxidation state present in combustion ash from commercial combustion plants is typically at or close to the detection limit (approx. 3% of the total chromium). Such findings provide justification for a reappraisal of whether or not chromium should be considered a significant HAP in coal combustion.

## INTRODUCTION

Chromium is listed as one of eleven inorganic hazardous air pollutants (HAPs), the so-called "air-toxics", in Title III of the 1990 Amendments to the Clean Air Act (1), largely because of the well-known toxicological and carcinogenic properties of the hexavalent oxidation state of chromium (2). This oxidation state is virtually always found in nature and the environment in the form of chromate ( $\text{CrO}_4^{2-}$ ) or dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) oxoanions. The other common oxidation state of chromium, Cr(III), is generally of much less concern to human health, and may in fact be essential in small quantities to mammals. Hence, in assessing potential health hazards posed by chromium in industrial emissions and wastes, it is clearly important that the chromium oxidation state be identified and determined quantitatively.

The different oxidation states of chromium in solids or any other state of matter can be readily distinguished in chromium X-ray absorption fine structure (XAFS) spectra by the intensity of the pre-edge peak (3,4,5). The pre-edge feature is generally very weak (typically less than 0.05 times the edge step) for trivalent chromium in an octahedral crystal-field of oxygen anions, whereas for hexavalent chromium oxoanions, the pre-edge peak is usually almost as intense as the edge-step. In this paper, a method for determining the oxidation states of chromium directly in solids is developed based on this difference in pre-edge peak intensity in chromium K-edge XAFS spectra and then the method is applied to the determination of chromium oxidation states in fly-ash and other products of coal combustion. Owing to the huge tonnages of coal used for electricity generation worldwide, coal combustion is viewed as a major potential source of release of many inorganic HAPs, including chromium, to the environment (6).

## EXPERIMENTAL

### *Chromium K-edge XAFS spectroscopy:*

XAFS spectroscopy is a synchrotron-based technique that provides information about the local structure and bonding around the absorbing element in a material from analysis of the fine structure associated with one of the element's characteristic X-ray absorption edges (7). For this study, experimental measurements were made at the chromium K-edge at both the National Synchrotron Light Source at Brookhaven National Laboratory, New York, and at the Stanford Synchrotron Radiation Laboratory, Stanford University, CA. Similar experimental practices were used at both synchrotrons. To record the chromium K-edge XAFS spectra, the monochromator was stepped from about 100 eV below the edge to as much as 1,000 eV above the edge and the intensity of the monochromatic x-ray beam before and after absorption by the sample was measured as a function of energy. All spectra were calibrated with respect to the first inflection point in the absorption spectrum of a thin chromium metal foil. This calibration point, which occurs at 5,989 eV, defines the zero-point of energy in the XAFS spectra shown in Figure 1 and other figures in this paper. The absorption spectra were measured in three different ways depending on the concentration of chromium in the material under investigation. For concentrated samples (Cr > 10wt%), measurements were made in absorption geometry, in which the intensity of the X-ray beam after attenuation by the absorption process in the sample was compared to the incident X-ray intensity. These measurements were made with ion chambers. For more dilute samples with chromium contents less than 5 wt% but more than about 0.1 wt% (1000 ppm), the intensity of the fluorescent X-rays emitted by the sample in response to the absorption process was measured with a Lytle detector (8). Finally, for chromium in ash samples, in which the concentration of chromium is very dilute (typically between 50 and 500

ppm), measurements were made using a 13-element germanium detector that collected X-rays only in a electronically gated energy interval set for fluorescent chromium X-rays (9). For the fluorescent measurements, a vanadium filter was normally used in association with Soller slits to enhance the signal/noise ratio. Spectral scans of about 30 mins were sufficient for most samples, except those for which the chromium content was much less than 500 ppm. Depending on the actual chromium concentration of such dilute samples, up to 10 separate scans were accumulated and summed to give a single spectrum.

The spectra have been analyzed in a conventional manner that is well described in the literature (7). Basically, the spectra are split into two distinct regions: a near-edge region that includes the fine structure associated with the edge itself, and an extended fine-structure region that consists of the weak oscillatory structure that may persist to as much as 1,000 eV above the edge. These two regions give rise to the X-ray absorption near-edge structure (XANES) spectra and the extended X-ray absorption fine structure (EXAFS) spectra, respectively. The XANES spectrum is generally used as a "fingerprint" to identify the form or forms of the element in the material under investigation, whereas the EXAFS region can be mathematically manipulated to yield a "radial structure function" (RSF) from which the local structure around the absorbing element may be inferred. In this work, only the XANES spectra will be discussed further as the EXAFS region of the spectrum is not used to determine the chromium oxidation states.

#### Determinative Method:

A calibration method for the XANES pre-edge peak was developed by measuring the XANES spectra of carefully prepared mixtures of potassium chromate ( $K_2CrO_4$ ) and potassium chromium(III) alum sulfate ( $KCr(SO_4)_2 \cdot 12H_2O$ ). Except for different standards in the mixtures, the current method is similar that described by Bajt et al. (4). The mixtures were prepared so that Cr(VI) constituted 0%, 5%, 10%, 15%, 20%, 25%, 50%, 75%, and 100% of the total chromium in the samples. In addition, the total chromium contents of all mixtures were reduced to 4.0 wt% by dilution of the mixtures in boric acid ( $HBO_3$ ).

Edge-step normalized XANES spectra of chromium in the boric acid pellets are shown in Figure 1 for all nine calibration mixtures. The spectra are offset vertically to highlight the systematic changes that occur with increasing Cr(VI) content. The pre-edge feature between 0 and 10 eV is the spectral feature that shows the most change and it is also the easiest to quantify. As shown by most Cr(III) standards, the pre-edge feature of the end-member K-Cr alum sulfate consists of two peaks: a weak peak at about 1.5 - 2.0 eV and a second, even weaker peak at about 4.0 eV. The chromate pre-edge peak consists of a single intense peak at about 4.0 eV. To quantify these changes, a least-squares iterative fitting program was used that fits the peaks to a mixed lorentzian-gaussian line shape and the background to an arctangent function. This program returns information on the intensity, width, and position of the peaks once the least-squares fitting has converged. These data are summarized in Table 1 for the pre-edge regions shown in Figure 1 and calibration curves were then prepared from the data for the peak at 4.0 eV. The variation of the normalized height of the pre-edge feature with Cr(VI) content was linear with a correlation coefficient ( $r^2$ ) in excess of 99% (Figure 2).

TABLE I  
Results from Least-Squares Fitting of Calibration Data

Cr(VI)/Total Cr	Peak at 2.0 eV			Peak at 4.0 eV		
	Height	Width	Area	Height	Width	Area
0	0.035	1.855	0.064	0.013	1.855	0.024
5	0.033	1.974	0.065	0.042	1.983	0.083
10	0.032	2.306	0.073	0.086	2.058	0.176
15	0.037	2.527	0.093	0.116	1.968	0.228
20	0.034	2.000	0.068	0.170	2.070	0.351
25	0.036	2.167	0.078	0.199	2.087	0.415
50	0.024	2.000	0.048	0.404	2.200	0.880
75	---	---	---	0.620	2.200	1.364
100	---	---	---	0.823	2.280	1.876

It should be understood that although the derived calibration curve has an extremely small standard error associated with it (<1% Cr), there are other significant sources of uncertainty that need to be addressed. These include possible variation of the pre-edge intensity with site distortion (10), thick absorber effects (7), dead-time corrections in the 13-Ge element detector

(9), and appropriateness of  $K_2CrO_4$  as the standard for Cr(VI) in ash. Such factors were not explicitly considered in the method described by Bajt et al. (4).

To circumvent all of these sources of uncertainty, it was decided to use the Cr(III) pre-edge peak at lower energy (1.5 eV) to calibrate any possible peak intensity enhancement due to these effects. This pre-edge peak is approximately three times the intensity of the pre-edge peak at about 3.5 - 4.5 eV for most  $Cr^{3+}$  materials. This relationship can then be used to define a zero Cr(VI) baseline that allows for possible experimental saturation effects and site distortion phenomena and, hence, for more precise estimation of the Cr(VI) content.

By using this approach for defining the intercept from the normalized height,  $h_2$ , of the peak at about 1.5 - 2.5 eV, a generalized equation can be derived for the relationship between the normalized height,  $h_4$ , of the peak at about 3.5 - 4.5 eV and the concentration of Cr(VI) in a sample, as follows:

$$\%Cr(VI) = 110 (h_4 - h_2/3) \quad (1)$$

The slope is derived not only from the linearity of the calibration data presented in Table 1, but is an average value that also takes into account the variation in pre-edge peak height exhibited by different chromate compounds. Consequently, any value of Cr(VI) determined from this equation has an uncertainty of up to  $\pm 10\%$ , because the probable forms of Cr(VI) in combustion ash samples are likely not well represented by any one chromate compound.

#### RESULTS AND DISCUSSION:

We have applied the above equation to measurements made on the Cr XANES spectra to estimate approximate values for Cr(VI) in various ash samples derived from coal combustion. Figure 3 shows the chromium XANES spectra for three commercial and one laboratory ash samples. Parameters (normalized height, width, area, position) for the pre-edge peaks were quantified by least-squares fitting using the program EDGFIT. Examples of the least-squares fitting are shown in Figure 4. The percentage of Cr(VI) present in the sample was estimated from the pre-edge peak heights using the above relationship (equation 1). The results of such fitting are summarized in Table 2 for all ash and slag samples examined.

Based on the spectra shown in Figures 3 and 4 and the results listed in Table 2 derived from least-squares fitting of the pre-edge peak, none of the fly-ash or bottom ash samples from either commercial coal combustion plants or laboratory experiments appears to contain significant Cr(VI) present in the samples, with the possible exception of the Pittsburgh drop-tube sample. All the results showed that the determined Cr(VI) content was typically around 1 - 5% of the total chromium. However, there is an estimated experimental uncertainty of  $\pm 3 - 5\%$  in such determinations from uncertainty in the determined heights of the peaks in the fitting procedure. Hence, 0% Cr(VI) is almost as significant a result as the determined value in many instances.

TABLE 2  
Results from Least-Squares Fitting of Cr XANES of Combustion Ashes

Ash Sample	Peak at 2.0 eV		Peak at 4.0 eV		Estimated Content of %Cr(VI)
	Height	Pos'n	Height	Pos'n	
<u>Commercial:</u>					
Cooper FA	0.044	1.5	0.030	3.8	2
NIST SRM 1633b	0.044	1.4	0.038	3.8	3
LET FA-1	0.050	2.4	0.034	4.1	2
LET BA-1	0.054	1.5	0.055	3.9	4
LET BA-2	0.040	1.6	0.035	3.3	3
LGE FA	0.042	1.9	0.054	3.9	5
LGE BA	0.053	2.1	0.033	4.1	1
<u>Laboratory:</u>					
Univ. Arizona Combuster:					
51-14-Coarse	0.063	2.3	0.061	4.8	3
51-14-Med	0.045	2.0	0.041	4.4	3
51-14-Fine	0.040	1.8	0.046	4.2	4
47-07-Coarse	0.039	1.9	0.020	4.4	1
PSIT Drop Tube:					
Pittsburgh Ash	0.031	1.7	0.091	3.6	9
Illinois #6 Ash	0.036	1.9	0.047	3.7	4

The Pittsburgh drop-tube sample (DECS-12) exhibits a value for Cr(VI),  $9 \pm 3\%$ , that is significantly higher than those determined for other ash samples. It should be noted that the Cr XANES spectrum (Fig. 3) for this sample was also one of the best quality so that this higher value can not be due to larger than normal experimental uncertainty. It is likely that this result can be attributed to the fact that the drop-tube experiments are normally carried out in excess air in comparison to conditions in the larger-scale combustors. Hence, a slight enhancement in the Cr(VI)/Cr(III) ratio may not be unusual given such circumstances. However, this observation would also appear to imply that conditions of coal combustion are not far removed from those that could result in significant formation of Cr(VI): Unusual furnace conditions (e.g. low temperatures, high oxygen fugacity) or possibly unusual slag chemistry may yet be found that result in the formation of significant Cr(VI) in combustion ash materials.

#### CONCLUSIONS

A direct and nondestructive method has been developed for speciating chromium in solid samples based on the normalized peak-height of the pre-edge feature in chromium XANES spectra. The method is capable of determining the relative percentages of the two major chromium oxidation states, with an uncertainty of  $\pm 10\%$ , down to as little as 5-10 ppm of chromium in relatively X-ray transparent solids such as combustion ash or coal. The only preparation necessary is to ensure that the sample has a particle size less than about 200 mesh (0.075 mm top size) and that it is representative over an X-ray beam spot size of between 4 and 10 mm<sup>2</sup>. No chemical separation is done on the sample nor is any method of pre-concentration used prior to analysis.

This spectroscopic method shows that the Cr(VI) content of all commercial ash samples so far examined is at or below the detection limit for Cr(VI), estimated to be about 3 - 5% of the total chromium, depending on concentration. These results are in agreement with data for fly-ash samples determined by ICP-AES, in which the Cr(VI) is complexed and extracted by ammonium hydroxide (11). Such findings imply that the behavior of chromium in coal combustion should be re-examined carefully to assess whether or not this element is a significant HAP. However, as the current results indicate for ash samples from small-scale laboratory combustion experiments, typical combustion conditions appear to be quite close to those that could promote formation of significant Cr(VI).

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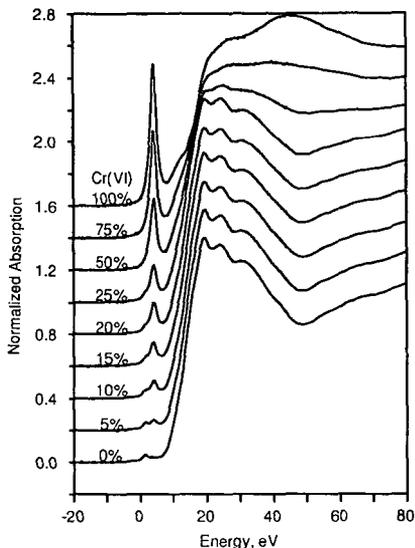


Figure 1: Chromium XANES spectra for mixtures of K-Cr(III) alum sulfate and  $K_2Cr(VI)O_4$ .

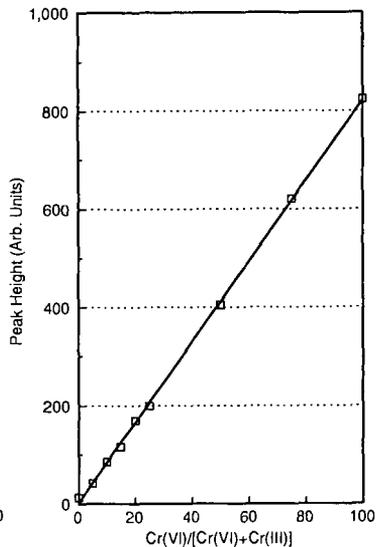


Figure 2: Calibration curve based on normalized peak height of least-squares fitted pre-edge peaks in Figure 1.

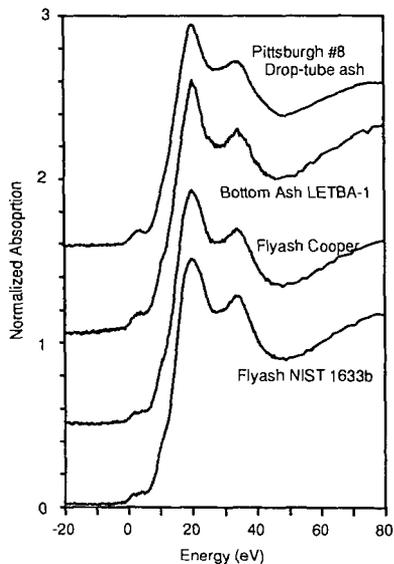


Figure 3: Chromium K-edge XANES spectra for three commercial ash products and a laboratory drop-tube ash.

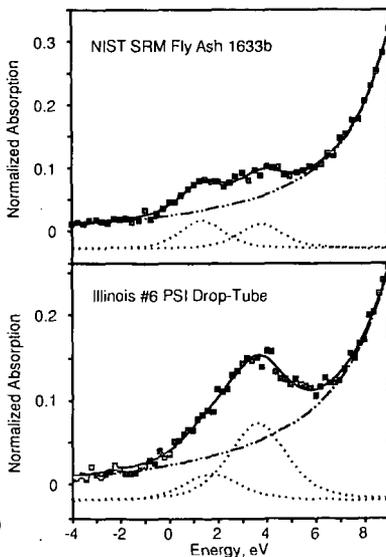


Figure 4: Examples of least-squares fitting of the pre-edge peak present in Cr XANES spectra of ash samples.

## SELENIUM SAMPLING AND ANALYSIS IN COAL COMBUSTION SYSTEMS

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Keywords: Selenium, Coal Trace Analysis

### BACKGROUND

The Clean Air Act Amendments of 1990 (CAAA) identified 189 elements and compounds that are classified by the U.S. EPA as hazardous air pollutants (HAPs). Among these are eleven inorganic trace elements found in coal. A provision of the CAAA required EPA to conduct a study of the health and environmental impacts of HAP emissions from electric utility generating units. EPA has completed a number of draft documents in compliance with this mandate. For trace element emission estimates, they have relied on a number of field tests which were conducted by a variety of organizations including the U.S. Department of Energy (DOE). The DOE program utilized the EPA Method 29 sampling train to measure the emissions of trace elements including Se. EPA Method 29 is validated for municipal waste combustor sampling but not for coal-fired combustion sources.

The DOE program involved measurements at eight coal-fired utilities selected to represent a cross-section of the coal-fired utility industry in regard to fuels and furnace configurations. Five sampling teams performed the testing. All of the test teams reported low material balance closures for Se.<sup>1</sup> CONSOL R&D participated at two of these test sites: Minnesota Power Clay Boswell and Illinois Power Baldwin stations. The Se balance closures for the Boswell plant ranged from 12% to 21% and averaged 18.5%.<sup>2</sup> The Se balance closures for the Baldwin plant ranged from 30% to 60% and averaged 50%.<sup>3</sup> Selenium is the only element that showed a material balance closure problem for both test sites, indicating either a sampling or analytical error. At the third DOE Air Toxics Working Group Meeting, the poor Se balances obtained from the eight station tests were discussed, but there were no clear answers as to the cause. The fact that all of these programs showed low Se balance closures is evidence of a sampling or analytical problem.

After reviewing these results, CONSOL R&D conducted a sampling and analytical program to determine the reasons for the poor Se material balances. This program focused on two areas: 1) the accuracy of sampling and analytical procedures for measuring Se in solids, and 2) the potential for Se losses within the combustion or sampling system.

### Selenium Properties

Among the eleven trace elements listed as HAPs, Se has unique volatility characteristics that could result in sampling problems. All of these eleven elements except mercury (Hg) and Se are predominantly (>99%) in the solid phase at coal-fired flue gas temperatures.<sup>4,5</sup> For these non-volatile elements, flue gas sampling is not required to complete a material balance. Because of its vapor pressure, almost all of the Hg released during combustion should be present as a vapor.

The equilibrium vapor pressure curve (Figure 1) for Se (as SeO<sub>2</sub>) indicates that this element can be present in both the gas and solid phases at normal utility flue gas temperatures.<sup>6</sup> The curve shows that there can be a large change in the partitioning of SeO<sub>2</sub> between the gas and solid phases in the temperature range of 200 °F to 300 °F. This temperature range is important because it encompasses the typical flue gas exhaust temperature for utilities (~280 °F to 300 °F) and the operating temperature of the EPA Method 29 probe and filter (258 °F ±20 °F). The Se content in the Illinois coal fired at the Baldwin plant was 4 ppm (whole coal basis). If all the Se in the coal volatilized during combustion, this would result in a gas phase Se concentration of approximately 97 ppbv. As the flue gas cools, some fraction of the gas phase Se would condense. Table 1 shows the theoretical distribution of Se between the vapor and condensed phases at various temperatures.

Selenium is the only Clean Air Act trace element that undergoes this phase transition in this temperature window. The implication of this phenomenon on Se sampling results is discussed below.

### Selenium in U.S. Coals

There is a limited amount of information on the Se contents of commercial (i.e., as-fired) coals. CONSOL has collected trace element data on over 250 coal samples representing a wide cross-section of U.S. coal production. This database shows a Se-in-coal concentration range of 0.5 to 6.5 ppm (whole-coal basis) with an average of ~1.5 ppm.<sup>7</sup> The recent DOE program involved nine coals with Se concentrations between 0.85 ppm and 3.25 ppm. In a DOE-sponsored coal analysis

round robin study conducted by CONSOL R&D, Se determinations for a NIST reference coal ranged from 0.75 ppm to 1.52 ppm compared to a certified value of 1.29 ppm. Accuracies ranged from 42% low to 15% high. Only one of the ten reported values was within 10% of the certified value.<sup>9</sup> The difficulty in obtaining an accurate Se-in-coal determination at concentrations typical for coal is certainly a contributing factor to the uncertainty in material balance closures.

#### Emission Factors

Trace element emission factors for combustion sources are developed by using the trace element concentration in the fuel and calculating a maximum uncontrolled emission rate. This value then is adjusted to account for bottom ash-to-fly ash partitioning, particulate-to-gas partitioning, and removal in control devices. In many cases these partitioning factors are estimated from the best available test data. If possible, the estimated emission factor is compared with emission measurements. The phase distribution of Se makes estimation of partitioning and removal factors difficult and uncertain.

The difficulty in closing Se balances around coal-fired power plants leads to uncertainty in the validity of the measured emissions and estimated emission factors based on these measurements. The accuracy of emission estimates is important because they ultimately will be used in risk assessments.

#### **RESULTS AND DISCUSSION**

This research program was focused on two areas of concern:

- Analysis of selenium in process stream samples,
- Se losses in the flue gas ducts and EPA Method 29 sampling train.

#### Analysis of Selenium in Process Stream Samples

There are three factors that contribute to good material balance closures: obtaining a representative sample, accurately measuring the process stream flow-rate, and an accurate chemical analysis. Assuming that the first two conditions are met, the chemical analysis becomes the most important step. However, the determination of selenium in process stream samples can be difficult.

Table 2 shows the results of Se analyses conducted on a NIST coal ash standard. These data show that the digestion step outlined in Method 29 procedures may not be suitable for all solid materials.<sup>4</sup> The Method 29 digestion (SW 846) involves the digestion of ~0.5 g of solids with 6 mL of concentrated HNO<sub>3</sub> and 4 mL of concentrated HF and either conventional heating in a Parr Bomb at 285 °F (six hours) or microwave heating. This digestion showed a low recovery for Se and for all of the HAPs elements. The CEM microwave procedure involves a multi-stage digestion using the same acids outlined in the Method 29 technique, but with larger volumes and longer digestion times. This technique showed a very good Se recovery. The open-vessel technique showed low recoveries for Se, although previous analyses of this ash standard have shown excellent recoveries for Se and the non-volatile trace elements. The low Se recoveries specific to this determination are thought to be a result of uncontrolled fluctuations in the temperature used in the digestion. Because of the low results for Se by open vessel digestion, CONSOL R&D analyzed a variety of solids for Se by first preparing the sample using hydrolysis. In this procedure, the solids are pyrolyzed in a stream of excess air and steam. The volatile Se is passed through a condenser and then into a NaOH scrubber solution for Se capture. This solution is analyzed by ICP-MS. The efficiency of this procedure has been verified by the analysis of SARM, NIST, and NBS standards.

The open-vessel digestion technique has several advantages. It is safer than the microwave technique, more time-efficient than the other procedures, and provides excellent elemental recoveries for most of the trace elements of interest (Hg determinations are obtained using a separate sample preparation technique). This work indicates that Se may be lost during the open vessel digestion step and additional work is being completed to determine the critical digestion temperature for this procedure for a variety of coal ash matrices.

Conclusions drawn from these data are that the Method 29 procedure does not provide a sufficiently rigorous digestion for coal ash samples. Typical coal fly ash has a strong clay-silicate matrix which requires either a more rigorous digestion or larger quantities of the acids. The same criticism applies to the analysis of the Method 29 solid fraction. These data indicate the front-half filter analysis can be biased low, which would lead to inaccurate material balance closures.

#### Selenium Losses in the Flue Gas Ducts and Sampling Train

Because the Se analyses of the coal, ash, and Method 29 front-half samples could be in error, Se material balances from the sampling programs at the Baldwin<sup>2</sup> and Boswell<sup>3</sup> plants were recalculated based on analyses obtained using the hydrolysis digestion techniques for the process stream (coal and ash) samples. The Method 29 samples were not available for repeat analyses. The ash samples showed somewhat higher Se concentrations, but the increase had only a small

effect on the Se balances. The selenium balances for the Baldwin testing are shown in Table 3.

These data indicate the Se material balance closures are low by -50%. The Se input value is based on the Se in the coal which averaged 3.73 ppm (whole-coal basis) for these tests. This analysis was verified as part of the DOE round robin which involved a comparative analysis by five labs. The Se values in the ESP ash samples were verified through replicate analyses and comparison with standard reference materials. The temperature of the flue gas entering the ESP was -340 °F and -330 °F at the sampling location. The vapor pressure curve for Se<sub>2</sub> at these temperatures indicates that all of the available Se should have been present in the vapor state. This is supported by the low level of Se in the ESP ash samples. The Method 29 procedure calls for a front-half (probe and filter) temperature of 258 °F ±20 °F. The vapor pressure curve at 250 °F predicts a gas phase Se concentration of 8 ppbv. This value is very close to the observed values (4, 6, and 7 ppbv).

A possible explanation for the poor Se balance for this utility is that at the Method 29 front-half sampling temperature (258 °F ±20 °F), the equilibrium between gas phase and solid phase Se is shifted to the solid phase. In reviewing the field sampling sheets, it was noted that the normal variations in the heater box gave temperatures as low as 240 °F. As shown in Figure 1, the selenium vapor pressure at 240 °F corresponds to a gas phase Se concentration of only 3.5 ppbv, which is well below what would be expected at the flue gas temperature. The speculation becomes more severe at lower temperatures and could be aggravated by insufficient heat to the sampling probe. If condensation occurs, the measurement of the Se emissions becomes a function of the accuracy of the front-half (solid) fraction. For this program, the front-half analyses were found to be unreliable,<sup>2,3</sup> and it was assumed that the particulate phase Se was represented by the ESP hopper ash samples. However, the ESP solids were collected at a point in the gas stream where the gas temperature is -340 °F. At this temperature, almost all of the Se is in the gas phase. It is likely that a significant fraction of the gas-phase Se condensed in the front-half of the Method 29 sampling train and was unaccounted for due to the inability to obtain an accurate front-half (particulate) Se analysis.

#### CONSOL Pilot-Scale Selenium Sampling Results

CONSOL R&D conducted a series of 12 Se measurements on the flue gas from a 1.5 MM Btu/hr pilot-scale coal combustor (Figure 2). All measurements were taken under tightly controlled combustion conditions using a constant coal source. The only variable was the flue gas temperature. The gas phase emission results from this test and the associated gas and sampling temperatures were compared. The test with the lowest flue gas temperature (200 °F) also showed the lowest concentration of gas phase Se (2.9 ppbv). The test with the highest flue gas temperature (335 °F) resulted in the highest gas phase Se concentration (9.3 ppbv).

The percent of the available Se found in the gas phase ranged from 11% to 34% and this value was dependent on the temperature of the flue gas and sampling equipment. Vapor pressure has an exponential dependence on temperature. However, because the temperatures are within a narrow range, a linear correlation analysis was conducted on the data to assess the co-variance of gas phase Se concentrations with flue gas and sampling temperatures. The following correlations were obtained from this data set:

Gas Phase Se Concentration Correlated to:	r <sup>2</sup>
Duct Temperature	0.77
Probe Temperature	0.51
Filter Temperature	0.23

These data show that the gas phase Se is moderately well correlated with the temperature of the flue gas and (more weakly) with the temperature at which the solids are collected in the Method 29 train. These data suggest that the partitioning between gas and solid phase is influenced by these temperatures and supports the mechanisms previously discussed. The data also show that cold spots in the flue gas handling system or the sampling probe can decrease the apparent gas phase Se concentration (Figure 2). A decrease in temperature between one sampling position to the next, in the temperature window of 200 °F to 300 °F could deplete the vapor phase Se by deposition on the sidewalls or on fly ash solids.

#### CONCLUSIONS

\* The Method 29 analytical procedure (including SW 846 digestion) shows a low bias for most trace elements commonly found in coal ash, including Se.

- \* Analytical bias (due to Se volatilization) can occur during the sample preparation (digestion) stage.
- \* Se partitioning is influenced by the gas and sampling temperatures.
- \* The Method 29 Sampling procedure can shift the apparent speciation between gas phase and solid phase Se.
- \* Material balance closures can be affected if vapor phase and solid phase samples are taken at different flue gas temperatures.
- \* The simultaneous sampling and analysis of Se in conjunction with the other elements as described in EPA Method 29 may lead to an inaccurate Se determination.

#### RECOMMENDATIONS

This work represents an initial step to a more complete understanding of Se sampling in coal combustion systems. There are a number of research areas that should be further investigated to improve this understanding and improve emission measurements. Recommendations for future research are as follows:

- \* Conduct comparative M-29 sampling with the front-half temperature at 258°F and at the actual duct temperature.
- \* Analyze M-29 front-half Se concentrations by both the SW-846 technique and the hydropyrolysis method.
- \* Investigate more effective digestion techniques for Se analysis of solid samples.
- \* Conduct a Se balance program around a well-controlled system using the suggested modifications.

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9. Private communication discussing trace element analysis of DOE Method 29 solid samples for the Baldwin and Boswell test sites from Barry Rayfield (Triangle Labs) to Barry Jackson (Roy F. Weston, Inc.), 10/12/93.

Table 1. Theoretical Phase Distribution for Se Emissions

Temperature, °F	Solid Phase (Fly ash)		Vapor Phase	
	ppmw (a)	% of Total	ppbv	% of Total
220	130	98%	1.9	2%
240	127	96%	3.5	4%
260	117	87%	13	13%
280	90	67%	32	33%
300	33	24%	74	76%

(a) Based on 10% ash in coal, 70% bottom ash - 30% overhead ash ratio, and no Se in bottom ash

Table 2. Comparison of Se Results on NIST 1633a

Element	Reference Value, ppm	SW-846 Digestion <sup>a</sup>	Microwave Digestion <sup>b</sup>	Open Vessel Digestion <sup>c</sup>
Arsenic	145	110	155	141
Beryllium	12*	2.1	11.2	12.7
Cobalt	46.0	7.7	109	42.6
Lead	72.4	12.7	50.9	74.0
Manganese	179	33.6	157	195
Nickel	127	17.3	113	117
Selenium	10.3	7.66	11.1	4.4
Vanadium	297	62.2	286	283

\*Designates informational values

- a) Digestion and analytical procedure described in M-29<sup>o</sup>
- b) Digestion and analytical procedure developed by CEM Corporation<sup>o</sup>
- c) Digestion and analytical procedure developed by CONSOL R&D<sup>2,3</sup>

Table 3. Selenium Mass Flowrates for the Baldwin Process Streams (unit is lb/hr\*)

	Test 1	Test 2	Test 3
Coal Input	1.82 (122)	1.78 (120)	1.39 (94)
Bottom Ash	0.03	0.03	0.03
Econ. Ash	0.00	0.00	0.00
ESP Ash	0.02	0.02	0.01
Stack Solids**	0.96 (64)	0.42 (28)	0.60 (40)
Stack Vapor**	0.09 (6)	0.06 (4)	0.10 (7)
Se Closure	60%	30%	53%

- \* The values inside the parentheses indicate the theoretical vapor phase concentration in ppbv if all of the Se present was volatilized
- \*\* Values obtained from the Method 29 sampling train

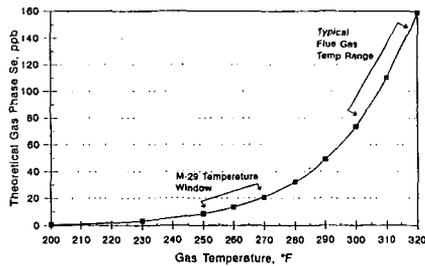


Figure 1. Vapor Pressure Curve for  $SeO_2$ .

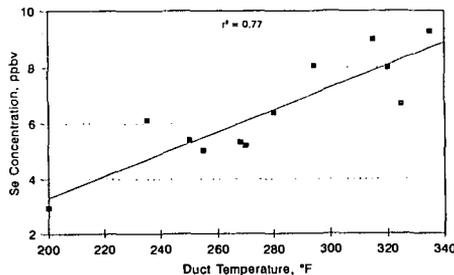


Figure 2. Gas Phase Se Concentrations vs Duct Temperature.

## A CONTINUOUS EMISSIONS MONITOR FOR TOTAL, ELEMENTAL, AND TOTAL SPECIATED MERCURY

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Key Words: Elemental Mercury, Speciated Mercury, Continuous Emissions Monitor

### ABSTRACT

ADA Technologies, Inc., is developing a continuous emissions monitoring system that measures the concentrations of mercury and volatile mercury compounds in flue gas. These pollutant species are emitted from a number of industrial processes. The largest contributors of these emissions are coal and oil combustion, municipal waste combustion, medical waste combustion, and the thermal treatment of hazardous materials. It is difficult, time consuming, and expensive to measure mercury emissions using current, manual sampling test methods. Part of this difficulty lies in the fact that mercury is emitted from sources in several different forms, such as elemental mercury and mercuric chloride. The ADA analyzer measures these emissions in real time, thus providing a number of advantages over existing test methods: 1) it will provide a real-time measure of emission rates, 2) it will assure facility operators, regulators, and the public that emissions control systems are working at peak efficiency, and 3) it will provide information as to the nature of the emitted mercury (elemental mercury or speciated compounds). This paper presents an overview of the CEM and describes features of key components of the monitoring system--the mercury detector, a mercury species converter, and the analyzer calibration system.

### THE NEED FOR A MERCURY CEM

Future strategies for controlling hazardous air pollutants will involve the use of continuous emissions monitoring systems. These systems provide a real-time measure of pollutants being emitted from sources and are needed in terms of assuring compliance with emissions regulations. They can also be used to help facilities operate pollution control equipment at peak efficiencies.

Mercury is a pollutant that has been receiving much attention in terms of monitoring and control strategies. The toxicity of mercury has prompted industry and regulators to develop methods to minimize its release to the environment. Continuous monitoring systems will play a key role in assuring that emissions of this hazardous material are minimized.

Mercury is emitted from industrial sources in a variety of chemical forms depending on the specific process and flue gas conditions. For example, mercury is known to exist as elemental mercury [ $\text{Hg}^0$ ] and as mercuric chloride [ $\text{HgCl}_2$ ] in most industrial flue gases that contain mercury.<sup>1</sup> A knowledge of the relative concentrations of the various forms of mercury will be required for air pollution control devices to operate effectively. An example of this principle is given in Table 1 for a coal-fired power plant.<sup>2</sup>

Current standard testing techniques rely on manual "grab samples" where flue gas is drawn through a series of impinger solutions to collect elemental and speciated forms of mercury.<sup>3</sup> The collected samples are analyzed in an analytical chemistry laboratory using complex techniques and instrumentation. These field sampling and analytical techniques are cumbersome, labor intensive, and expensive. A 1-week comprehensive sampling program can cost in the range of \$25,000-\$50,000.

A continuous mercury monitoring system should address the following needs:

- Since the optimum control device depends on the specific chemical form of the mercury, an analyzer that can distinguish between the chemical forms is needed to assure effective operation of the APCD.
- An analyzer is needed that will assure the APCD is working properly.
- An analyzer is needed that can be used to control the feed rate of a process generating the mercury emission.
- An analyzer is needed that will help assure the public and regulatory agencies that facilities which produce mercury emissions are in compliance with regulatory limits.

#### DESCRIPTION OF CEM

In response to the need for monitoring mercury emissions in real-time, ADA Technologies has developed a continuous emissions monitoring system that is capable of measuring total mercury, elemental mercury, and (by difference) total speciated mercury. The system features a sensitive mercury detector, a mercury species converter, and a calibration system. Figure 1 shows the components in a typical CEM arrangement.

The "converter" is used to change speciated mercury compounds to elemental mercury. When the sample gas is placed through the converter, a measure of the total mercury content of the flue gas is obtained. When the converter is bypassed, only elemental mercury is measured in the gas sample. The difference between the two measurements is the concentration of total speciated mercury content.

A heated, non-reactive sample transport line is used to convey the gas sample to the analyzer. Calibration gas is introduced to the end of the sample line in order to assure that the entire sampling system and the analyzer are calibrated as a single unit.

#### DESCRIPTION OF COMPONENTS

##### Mercury Detector

The analyzer uses a unique ultraviolet absorption technique to quantify the mercury. Proprietary optical components are incorporated that provide a measurement sensitivity below  $1 \mu\text{g}/\text{m}^3$  (less than approximately 150 ppt v/v). The analyzer has a linear response to a concentration of greater than  $100 \mu\text{g}/\text{m}^3$ . The optical design also eliminates the effects of interfering gases such as sulfur dioxide.

Figure 2 shows the analyzer response when elemental mercury was introduced at a concentration of  $2.6 \mu\text{g}/\text{m}^3$  (390 ppt v/v). Also shown in the figure is the signal when zero gas was introduced into the analyzer. Based on the peak-to-peak noise level observed, a minimum level of detection (defined as 2x noise level) of  $0.39 \mu\text{g}/\text{m}^3$  (58 ppt v/v) is calculated. Operation with detection limits as low as 45 ppt have been observed under ideal conditions.

The ADA analyzer incorporates a unique optical design that eliminates the effects of interfering gases such as sulfur dioxide. Figure 3 shows the response of the detection system when measuring mercury at a concentration of  $8.1 \mu\text{g}/\text{m}^3$  (1.2 ppb v/v) in the presence of sulfur dioxide at a concentration of 1000 ppm. Within the uncertainty of the measurement, the analyzer corrects for the  $\text{SO}_2$  absorption perfectly.

Figure 4 shows the response of the analyzer over a concentration range of 0 to 6 ppb (v/v). This range is expected to cover most concentrations expected in coal-fired and municipal solid waste generated flue gases. A dilution probe is used on the analyzer for situations in which high concentrations of mercury are present, such as when monitoring uncontrolled emissions ahead of an APCD.

### Converter

A mercury species converter is another key component of the CEM system. The converter is used to distinguish between concentrations of elemental and "total" mercury found in the flue gas. Since the mercury detector measures only elemental mercury, the converter is needed to change speciated forms of mercury present in the flue gas to elemental mercury. Total mercury is, therefore, measured by passing the flue gas sample through the converter. Elemental mercury concentrations are measured by the CEM when the flue gas sample bypasses the converter. Total speciated mercury is then determined as the difference between the measured total mercury concentration and the elemental mercury concentration.

The converter uses a unique design that eliminates the need for expendable chemicals to reduce the speciated forms of mercury. Figures 5 and 6 show the response of the analyzer to two surrogate speciated mercury compounds--mercuric chloride and dimethyl mercury. The test sequence repeatedly injected the mercury species through the converter to allow measurement of the resulting elemental mercury and then bypassed the converter to demonstrate the converter effectiveness. Note the slower response time of the analyzer for the speciated forms relative to elemental mercury. This is due to adsorption of the "sticky" speciated forms of mercury on the walls of the tubing and gas cells. Heat tracing of the gas handling system mitigates this problem to some extent. This becomes important in the final analyzer system as it will limit how quickly one can calibrate the analyzer for speciated forms of mercury and therefore how often this procedure can be done.

### Calibrator

ADA Technologies developed a calibrator for use with the mercury CEM. The calibrator is based on the use of permeation tubes to provide known and accurate concentrations of elemental mercury and mercuric chloride. These devices are considered primary standards for calibrating continuous monitors and they are used to calibrate ambient air analyzers. ADA has developed a two-channel calibrator--one channel is used to calibrate the elemental mercury detector and the other is used to calibrate the converter.

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### TABLES

**Table I. Mercury Removal Under Different Process Conditions**

Plant	Ash Loading to Spray Dryer	Coal Cl	% Mercury Removed
A	High	Low	14
B	High	Low	23
C	High	Low	6
G	High	Low	16
E	Low	High	55
H	Low	High	44
F	Medium	High	89
D	High	High	96

FIGURES

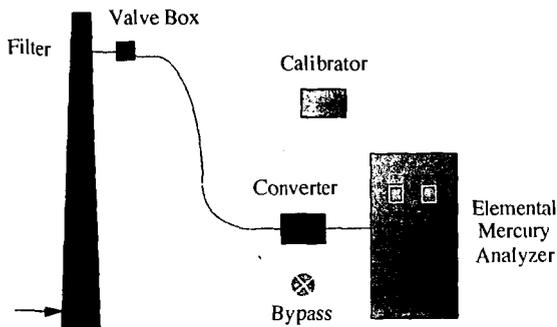


Figure 1. Mercury CEM arrangement.

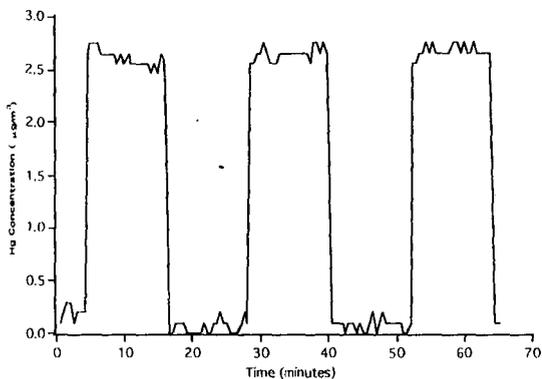


Figure 2. Response of the analyzer to  $2.6 \mu\text{g}/\text{m}^3$  of mercury.

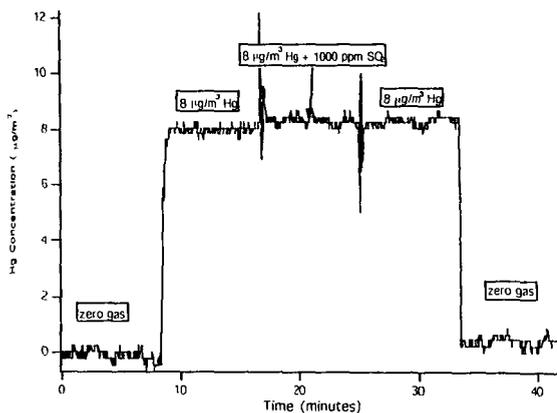


Figure 3. Mercury detector response when measuring mercury in the presence of sulfur dioxide.

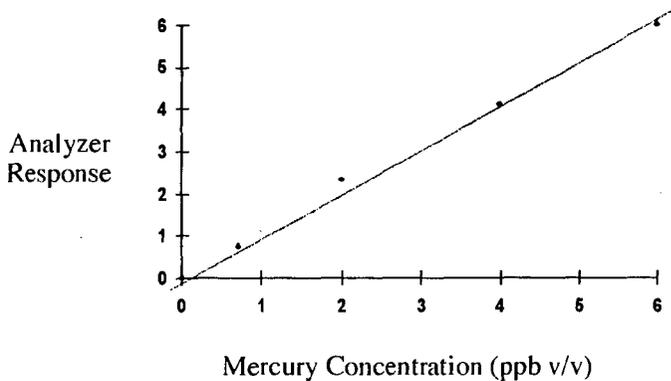


Figure 4. Linearity of the mercury detector.

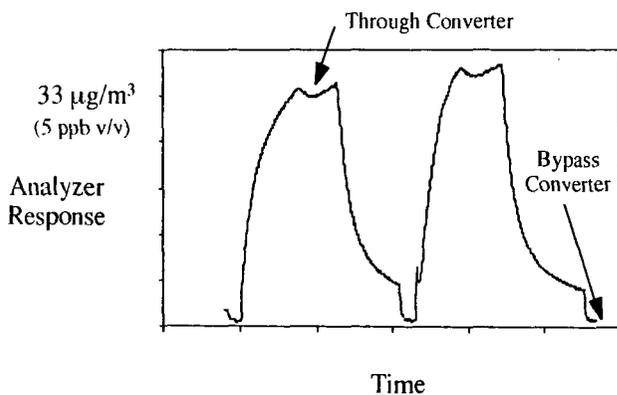


Figure 5. Mercuric chloride being converted to elemental mercury.

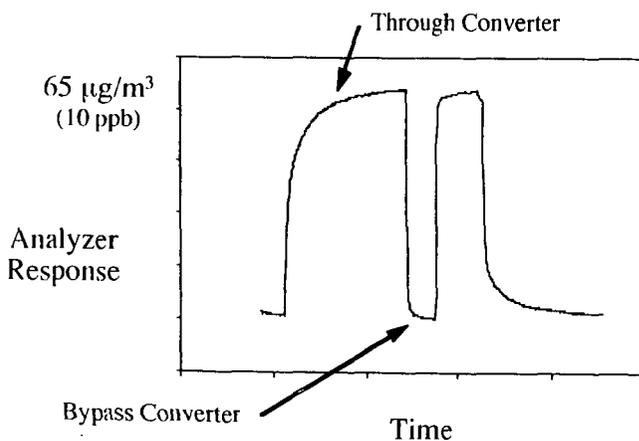


Figure 6. Dimethyl mercury being converted to elemental mercury.

## PRECOMBUSTION CONTROL OPTIONS FOR AIR TOXICS

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**Keywords:** Trace Elements, Coal Cleaning, and Air Toxics Control

### INTRODUCTION

Coal cleaning reduces the ash and sulfur content of coal by removing ash-forming and sulfur-bearing minerals. Coal cleaning can also reduce the concentration of most of the elements named as hazardous air pollutants in the 1990 Amendments to the Clean Air Act because many of these elements are associated with mineral matter. For example, arsenic is commonly associated with pyrite; cadmium with sphalerite; chromium with clay minerals; mercury with pyrite and cinnabar; nickel with millerite, pyrite, and other sulfides; and selenium with lead selenide, pyrite, and other sulfides (Finkelman, 1980). There are also cases in which some of these elements are organically bound. Just as both organic and pyritic sulfur can be found in the same coal, the same trace element may be both organically bound and present as part of a mineral in the same coal. Organically bound trace elements are not removed by currently used methods of cleaning coal.

Trace elements removed by coal cleaning will not be released into the atmosphere during combustion. Also, coal cleaning reduces the ash content of the coal and increases the heating value, reducing transportation costs and increasing boiler efficiency. Finally, coal cleaning provides other environmental benefits by reducing the sulfur dioxide emissions potential of the coal and the amount of ash for collection and disposal.

As an air toxics control measure, coal cleaning offers several advantages to utilities. Because physical coal cleaning is a relatively inexpensive technology, it may prove to be the lowest-cost control option in many cases. Also, coal cleaning is currently the only commercially available control technology for the highly volatile trace element mercury. Finally, removing trace elements before combustion reduces the concentration of these elements in utility solid wastes, reducing possible long-term environmental liability.

### TRACE ELEMENT REDUCTION BY CONVENTIONAL CLEANING

In the US, work by CQ Inc., Southern Company Services, Inc. (SCS), Consolidation Coal Company (CONSOL), and Bituminous Coal Research Inc. (BCR) has demonstrated that conventional methods of coal cleaning can produce large reductions in the concentration of many trace elements (Akers and Dospoj, 1993; CQ Inc. and SCS, 1993; DeVito et al., 1993; and Ford and Price, 1982). Combined, these sources provide trace element reduction data from 16 commercial and ten commercial-scale cleaning tests. This data is summarized for arsenic and mercury in Table 1. As no attempt was made to enhance removal of any trace element, these results are representative of trace element reductions that occur as a by-product of cleaning for ash and sulfur reduction.

The data in Table 1 demonstrate that physical coal cleaning is effective in reducing the concentration of these two trace elements, although the degree of effectiveness varies. For example, arsenic reduction varies from 20 to 85 percent and mercury reduction from -191 (an increase) to 78 percent. Part of the observed variability in trace element reduction is caused by poor analytical precision. The accurate measurement of elements present in trace concentrations in coal is challenging and even well qualified laboratories can produce faulty results (Akers et al., 1990). However, most of the variability appears to relate to the interactions between the total amount of mineral matter removed by cleaning, the method by which the coal is cleaned, and the mode of occurrence of the trace element bearing-mineral matter.

The primary economic motive for cleaning coal is to remove ash-forming mineral matter to reduce coal transportation costs, lower ash collection, handling and disposal costs, and increase combustion efficiency. Coals are cleaned to a variety of ash levels to meet local and regional market demands. The ash reduction achieved by a cleaning plant is directly related to the total amount of mineral matter removed. Not surprisingly, trace element reduction tends to increase with ash reduction. However, factors other than ash reduction impact the reduction of many elements including the degree of liberation of the trace element bearing mineral and the ability of the coal cleaning equipment utilized to remove the mineral.

Mineral matter occurs in coal in a variety of forms. For example, pyrite, the most studied coal-associated mineral, can occur as anything from a massive fracture fill several centimeters in size to discrete euhedral crystals a few microns in size. Some conventional coal cleaning operations crush the raw coal before cleaning to protect equipment from oversized material and to liberate ash- or sulfur-bearing minerals. While crushing is minimized to avoid producing excess fines, it can liberate larger mineral forms. It can also liberate trace element-bearing mineral matter.

CQ Inc. performed a washability study of Kentucky No. 11 Seam coal. During this study, a comparison was made of uncrushed coal with coal crushed to 9.5 mm topsize. In this case, additional arsenic liberation occurs when the raw coal is crushed to a topsize of 9.5 mm. For example, cleaning the uncrushed coal at 90 percent energy recovery produces an 86 percent arsenic reduction, while cleaning the crushed coal at the same energy recovery produces a 97 percent arsenic reduction. In this example, crushing increased the liberation of the arsenic-bearing mineral(s) in the coal allowing additional quantities to be removed without any sacrifice of energy recovery.

The type of equipment used in a cleaning plant can also affect trace element reduction. Table 2 contains a comparison of a heavy-media cyclone and froth flotation for trace element reduction. In this case, Pratt Seam coal from Alabama was cleaned by both technologies. Here, chromium reduction is roughly proportional to ash reduction for both cleaning devices; however, while mercury is reduced by the heavy-media cyclone, it is increased by froth flotation.

The comparison of froth flotation to heavy-media cycloning illustrates the concept that physical cleaning processes do not remove trace elements as such, but rather remove trace element-bearing minerals. Mercury commonly occurs in coal within the structure of the mineral pyrite. As pyrite is a very dense mineral, it is easily removed by a density-based process such as a heavy-media cyclone. However, cleaning processes such as froth flotation remove minerals based on surface characteristics. Because coal and pyrite have similar surface characteristics, conventional froth flotation may not provide high reductions of either pyrite or pyrite-associated trace elements such as mercury.

#### **TRACE ELEMENT REDUCTION BY ADVANCED CLEANING**

Advanced coal cleaning technologies may offer advantages over conventional technologies in reducing trace elements. Advanced processes typically involve crushing coal to increase the chance of liberating sulfur-bearing and ash-forming mineral matter, possibly also liberating trace element-bearing mineral matter. Also, advanced processes are specifically designed to clean fine-sized coal, making them more efficient than conventional processes in removing mineral matter from this material.

In an evaluation of Sewickley Seam coal, CQ Inc. compared an advanced coal cleaning process developed by Custom Coals International to conventional coal cleaning techniques (Akers and Dospoy, 1993). The Custom Coals' process is characterized by several innovative components including a fine-coal heavy-media cyclone separation circuit. A conventional coal cleaning plant using heavy-media vessels and water-only cyclones was used for comparison. As part of this evaluation, extensive washability and liberation tests were performed on the coal. CQ Inc. engineers developed computer models of a conventional coal cleaning plant and a plant using the advanced process with middlings crushing for liberation. This information was used to produce a laboratory-simulated clean coal by combining the appropriate size and density fractions of the raw coal in the proportions predicted by the models to produce both the conventional and the advanced clean coal.

The results of this evaluation are presented in Table 3. Conventional cleaning techniques reduced the concentration of antimony, arsenic, chromium, cobalt, lead, mercury, and nickel and advanced techniques provided a further reduction in all cases except mercury. For example, conventional cleaning reduced the arsenic concentration of the coal from 14 to 7 ppm, while advanced cleaning provided a further reduction to 4 ppm.

#### **CONCLUSIONS**

Coal cleaning techniques are effective in removing ash-forming mineral matter along with many mineral-associated trace elements from coal. Data gathered from commercial and commercial-scale cleaning tests indicate that trace element reduction tends to increase as ash reduction increases. However, factors such as the mode of occurrence of the trace

element-bearing mineral and the type of cleaning equipment employed also affect trace element reduction. Furthermore, there is some evidence that advanced coal cleaning processes can provide higher reductions of some trace elements than conventional processes. Knowledge of the interplay between the characteristics of the trace element-bearing mineral and various types of coal cleaning equipment can be used to enhance trace element removal during coal cleaning.

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**Table 1. Trace Element Reduction by Conventional Coal Cleaning**

<u>Seam</u>	<u>Data Source</u>	<u>Ash Reduction (%)</u>	<u>Arsenic Reduction (%)</u>	<u>Mercury Reduction (%)</u>
Central App. A	CONSOL	87	58	22
Central App. B	CONSOL	88	49	39
Illinois No. 6	CONSOL	87	62	60
Pittsburgh - A	CONSOL	52	68	33
Pittsburgh - B	CONSOL	79	74	50
Pittsburgh - C	CONSOL	82	75	30
Pittsburgh - D	CONSOL	76	83	12
Pittsburgh - E	CONSOL	78	63	41
Pittsburgh	SCS	84	81	42
Upper Freeport	SCS	24	40	-191
Lower Kittanning	BCR	74	72	38
Sewickley	BCR	65	51	25
Pittsburgh	BCR	69	61	27
Pittsburgh	BCR	34	30	14
Illinois No. 6	BCR	57	20	12
Kentucky No. 9&14	BCR	51	46	24
Pratt/Utley	CQ Inc.	75	43	39
Pratt	CQ Inc.	66	42	22
Utley	CQ Inc.	43	29	26
Pratt	CQ Inc.	75	28	45
Upper Freeport	CQ Inc.	83	83	78
Upper Freeport	CQ Inc.	86	85	76
Illinois 2,3,5	CQ Inc.	61	39	28
Illinois 2,3,5	CQ Inc.	57	54	50
Kentucky No. 11	CQ Inc.	86	66	--
Kentucky No. 11	CQ Inc.	90	43	48

CONSOL - Consolidation Coal Company  
SCS - Southern Company Services, Inc.  
BCR - Bituminous Coal Research  
App - Appalachian

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**Table 2. Equipment Performance Comparison (Percent Reductions)**

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	<u>Heavy-Media Cyclone</u>	<u>Froth Flotation</u>
Ash	70	62
Chromium	63	56
Mercury	26	-20

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**Table 3. Conventional and Advanced Cleaning (ppm except where noted)**

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	<u>Raw</u>	<u>Conventional Cleaning</u>	<u>Custom Coal Advanced Process</u>
Ash Content (Wt %)	29.2	15.2	14.0
Antimony	0.80	0.48	0.26
Arsenic	14.0	7.2	3.5
Cadmium	0.20	0.63	0.34
Chromium	16.07	8.35	8.22
Cobalt	0.27	0.24	0.22
Lead	14.73	6.96	6.16
Mercury	0.16	0.14	0.14
Nickel	13.39	9.13	8.21
Selenium	1.14	1.54	1.24

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## POTENTIALLY HAZARDOUS TRACE ELEMENTS IN KENTUCKY COALS

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Keywords: Trace elements, coal cleaning, elemental partitioning

### INTRODUCTION

The minor and major trace elemental content of coal is of great interest because of the potentially hazardous impact on human health and the environment resulting from their release during coal combustion. Of the one billion tons of coal mined annually in the United States, 85-90% is consumed by coal-fired power plants.<sup>1</sup> Potentially toxic elements present at concentrations as low as a few  $\mu\text{g/g}$  can be released in large quantities from combustion of this magnitude.

The 1990 Amendments to the Clean Air Act listed 12 elements found in coal as being potentially subject to control: Sb, As, Be, Cl, Cd, Co, Cr, Pb, Hg, Mn, Ni, and Se. In this study the partitioning of these and other elements during coal combustion and advanced cleaning processes has been investigated. Elemental concentrations were measured in the fractions obtained before and after combustion or cleaning using external beam particle induced X-ray emission (PIXE). PIXE is a rapid, instrumental technique that, in principle, is capable of analyzing all elements from sodium through uranium without chemical interference effects. In practice more than 20 elements are routinely determined with sensitivities as low as 1  $\mu\text{g/g}$ .

### EXPERIMENTAL

#### Sample Preparation

**Combustion studies.** Samples of feed coal, fly ash, and bottom ash were collected from two western Kentucky coal-fired power plants (Plants A and B). Each sample was ground to -225 mesh and dried at 105°C overnight. The ash samples were mixed with dried, high-purity graphite to obtain ~30% by weight of ash. Each coal and ash/graphite sample was pressed into a 1 mm x 19 mm pellet.

**Coal cleaning studies.** A sample of run of mine coal from the Kentucky #9 seam was collected at the mine site, and split into subsamples as needed. Each subsample was ground to -325 mesh and a 5% (w/v) slurry was prepared. The slurry was subjected to Denver floatation, and the float fraction was further subjected to hydrothermal leaching using either a NaOH or HNO<sub>3</sub> solution. The duration, temperature, and pressure of the leaching process were varied to ascertain their influence, if any, on the removal of trace elements. The clean coal was dried at 50°C overnight, and pressed into a pellet as described above.

#### Experimental Setup

The samples were irradiated with an external 1.6 MeV and 2.1 MeV proton beam. The beam, at an angle of 23° relative to the sample surface, was swept over the target to irradiate a 16 mm diameter area. The sample chamber was flushed with helium at atmospheric pressure to reduce sample heating and charging. X-rays were detected with a Si(Li) detector (FWHM resolution of 160 eV at 5.90 keV) placed at an angle of 45° relative to the incident beam. The irradiation time for each sample was 15 minutes. A typical PIXE spectrum of a coal sample is shown in Figure 1. Similar spectra are obtained from the analysis of fly ash and bottom ash. Data analyses were performed using the GUPIX<sup>2</sup> PC-based software.

### RESULTS & DISCUSSION

**Combustion studies.** Enrichment factors, shown in Figures 2 and 3, are used to illustrate the partitioning behavior of elements during coal combustion. The enrichment factor, EF, for element X is given by:

$$EF = \frac{[X]_{ash} / [X]_{feed\ coal}}{[Al]_{ash} / [Al]_{feed\ coal}}$$

The ratio of the concentration of X in the ash and feed coal is calculated relative to the ratio of the concentration of Al in the same

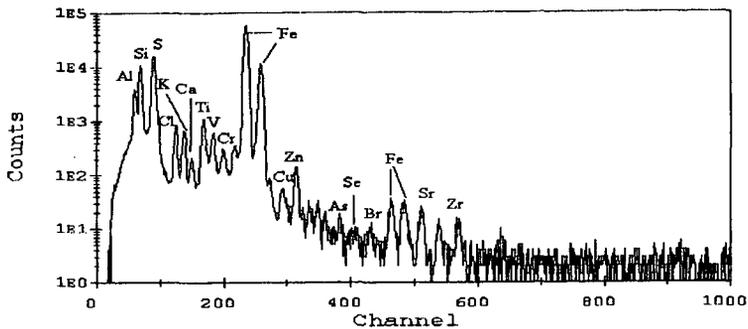


Figure 1. Typical PIXE spectrum of coal.

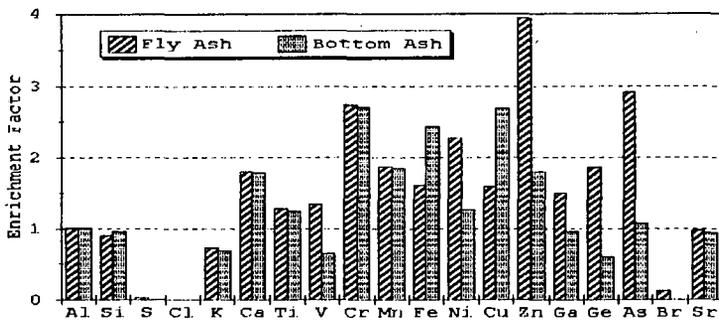


Figure 2. Enrichment factors for Plant A.

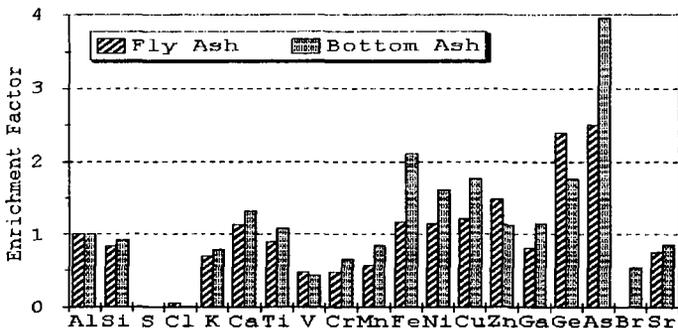


Figure 3. Enrichment factors for Plant B.

ash and feed coal samples because Al is known to partition equally between the fly ash and bottom ash. The partitioning of elements observed in Plant A is consistent with accepted partitioning behavior.

However, different results were obtained from Plant B samples. Figure 3 illustrates that the majority of the elements were more enriched in the bottom ash than in the fly ash: Ca, Ti, Cr, Mn, Fe, Ni, Cu, Ga, As, and Br. This unusual enrichment in the bottom ash was thought to be due to the addition of tailings from the coal cleaning processes to the bottom ash. Plant operators later confirmed the use of this practice at the plant.

**Coal cleaning studies.** Concentration factors were used to evaluate the effectiveness of the hydrothermal leaching coal cleaning process. The concentration factor, CF, for element X is given by:

$$CF = \frac{[X]_{\text{clean coal (hydrothermal leaching)}}}{[X]_{\text{float fraction (Denver floatation)}}$$

Thus, a  $CF < 1$  indicates a reduction in the concentration of that element as a result of hydrothermal leaching. A comparison of the CFs obtained using NaOH and  $HNO_3$  as the chemical leaching agents is shown in Figure 4. The increase observed in the concentration of some elements (i.e.  $CF > 1$ ) could be the result of these elements being leached from reactor components. The increase may also be due to a contaminated leaching solution. It should be noted, however, that the elements whose concentration did increase are not of significant environmental concern.

$HNO_3$  was more effective than NaOH in reducing elemental concentrations for all elements except V and Ga. When  $HNO_3$  was the leaching agent most elements were removed very efficiently ( $CF < 0.5$ ). The degree to which elements are removed by coal cleaning processes depends to a great extent on their mode of occurrence or chemical association in the coal. Although the exact composition can vary greatly from one coal to the next, generalizations have been made concerning common modes of occurrence for trace elements in coal.<sup>3,4,5</sup> Mg, Ca, Mn, and Sr have a carbonate association in some coals. This would explain their efficient removal since the solubilities of carbonates increase in acidic solutions. Elements known to have an association with pyrite, Fe, S, As, Zn, Ni, and Ga, all show a significant decrease in concentration. Similarly, a considerable reduction in elements known to be strongly associated with silicates, Si, Al, Mg, and K, was observed. The reduction in Cl and Br concentrations by both NaOH and  $HNO_3$  treatment could indicate they are present as soluble salts.

Elements thought to have a significant organic association were removed less efficiently by  $HNO_3$ . In these samples, those elements were

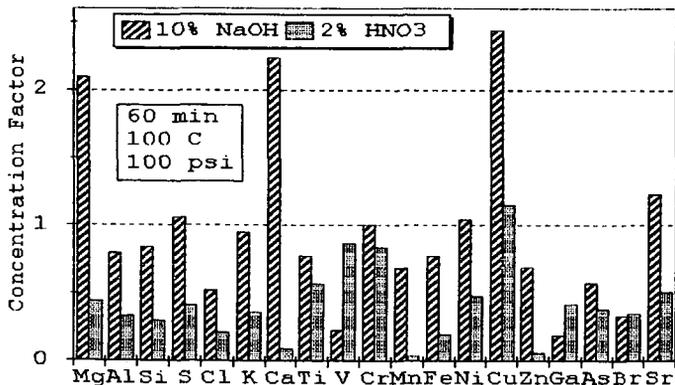


Figure 4. Concentration factors for NaOH and  $HNO_3$ .

V, Cr, Ti, and Cu. X-ray absorption fine structure spectroscopy of Kentucky #9 coal has indicated a partial organic association for V, Cr, and Ti. Although the association of Cu has not been determined in these samples, Cu is known to have partial organic associations in other coals.

The effect of other variables in the hydrothermal leaching process are illustrated in Figures 5-7. Increases in the duration, pressure and temperature of the hydrothermal leaching process showed essentially no improvement in the reduction of elemental concentrations for some elements and only slight improvements for others. Thus, it appears these variables have minimal impact on the effectiveness of this coal cleaning process.

**SUMMARY**

The partitioning of elements during coal combustion is influenced by the mode of occurrence of the elements in the feed coal, boiler characteristics, and the volatility of the species present. Therefore it is not unusual to observe differences in the partitioning of elements

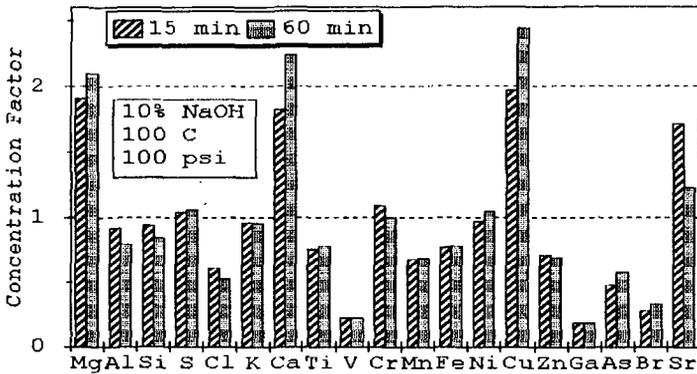


Figure 5. Concentration factors for different leaching time periods.

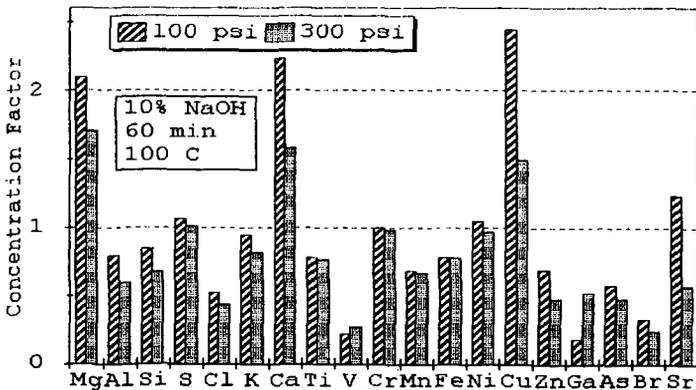


Figure 6. Concentration factors for different pressures.

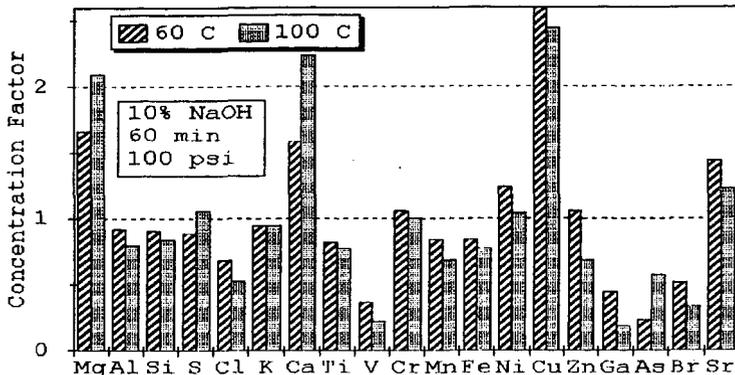


Figure 7. Concentration factors for different temperatures.

at different coal-fired power plants using different feed coal. Nevertheless, the differences observed in this study are more likely caused by the addition of wastes from coal cleaning processes to the bottom ash of Plant B.

The variable with the greatest impact on hydrothermal leaching appears to be the leaching chemical itself. A significant reduction in the concentration of many elements was observed with the use of  $\text{HNO}_3$  as the leaching agent. Present data suggests other variables in the process have only slight impact on the removal of hazardous elements in coal. Work is ongoing to optimize the overall system to obtain the lowest possible elemental concentrations.

Of the 12 "air toxics" listed in the 1990 Clean Air Act Amendments Cl, Cr, Mn, Ni, and As were analyzed in this work. The remaining seven elements not analyzed were present at levels below the sensitivity of our experimental system, however future work on these samples will include analyzing for these elements using neutron activation analysis.

#### ACKNOWLEDGEMENTS

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# SCREENING OF CARBON-BASED SORBENTS FOR THE REMOVAL OF ELEMENTAL MERCURY FROM SIMULATED COMBUSTION FLUE GAS

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**Keywords:** Sorbents, Mercury, Flue Gas

## ABSTRACT

A fixed-bed reactor system with continuous Hg<sup>0</sup> analysis capabilities was used to evaluate commercial carbon sorbents for the removal of elemental mercury from simulated flue gas. The objectives of the program were to compare the sorbent effectiveness under identical test conditions and to identify the effects of various flue gas components on elemental mercury sorption.

Sorbents tested included steam-activated lignite, chemically activated hardwood, chemically activated bituminous coal, iodated steam-activated coconut shell, and sulfur-impregnated steam-activated bituminous coal. The iodated carbon was the most effective sorbent, showing over 99% mercury removal according to U.S. Environmental Protection Agency (EPA) Method 101A. Data indicate that adding O<sub>2</sub> at 4 vol% reduced the effectiveness of the steam-activated lignite, chemically activated hardwood, and sulfur-impregnated steam-activated bituminous coal. Adding SO<sub>2</sub> at 500 ppm improved the mercury removal of the sulfur-impregnated carbon. Further, the presence of HCl gas (at 50 ppm) produced an order of magnitude increase in mercury removal with the chemically activated and sulfur-impregnated bituminous coal-based carbons.

## INTRODUCTION

Coal combustion and gasification processes together with industrial and commercial operations, such as waste incineration, emit significant quantities of trace elements to the atmosphere each year (1). The 1990 Clean Air Act Amendments have identified eleven trace elements (beryllium, chromium, manganese, cobalt, nickel, arsenic, selenium, cadmium, antimony, lead, and mercury) for control because of their potential harmful effects to the ecosystem. Mercury (along with arsenic and selenium) is of particular concern because it can occur in vapor or submicron fume form, and as such conventional collection devices (precipitators and baghouses) are marginally effective for its removal (2).

Trace element control strategies have recently focused on disposable or regenerable sorbents (activated carbons, coke, limestone) that can be injected as powders directly into flue gas streams or utilized in fluid-bed or fixed-bed reactors. However, homogeneous or heterogeneous reactions with other flue gas constituents (HCl, O<sub>2</sub>) can occur. Identifying and controlling these reactions are important in determining the effectiveness of sorbents to capture particular species, e.g., metallic mercury, mercuric chloride, or mercuric oxide. Further, other gases such as carbon monoxide, nitrogen dioxide, and sulfur dioxide have the potential to interfere with the effective sorption of mercury species.

The overall objective of the ongoing project is to identify the conditions (temperature and flow rates) and the controlling processes (mercury species and concentration, flue gas components) for the most effective capture of trace elements by carbon sorbents in combustion and gasification systems.

## EXPERIMENTAL

### *Apparatus and Procedure*

The mercury sorbent test apparatus consists of four main subsystems: 1) flue gas generation, 2) mercury injection, 3) sorbent-flue gas contactor, and 4) effluent gas mercury analysis (with data logging). A diagram of the test apparatus is presented in Figure 1.

The simulated flue gas, which can contain N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, HCl, and NO<sub>2</sub>, is generated in a manifold system; rotameters provide volume flow control. Elemental mercury vapors are generated with a permeation tube(s). The permeation tube mercury desorption rate, and consequently, the simulated flue gas mercury concentration, is a function of the permeation tube's N<sub>2</sub> sweep gas equilibrium temperature. Permeation tube temperature control, to within 0.1°C of setpoint, is provided by a condenser heated with circulating heat-transfer fluid.

A U.S. Environmental Protection Agency (EPA) Method 5 in-stack particulate sampling filter is used as a sorbent bed containment device. The interior of the filter assembly, including filter support grid, and all other components in contact with the mercury-laden gas are Teflon-coated. The filter assembly and influent tubing are electrically heated to maintain the desired temperature and prevent condensation. A downflow configuration is used to minimize entrainment of powdered sorbents. The filter static and

differential pressures are monitored using pressure gauges. The filter assembly can be equipped with a thermocouple to measure the flowing gas temperature.

The elemental mercury concentration in the simulated flue gas stream is continuously monitored using a DuPont Model 400 ultraviolet (253.7 nanometer) photometric analyzer. A Buck Scientific Model 400 cold-vapor ultraviolet analyzer has also been used to monitor the filter inlet mercury concentration. Mercury concentration values from the analyzers are continuously logged to a chart recorder; a data acquisition unit coupled with a lap-top computer has been used to log mercury analyzer output data and select system temperatures. Diaphragm-type and bubble-type gas meters have been used to measure the total gas rate.

#### *Sorbents*

The following five commercial activated carbons were evaluated as elemental mercury sorbents: 1) chemical-activated hardwood (AC1), 2) steam-activated lignite (AC2), 3) 5% sulfur-impregnated steam-activated bituminous coal (AC3), 4) chemically activated bituminous coal (AC4), and 5) 10% iodine-impregnated steam-activated coconut shell (AC5). The activated carbons were tested as powders; the sulfur and iodine impregnated carbons were obtained in granular form and then comminuted to a nominal 200-mesh (75-micron) top size.

#### *Tests Performed*

Twenty-seven tests were performed using the five sorbents. Test variables included sorbent type, O<sub>2</sub> concentration (0 or 4 vol%), SO<sub>2</sub> concentration (0 or 500 ppm), and HCl concentration (0 or 50 ppm). Common test parameters were as follows: a nominal mercury concentration of 100 µg/m<sup>3</sup>, gas rate of 26 scfh, filter assembly gas temperature of 150°C (300°F), and sorbent mass of 0.20 g. The tests are summarized below.

- Six tests, one each with AC1 and AC2 and two each with AC3 and AC5, used 100 vol% N<sub>2</sub> as the simulated flue gas
- Five tests, one each with AC1, AC2, AC3, AC4, and AC5, used 4 vol% O<sub>2</sub>, 96 vol% N<sub>2</sub> as the simulated flue gas
- Thirteen tests, two each with AC1 and AC2 and three each with AC3, AC4, and AC5, used a simulated flue gas composed of 4 vol% O<sub>2</sub>, 96 vol% N<sub>2</sub>, plus 500 ppm SO<sub>2</sub>
- Three tests, two with AC3 and one with AC4, used 4 vol% O<sub>2</sub>, 96 vol% N<sub>2</sub>, plus 500 ppm SO<sub>2</sub> and 50 ppm HCl as the simulated flue gas

EPA Method 101A (3) was applied to the filter assembly influent and effluent simulated gas streams during one test with the AC5 (iodated carbon) in the presence of O<sub>2</sub> + SO<sub>2</sub>. This test was performed to quantify total mercury removal by the carbon and to compare the result against the general trend of the ultraviolet analyzer output. Further, the test was applied to assess if elemental mercury was being converted to an oxidized form in the presence of AC5, and thus not adsorbed by the carbon or detected by the ultraviolet analyzer, but collected by the permanganate solution of EPA Method 101A.

Similarly, EPA draft Method 29 (4) was applied to the filter effluent stream in the single test with the AC4 (chemically activated bituminous coal) in the presence of O<sub>2</sub> + SO<sub>2</sub> + HCl. Similarly to the test with AC5, this test was applied to assess if elemental mercury was being converted to oxidized and/or chloride forms in the presence of AC4. With this test, chloride forms of mercury would be collected in the peroxide solution.

The test duration for each EPA method was one half-hour. The EPA Method 101A permanganate solution and draft Method 29 peroxide and permanganate solutions were analyzed by cold-vapor atomic adsorption using a Leeman Labs PS200 automated mercury analyzer.

## **RESULTS AND DISCUSSION**

The effluent gas from the filter assembly was monitored for <100% mercury capture and 0% mercury capture (breakthrough). Adsorption curves, which show the mercury removal efficiency as a function of gas-sorbent contact time, are presented in Figures 2 and 3 for tests conducted with 0 and 4 vol% O<sub>2</sub>, respectively.

Tests at 0 vol% O<sub>2</sub> indicated that AC1 and AC3 each exhibited an instantaneous lowering of Hg<sup>0</sup> removal efficiency to 46% and 10%, respectively. Breakthrough with these respective carbons was achieved in approximately 4 and 24 minutes. The AC2 exhibited a slower loss of mercury removal efficacy, achieving breakthrough in approximately 30 minutes. Tests with 4 vol% O<sub>2</sub> indicated that AC1, AC2, and AC3 showed similar instantaneous losses of mercury removal efficiency but with more rapid attainment of breakthrough, 0.5, 18, and 10.5 minutes, respectively, than tests without oxygen. The AC4, first used in tests with O<sub>2</sub>, exhibited superior mercury removal efficiency relative to the AC1, AC2, and AC3 sorbents, achieving breakthrough after 94 minutes.

The AC5 iodated carbon appeared to be vastly superior to the other carbons in tests with and without O<sub>2</sub>. The baseline analyzer output indicates that elemental mercury was 100% adsorbed when using 0 vol% oxygen after over 20 hours; a replicate test produced identical results. As was observed with AC5 in tests without O<sub>2</sub>, elemental mercury was 100% adsorbed even after 112 minutes, a test duration almost 20 minutes longer than the next most effective sorbent.

The addition of SO<sub>2</sub> appeared to have a selective influence on mercury removal efficiency relative to that of O<sub>2</sub>. A plot of the sorbent contactor effluent gas mercury concentration is shown in Figure 4 for tests performed using 4 vol% O<sub>2</sub> and 500 ppm SO<sub>2</sub> combined. Trends are similar to those from tests performed without SO<sub>2</sub> in that AC1 and AC2 are the least effective sorbents, showing an instantaneous loss in removal efficiency and the most rapid attainment of breakthrough. Similarly to tests without SO<sub>2</sub>, AC5 (iodated carbon) retained essentially 100% removal efficiency. However, AC3 showed a slower loss of effectiveness relative to AC1 and AC2, with a breakthrough time 50% longer than that with AC2.

The EPA Method 101A test using AC5 indicated that elemental mercury was removed by this carbon at a high level of effectiveness. The mass concentration of mercury in the effluent and influent permanganate solutions, 78 µg and 0.2 µg per one-half liter, respectively, indicated that mercury removal was over 99 wt%, agreeing well with analyzer output data. However, the sorption data or its analyses do not provide evidence of any conversion of mercury to oxidized form.

The results of tests performed with AC3 and AC4 using 50 ppm HCl indicated evidence of interaction or reactions that enhance mercury removal efficiency. A monitoring plot of effluent gas mercury concentration as a function of gas contact time (or total mercury flow) is presented in Figure 5 for a test performed with AC3. The sawtooth curve shows the change in mercury concentration, and presumably mercury removal efficiency, effected by starting and stopping the HCl gas flow. The straight baseline, which indicated nearly 100% mercury removal with flowing HCl, contrasts with the curve for AC3 in Figure 4, generated without HCl. During the periods without HCl injection, the mercury concentration curve exhibited a similar, slow degradation in mercury removal as seen in Figure 4. Upon injection of HCl, the return to essentially 100% mercury removal was immediate.

A replicate test with AC3 and a single test with AC4 using 50 ppm HCl produced similar results. The EPA (draft) Method 29 with AC4 showed that elemental mercury was removed at a high level of effectiveness. The mass concentration of mercury in the effluent peroxide and permanganate solutions, 0.3 and 1.9 µg per one-half liter, indicated that mercury removal was over 97 wt%, agreeing with the analyzer output. The quantitation of mercury in the peroxide trap further suggests that chloride forms of mercury were produced, and, as such, were removed by the AC4.

## CONCLUSIONS

The AC5 (iodated) activated carbon appeared to be the consistently superior sorbent regardless of the simulated flue gas atmosphere; AC1 (chemically activated hardwood) was consistently the least effective. Adding O<sub>2</sub> at 4 vol% apparently reduced the effectiveness of all carbons except the iodated carbon. The effect of adding SO<sub>2</sub>, however, appeared to more selective, increasing the effectiveness of the sulfur-impregnated carbon relative to the other carbons. Adding HCl at 50 ppm had the apparent effect of enhancing the mercury removal efficiency of the sulfur-impregnated and chemically activated bituminous coals to a level comparable to the iodated carbon.

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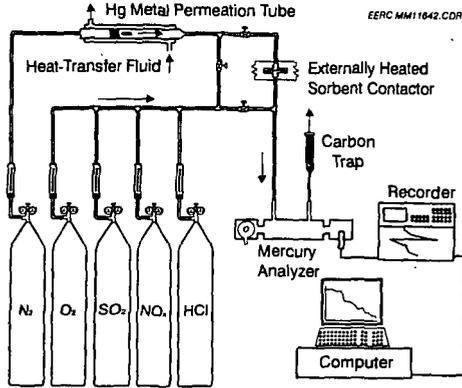


Figure 1. Mercury sorbent test apparatus.

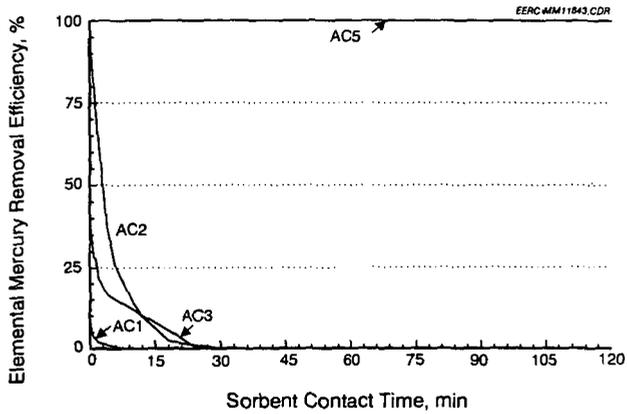


Figure 2. Mercury removal efficiency curve, 0 vol% O<sub>2</sub>.

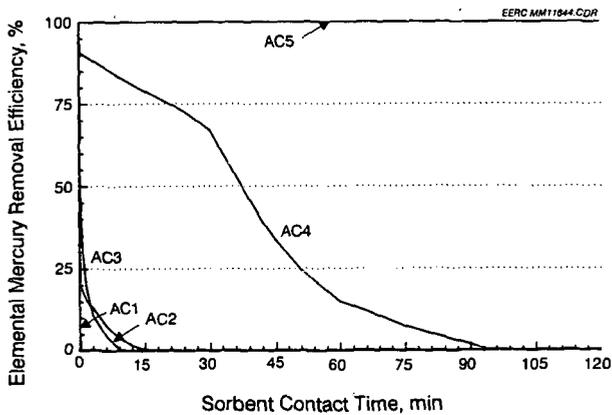


Figure 3. Mercury removal efficiency curve, 4 vol% O<sub>2</sub>.

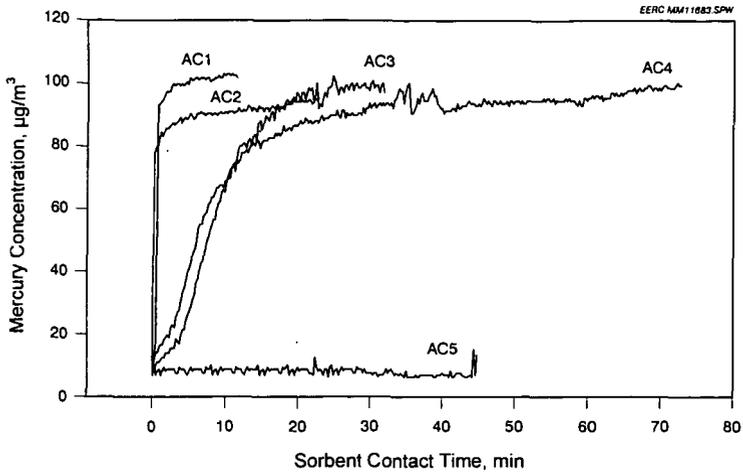


Figure 4. Comparative effectiveness of activated carbons for elemental mercury sorption; 4 vol% O<sub>2</sub> and 500 ppm SO<sub>2</sub>.

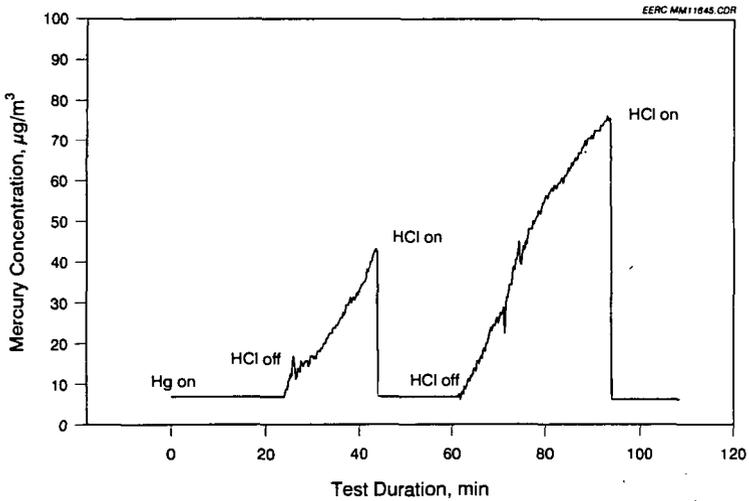


Figure 5. Mercury sorption by sulfur-impregnated steam-activated bituminous coal (AC3); 4 vol% O<sub>2</sub>, 500 ppm SO<sub>2</sub>, 50 ppm HCl.

## PRODUCTION OF ACTIVATED CHAR FOR CLEANING FLUE GAS FROM INCINERATORS

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Keywords: Incinerator flue gas cleaning, activated carbon, dioxins and furans

### ABSTRACT

A granular activated coal char suitable for removing dioxins, furans, mercury, particulate matter, HCl, HF and SO<sub>2</sub> from incinerator flue gas has been produced from the Colchester (Illinois No. 2) coal. Tests with 250 kilogram of this adsorbent on flue gas from a commercial incinerator in Europe demonstrated that its efficiency for removing dioxins and furans was 99.72% to 99.98%. Mercury concentration in the flue gas after the adsorbent was too low to be detected; an efficiency for mercury removal could not be calculated. This adsorbent was produced in three steps from 1 mm by 6.4 mm coal obtained from a commercial Illinois washing plant. The projected cost for manufacturing the adsorbent is lower than that of carbon adsorbents commercially available in the United States (U.S.). The estimated break even cost for the adsorbent from an 80,000 ton/year plant is \$326/ton with a 20% return on investment and a cash flow for 20 years discounted 20% annually.

### INTRODUCTION

The U.S. is expected to follow the European lead by imposing low limits for several pollutants from incinerators. The legal emission limits for European waste incinerators were tightened significantly in the late 1980's. Current regulations impose a drastic lowering of the emissions of HCl, HF, SO<sub>2</sub>, and mercury on all new incinerators (Table 1) [1]. These regulations apply to existing incinerators in Germany and the Netherlands now, and in Austria by 1996. For the first time emissions of dioxins and furans have been targeted, and are not to exceed 0.1 ng Toxicity Equivalents (TE)/m<sup>3</sup> Standard Conditions (SC).

An activated carbon process, developed in the 1970's by STEAG AG of Essen, Germany, to eliminate SO<sub>x</sub> and reduce NO<sub>x</sub> emissions, has also shown high removal efficiencies for inorganic and organic compounds such as HCl, heavy metals, dioxins and furans (Table 2) [1]. The first commercial plant using STEAG's activated carbon technology (/a/c/t<sup>TM</sup>) for cleaning flue gas from a waste incinerator began operation in 1991. Other medical, hazardous and municipal waste incinerators with flue gas outputs of 6,500 m<sup>3</sup>/h SC to 155,000 m<sup>3</sup>/h SC have been equipped with this process. Four plants were operating in Europe in 1993 using STEAG's /a/c/t<sup>TM</sup>-process and three more will be on line cleaning an additional 1.3 MM m<sup>3</sup>/h by year's end. STEAG has begun licensing its process in the U.S.

Staff members of the Illinois State Geological Survey (ISGS) became aware in 1993 that a U.S. supplier of a carbon adsorbent suitable for STEAG's /a/c/t<sup>TM</sup>-process was needed [1]. To be acceptable the adsorbent must pass a NO<sub>x</sub> self heating test. In this test, the adsorbent is saturated with nitric oxide and the gas flow is discontinued. The temperature rise due to the heat of reaction is measured. It is typically related to the surface area. STEAG's European licensees use adsorbent called German Herdofenkoks that is manufactured from a German brown coal (lignite). This adsorbent has a surface area less than 300 m<sup>2</sup>/g (N<sub>2</sub> BET). Carbons commercially available in the U.S. have higher surface areas and are reported to fail this test. Not only this safety problem but also the prices for U.S. carbons preclude their use in STEAG's once-through process. The Herdofenkoks adsorbent was reported to sell in Europe for the equivalent of \$300(U.S.)/ton in May 1995.

Mild gasification (MG) of Illinois coals and research on the char that accompanies this process have been active areas of research at the ISGS since the early 1980s [2]. Recent results show that, by selecting appropriate conditions during MG and following MG with a low temperature (< 475°C) oxidation step, a high-sulfur Illinois coal that emits more than 5 lbs SO<sub>2</sub>/MMBtu can be converted to char that emits less than 2.5 lbs SO<sub>2</sub>/MMBtu [3,4,5]. This partial gasification by low temperature oxidation not only lowers the sulfur content but also activates the chars providing a product that has as much as 300 m<sup>2</sup>/g N<sub>2</sub> BET surface area [6]. These results encouraged ISGS researchers to believe an adsorbent satisfactory for a STEAG /a/c/t<sup>TM</sup> type process could be produced from an Illinois coal without the extensive cleaning to remove ash, extensive preoxidation times ("baking") and the briquetting that are a part of costly steps required to make high surface area activated carbon.

### EXPERIMENTAL

#### Coal

Freeman United Coal Company has a size consist of zero by 6.4 mm at one point in its plant that cleans the Colchester seam coal mined near Industry, Illinois. Twelve barrels of this size consist was made available by Freeman United Coal Company for the work described herein. It was spread at about two to four inches depth on the floor to dry overnight before removing the minus 16 mesh (< 1 mm) material by screening. A typical analysis for the Colchester coal appears in Table 4.

#### Equipment

Pound quantities of activated char were produced in a Model RT-472-104 continuous feed rotary tube kiln (CFRK), manufactured by the Pereny Equipment Company, Inc., of Columbus, Ohio. The CFRK consists of a 10.2 cm ID, 1.83 m long rotating tube of HX alloy. The center portion of the tube (1.4 m) is heated by three separate electrically heated furnaces. The sample is introduced into the tube using a screw type feeder.

A **continuous feed charring oven (CFCO)** was also used in the pyrolysis step because it was better suited to handle large amounts of tar evolved in longer runs. The coal sample was conveyed through a 15.2 cm x 15.2 cm x 69 cm oven on a belt of close-fitting, overlapping, stainless-steel trays (12.7 cm wide) attached to links of a chain drive and heated above and below by tubular electric heating elements. A hopper that controls the bed depth fills the trays as they enter the oven. Evolved gases are removed counter to the direction of the coal and are drawn out an exhaust pipe where volatile materials are burned before being released into the fume hood. All areas outside the heating zone are enclosed in a reasonably tight sheet-metal housing which may be purged with nitrogen to exclude air and avoid loss of char due to burning. Chars were prepared in the CFCO using feed rates of 1-4 pounds per hour, bed depths of 8-20 mm, temperatures of 400-500°C and residence times of 0.25-0.75 h.

A 50 cm I.D. x 1.22 m long (19.5" x 4') (active heated length), stainless steel shell, **batch rotary kiln (BRK)** manufactured by AMS was heated by natural gas burners. It had internal material bed disturbers, bed and gas thermocouples, system thermocouples, and off-gas combustion chamber. Nitrogen or steam purging and a nitrogen cooled sampling probe were available. The maximum operating temperature was 1000°C. A 10% loading required 0.83 cubic feet of coal.

A 20 cm x 0.91 m (8"x36") **continuous feed rotary kiln (CFRK)** was heated by 7 gas burners monitored by three external and two internal thermocouples. The feeder was an AMS fashioned volumetric belt that fed 13.2-15.4 kg (6-7#/h) and the cooler a 35.5 cm x 2.29 m long (14" x 7.5') kiln. The off-gas combustor was the one described for the BRK.

A 48 cm x 3 m (18"x10'), indirect fired, **continuous feed rotary kiln (CFRK)** had a variable rotational speed, adjustable slope and a high velocity pulsating burner system (4 burners in the first two zones, 3 in the last zone). The Inconel 601 shell, No. 10 gage thickness, had six 2.54 cm high anti-slide bars. Auxiliary equipment included a 38 cm x 3.7 m (15"x12') rotary cooler (direct air or indirect water), secondary combustion chamber, and a 24 point continuous data logger. This CFRK could accommodate about 200 kg/h (90#/h) feed rate.

Single-point **BET surface areas** of prepared chars were determined from N<sub>2</sub> (77 K) adsorption data obtained at a relative pressure ( $P/P_0$ ) of 0.30 with a Monosorb flow apparatus (Quantachrome Corporation).

The kinetics of **SO<sub>2</sub> adsorption** on selected chars was determined using a Cahn TG-131 thermogravimetric analyzer (TGA) system. In a typical run, a 30-50 mg char sample was placed in a platinum pan and heated at 20°C/min to 120°C in flowing nitrogen. Once the temperature stabilized, the nitrogen flow was switched to one containing 5% O<sub>2</sub>, 10% H<sub>2</sub>O and the balance nitrogen. Once the weight stabilized, the SO<sub>2</sub> was added in concentrations representative of a typical flue gas (e.g. 2500 ppmv SO<sub>2</sub>). The weight gain versus time was recorded by a computerized data acquisition system.

## DISCUSSION OF RESULTS

Colchester coal, a high volatile C bituminous coal with a free swelling index of 3 or more, swells, melts, and agglomerates while being charred if it has not been air oxidized. An oxidation step was necessary (1) to maintain approximately the same particle size in the final product as that existing in the 1 mm by 6.4 mm starting material and (2) to retain sufficient initial pore structure to produce the porosity needed in the final product by partial gasification of the char. Surface area is difficult to develop if coal has passed through a melting stage, but loss of particle strength occurs if too much preoxidation occurs. To achieve the desired result in as short a residence time as practical, as high an air oxidation temperature as possible was selected while allowing a margin of safety in avoiding a loss of control due to burning. Conditions of time and temperature during oxidation were selected that gave a preoxidized coal that could be pyrolyzed at 450 to 500°C to provide char that could be activated at 850°C in CO<sub>2</sub> to increase surface area to 150-250 m<sup>2</sup>/g (N<sub>2</sub> BET)(Table 3) [7,8]. Observe that decreasing the amount of oxidation either by lowering the temperature or decreasing the time resulted in less surface area. The selection of carbon dioxide for developing added porosity at 850°C was influenced by previous experience [9]. This gas provided a flexibility in temperature control not available with steam.

After demonstrating the three-step preparation (preoxidation, pyrolysis and activation) at the ISGS, Allis Mineral Systems (AMS) was engaged to scale up production in equipment located at its Process Research and Test Center in Oak Creek, Wisconsin [10]. The first successful production level at Oak Creek was preoxidation in a 50 cm diameter batch rotary kiln (BRK) with pyrolysis and activation in a 20 cm CFRK. The largest scale production of adsorbent at Oak Creek involved performing all three steps in succession in the 48 cm diameter CFRK which accommodated a feed rate as high as 90 lbs/h. An attempt to conduct all three steps in the batch kiln was unsuccessful; the tar was not removed at a rate sufficient to avoid agglomeration. The importance of removing volatile components as quickly as possible was reinforced during the transition from the preoxidation step to the pyrolysis step in the 48 cm CFRK. About 90 pounds of preoxidized coal remained in the kiln when the kiln temperature was increased rapidly to the pyrolysis temperature. Some agglomeration occurred which may have approached 7 wt% of the final product.

The Oak Creek kilns had dams at the exit end that maintained a bed occupying 10% of the cross sectional area. The ISGS kiln did not have a dam and the bed occupied considerably less than 10% of the cross sectional area. The thicker bed depth decreased the amount of solids exposed to

reaction gas in the preoxidation and activation steps. This meant that each progression to a larger kiln required more time to achieve equivalent products.

A comparison of properties of the German Herdofenkoks and the ISGS Colchester adsorbent is presented in Table 5. The lower density of the ISGS Colchester adsorbent reflects a lower level of preoxidation than ideal (some swelling). The lower surface area, 110 m<sup>2</sup>/g, than those obtained in the lab scale of operation, 151-236 m<sup>2</sup>/g (Table 3) reflect a combination of less preoxidation and less activation in the larger kiln. The SO<sub>2</sub> adsorption profiles shown in Figure 1 confirm that the scale up fell short of reaching the full potential of SO<sub>2</sub> capacity possible with Colchester coal. Additionally, this profile shows a much higher rate of SO<sub>2</sub> adsorption in the first few hours. The initial SO<sub>2</sub> uptake is best correlated with active sites, those responsible for the oxidation of SO<sub>2</sub> to SO<sub>3</sub> [11]. Another factor to be considered in the difference in filling rate is the pore structure. There is reason to believe that the pore structure of the Colchester adsorbent differs significantly from that of the Herdofenkoks adsorbent [11]. It remains to be shown how much of this difference in SO<sub>2</sub> adsorption behavior is due to active sites and how much is related to a special network geometry in which outer macro pores feed into interior micro pores. Of practical importance for use in a STEAG /a/c/t<sup>TM</sup>-process, is the lower rate of uptake of nitric oxide (Figure 2) by the ISGS Colchester adsorbent.

The preliminary effort to establish a break even cost was based on the flow diagram shown in Figure 3. While the estimate of \$326/ton (Table 7) for product from an 80,000 ton/year plant is very preliminary, it is encouraging for at least one reason. The flow diagram does not reflect economics in residence time under conditions of better gas/solid contact that are known to accompany the use of modified kilns or other types of equipment. The data (Table 6) in STEAG's pilot scale adsorbent, including passing the NO<sub>x</sub> self heating test (not shown), qualify this material for use in STEAG's /a/c/t<sup>TM</sup>-process.

## CONCLUSIONS

Research has demonstrated that Colchester (Illinois No. 2) coal is a promising feedstock for producing an activated char adsorbent for removing pollutants from incinerator flue gas. Not only are the properties of this adsorbent those desired, its estimated break even cost in a dedicated commercial facility, \$326/ton, could make it highly competitive for use in cleaning incinerator flue gas in the U.S. The ISGS Colchester adsorbent is the first adsorbent to be made in the U.S. from a domestic coal that meets requirements of the STEAG /a/c/t<sup>TM</sup>-process.

## ACKNOWLEDGEMENT & DISCLAIMER

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Table 1. Emission Limits for European Waste Incinerators [1]

	Germany One day mean values	Netherlands One hour mean values	Austria Half hour mean values
Total Dust (mg/m <sup>3</sup> )	10	5	15
HCl (mg/m <sup>3</sup> )	10	10	10
HF (mg/m <sup>3</sup> )	1	1	0.7
SO <sub>2</sub> (mg/m <sup>3</sup> )	50	40	50
NO <sub>x</sub> (mg/m <sup>3</sup> )	200 <sup>1</sup>	70	100
Hg (mg/m <sup>3</sup> )	0.05	0.05	0.05
Dioxins & Furans (ng TE/m <sup>3</sup> )	0.1	0.1	0.1

<sup>1</sup> Federal standards, local standards generally at 100 mg/m<sup>3</sup>

Table 2. Experience with STEAG's /a/c/t/<sup>TM</sup>-Process [1]

	Medical Waste Incinerator Germany	Medical Waste Incinerator Netherlands	Hazardous Waste Incinerator Netherlands
Total Dust (mg/m <sup>3</sup> )	< 2	1	< 0.5
HCl (mg/m <sup>3</sup> )	< 1	< 2.2	< 0.19
HF (mg/m <sup>3</sup> )	< 0.05	< 0.05	< 0.05
SO <sub>2</sub> (mg/m <sup>3</sup> )	< 2	< 0.6	< 6
NO <sub>x</sub> (mg/m <sup>3</sup> )	65	343 <sup>1</sup>	177 <sup>1</sup>
Hg (mg/m <sup>3</sup> )	< 0.01	< 0.00031	< 0.002
Dioxins & Furans (ng TE/m <sup>3</sup> )	0.003	0.00031	0.002

<sup>1</sup> Not equipped with SCR

Table 3. Lab Scale Adsorbent Preparation at the ISGS

Run #	Preoxidation in the CFRK	Pyrolysis	Activation in the CFRK	Surface Area N <sub>2</sub> BET (m <sup>2</sup> /g)
11	Air, 300°C, 2 h	CFRK, CO <sub>2</sub> , 450°C, 1 h	CO <sub>2</sub> , 850°C, 1 h	235
12	Air, 280°C, 0.5 h	CFRK, N <sub>2</sub> , 410°C, 0.5 h	CO <sub>2</sub> , 850°C, 1 h	151
13	Air, 330°C, 0.75 h	CFRK, CO <sub>2</sub> , 475°C, 1 h	CO <sub>2</sub> , 850°C, 1 h	236
14	Air, 220°C, 0.75 h	CFRK, CO <sub>2</sub> , 475°C, 1 h	CO <sub>2</sub> , 850°C, 1 h	179
15	Air, 220°C, 1.5 h	CFKO, N <sub>2</sub> , 475°C, 0.75 h	CO <sub>2</sub> , 850°C, 0.75 h	230
16	Air, 220°C, 0.75 h	CFKO, N <sub>2</sub> , 475°C, 0.75 h	CO <sub>2</sub> , 850°C, 0.75 h	180

Table 4. Typical Analysis  
Colchester Coal

Moisture	14.4%
Vol. Matter	39.9%
Fixed Carbon	53.3%
H-T Ash	6.8%
Carbon	74.3%
Hydrogen	5.3%
Nitrogen	1.4%
Oxygen	8.9%
Total Sulfur	3.3%
Sulfatic	0.1%
Pyritic	2.2%
Organic	1.1%
Btu/lb	13,645
FSI	3.8%

Table 5. Comparison of Properties  
(Yield: 48% [277 kg from 581 kg coal])

Property	German Herdfenkoks sorbsent	ISGS/AMS Colchester sorbsent
Bulk density lbs/ft (kg/m <sup>3</sup> )	29.8 (413)	23.8 (378)
PROXIMATE (moisture free)		
Hi-Temp. Ash, wt%	8.68	8.27
Volatile Matter, wt%	7.71	4.74
Fixed Carbon, wt%	83.61	86.98
N <sub>2</sub> BET Surface Area, m <sup>2</sup> /g	277	110

Table 6. Results of Testing ISGS Colchester Adsorbent in STEAG's Test Module

	Before Reactor	After Reactor	Adsorption Efficiency
<b>Total Dioxins &amp; Furans</b>			
Test 1 (ng/m <sup>3</sup> )	333.3	0.062	99.98 %
Test 2 (ng/m <sup>3</sup> )	337.9	0.052	99.98 %
Test 3 (ng/m <sup>3</sup> )	282.3	0.789	99.72 %
<b>Cd + Tl</b>			
Test 1 (mg/m <sup>3</sup> )	0.0140	0.0012	91 %
Test 2 (mg/m <sup>3</sup> )	0.0062	0.0012	81 %
Test 3 (mg/m <sup>3</sup> )	0.0052	0.0004	92 %
<b>Hg</b>			
Test 1 (mg/m <sup>3</sup> )	0.0177	below det. limit	
Test 2 (mg/m <sup>3</sup> )	0.0384	below det. limit	
Test 3 (mg/m <sup>3</sup> )	0.0223	below det. limit	
<b>Sb, As, Pb, Cr, Co, Cu, Mn, N, V, Sn</b>			
Test 1 (mg/m <sup>3</sup> )	0.2698	0.0744	72 %
Test 2 (mg/m <sup>3</sup> )	0.0805	0.0347	57 %
Test 3 (mg/m <sup>3</sup> )	0.0634	0.0185	71 %

Table 7. Estimated Break Even Cost in an 80,000 Ton/Year Plant<sup>1</sup>

Land purchase price (\$)	100,000	Cost of coal (\$/y)	7,466,667
Building cost (\$) <sup>2</sup>	5,000,000	Cost of Natural Gas (\$/y)	2,626,000
Equipment (\$) <sup>2</sup>	16,000,000	Cost of Electricity (\$/y)	526,000
Installation (\$)	8,500,000	Cost of lime (to neutralize SO <sub>2</sub> )	300,000
Carbon production (\$)	80,000	Water (2.45MM gal @ \$1/Mgal)	2,450
Percent yield	45	Labor cost	1,540,000
Coal input (t/yr)	177,778	Maintenance cost (5% of \$21MM) <sup>3</sup>	1,050,000
Coal price f.o.b. mine, sized 1 mm by 6.4 mm (\$/t)	34	Real estate taxes (\$)	153,000
Coal transportation cost (\$/t)	8	<b>BREAK EVEN COST (\$/ton)<sup>4</sup></b>	<b>326</b>

<sup>1</sup> Assume it takes one year to construct the plant, and the plant produces at design capacity thereafter.

<sup>2</sup> Depreciation (7 Yr st. line) on \$21MM.

<sup>3</sup> Operating costs are raised 3% per year.

<sup>4</sup> Interest on undepreciated value at 20%/yr, net present value at 20% discount rate, 20 years of operation.

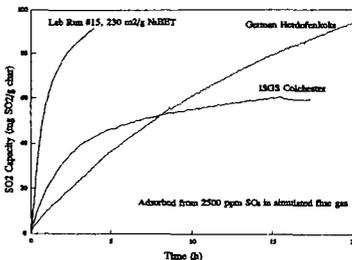


Figure 1. SO<sub>2</sub> Adsorption

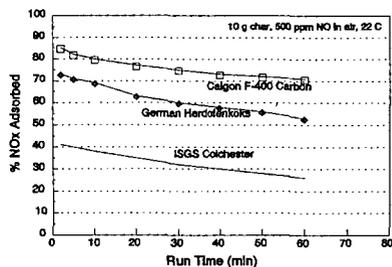


Figure 2. NO<sub>x</sub> Removal

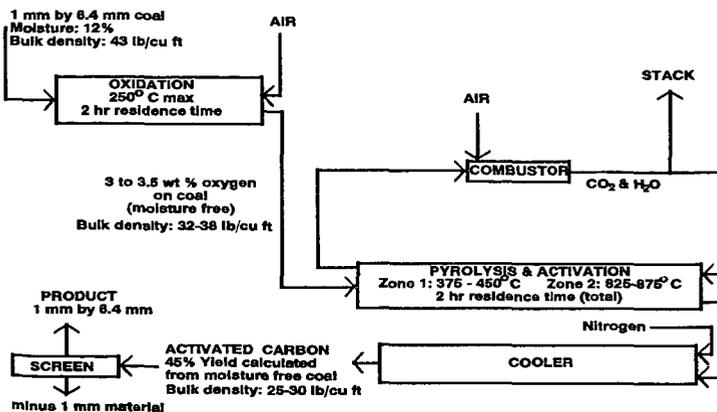


Figure 3. Flow Diagram for a Plant Producing Adsorbent from Colchester (Illinois No. 2) Coal

## PILOT PLANT STUDY OF MERCURY CONTROL IN FLUE GAS FROM COAL-FIRED BOILERS

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Keywords: Mercury control, coal-fired boilers, flue gas analysis

### BACKGROUND

Mercury control technology options for coal-fired boilers are ill-defined. Commercial development of mercury emissions control technologies has centered on high concentrations of mercury compared to the levels present in the flue gas from coal combustion, typically 5 to 10  $\mu\text{g}/\text{m}^3$ . In addition, most mercury in these commercial applications (medical waste and municipal solid waste incinerators)<sup>1,2,10</sup> is in the form of  $\text{HgCl}_2$ ; flue gas from coal-fired units contains both ionic and elemental mercury. Reaction mechanisms may be different for these two species. Development work at the lower concentrations has centered on small scale, fixed-bed, laboratory studies.<sup>3,5,7,8,9,12</sup> Recent tests at coal combustion sources with sorbents such as lime<sup>3,5,7</sup> and activated carbon<sup>8</sup> have shown some mercury removal. However, neither the laboratory nor combustion tests completely address process design issues. In the laboratory studies, the actual process conditions are very different from those with coal; while in the combustion tests, it is difficult to vary the conditions. In addition, data reliability is poor because of the difficulty of mercury sampling and analysis.

Development of mercury control technology for coal-fired flue gas requires:

1. Accurate and reliable sampling and analytical techniques, including speciation of mercury,
2. A thorough understanding of the effects of the combustion conditions and of the speciation of mercury on mercury removal,
3. Identification of sorbents and process configurations for removal of mercury at the low levels present in coal-fired flue gas, and
4. Waste management studies and economic evaluation of control technologies.

Each of these factors is important in developing a process to control mercury emissions. To this end, a 0.2 MWe equivalent, continuous flow pilot plant was constructed at CONSOL R&D to evaluate the efficiency and cost of sorbent injection technology for mercury control, and to verify mercury sampling and analysis techniques.

### DESCRIPTION OF THE FACILITY

The 0.22  $\text{Nm}^3/\text{s}$  (500 scfm) pilot plant is of sufficient size to provide a realistic process simulation while maintaining the capability to study the effect of potentially important variables such as sorbent/flue gas residence time, fly ash loading, and mass transport phenomena. It provides accurate and independent control of key process variables, including mercury concentration and speciation. The flue gas mercury concentration can be varied between 2 and 20  $\mu\text{g}/\text{m}^3$ , a range typical of coal combustion. By adding actual coal fly ash, the physical and chemical fly ash/sorbent interactions are realistically simulated. Because the pilot plant is a flow system, the mass transfer conditions, temperature/time history, and gas/solid interactions can be varied to simulate conditions in a coal-fired power plant.

The sorbent injection pilot plant accurately simulates flue gas downstream of the air preheater in a coal-fired boiler. The plant was designed to simulate a wide range of site-specific conditions by burning natural gas and by injecting the deficient components such as fly ash,  $\text{CO}_2$ ,  $\text{SO}_2$  and mercury compounds. Independent control of the temperature (38-205  $^\circ\text{C}$ , 100-400  $^\circ\text{F}$ ), humidity, sorbent injection and sorbent recycle rate is maintained. The pilot plant was proven to be a reliable, accurate tool for desulfurization studies when its results for the Coolside process were scaled up to a 105 MWe demonstration at the Ohio Edison Edgewater plant.<sup>13</sup>

Figure 1 is a schematic of the 0.22  $\text{Nm}^3/\text{s}$  (500) scfm sorbent injection pilot plant. Originally used in the development of the Coolside and Advanced Coolside desulfurization processes,<sup>15</sup> it was modified for mercury control studies. The plant consists of a flue gas generation system, a flue gas conditioner for temperature and humidity control, a mercury spiking system, fly ash and sorbent injection systems, a sorbent recycle system, flue gas duct work, particulate removal systems (cyclones and a baghouse), a waste handling system, and flue gas

analysis systems. The pilot plant provides accurate and independent control of flue gas temperature and composition. Accurate control of mercury concentration and speciation in the simulated flue gas is maintained independently of the bulk flue gas composition. The feed and effluent sorbent streams and flue gas stream can be sampled. The pilot plant is instrumented and automated for process control and data collection. A natural gas combustor, a steam injection system and the flue gas conditioner are used to control flue gas humidity and temperature independently. Control loops on these systems allow flue gas temperature to be maintained automatically between 38 and 205 °C within  $\pm 0.5$  °C (100 and 400 °F within  $\pm 1$  °F) and the approach to adiabatic saturation to be controlled within  $\pm 0.5$  °C ( $\pm 1$  °F).

The feed system for elemental mercury consists of mercury-containing permeation tubes, a constant temperature bath and an inert carrier gas. The tubes are commercially available, and are an accurate, reproducible method for feeding mercury. The temperature of the tubes is controlled to within  $\pm 0.01$  °C ( $\pm 0.02$  °F) by a constant temperature bath. The permeation rate for the tubes is calibrated by weighing the tubes over a known period. In long-term tests, weight loss of the tubes is used to verify the mercury material balance. Mercuric chloride is fed by a separate, similar subsystem. Similar calibrations were carried out on the HgCl<sub>2</sub> feed system. By adding Hg<sup>0</sup> and HgCl<sub>2</sub> to the flue gas independently, the amount and speciation of mercury are controlled to within 5%.

The solids are collected using a cyclone or a baghouse. The sorbent collected by the cyclone is almost instantaneously removed from contact with the flue gas stream. This allows solids to be collected after a short, well-controlled contact time with the flue gas (1-3 sec). With two parallel particulate collecting devices, in-duct removal can be measured separately from baghouse removal. The in-duct mercury removal allows estimation of the Hg removal in an ESP-equipped unit.

Recycling the flue gas reduces reagent costs and assists in maintaining a consistent flue gas composition. A large fixed-bed carbon filter prevents recycle of Hg<sup>0</sup> or HgCl<sub>2</sub> not removed by the sorbent.

For all the flue gas sampling tests, the simulated flue gas contained 1000 ppmv SO<sub>2</sub>, 10% O<sub>2</sub>, and 10% CO<sub>2</sub>, and had a saturation temperature of 52 °C (125 °F). The flue gas flow was accurately controlled and monitored with a thermal dispersion mass flowmeter, and checked by standard manual procedures (pitot tube/differential pressure gauge). The gas sampling was conducted in a section of the pilot plant duct located approximately 16.8 m (55 ft) downstream of the mercury injection point. There are a gas distribution plate in the duct just downstream of the injection point and several direction changes of the flue gas (90° bends) prior to sampling to distribute mercury in the flue gas.

#### **TEST PROGRAM**

##### **Initial Operations**

Verification and, if necessary, improvement of sampling/analytical techniques is the first task in the experimental program. Accuracy and reliability are critical for measuring flue gas mercury concentration, for determining speciation, to provide reliable data for process development, and for scale-up to commercial application. Because the mercury concentration and speciation are accurately controlled in the pilot plant, any error in the sampling/analytical methods can be determined.

##### **Sorbent Evaluation/Development**

Identification of an inexpensive, effective sorbent is a primary objective of this work. Understanding the effects of temperature, humidity and mercury speciation on sorbent performance is critical for designing a viable process. To achieve this, statistically designed screening tests will be performed on each candidate sorbent. For candidate sorbents, significant process variables will be explored in more detail. Steady-state tests, with sorbent recycle, will be made with the most cost-effective sorbents. These runs will last two to three days, until steady-state conditions are demonstrated by solid analysis.

##### **Waste Management Studies**

Several important technical issues involve waste management. These include mercury leaching, revolatilization and the impact of mercury on ash utilization. However, utilization of solid waste is preferable to disposal and can accelerate commercialization. The program will evaluate options for waste utilization, with emphasis on the high volume use of the material in construction. A successful approach to eliminate or reduce the need for waste disposal represents a substantial improvement in the state of sorbent injection processes.

##### **Economics**

Engineering and economic studies will be conducted to determine the feasibility of process operations. Sorbent injection processes have inherently low capital costs; therefore, sorbent cost is a key issue. Hydrated lime may be effective

for removing some ionic mercury and is low in cost; however it may not be effective in removing elemental Hg. High surface area activated carbons are expensive (\$0.50-0.80/kg (\$450-1000/ton)), and chemically impregnated sorbents are even more expensive by a factor of five. The minimum amount of sorbent required is not known and likely will vary among applications. The potential of recycle to increase sorbent utilization also will be addressed. Integration of mercury control with other flue gas treatment systems represents a significant improvement in the process economics. Process economic studies also will allow research to focus on areas of the most potential benefit to process economics.

## INITIAL RESULTS

### Mercury Feed System

Calibration of the elemental mercury ( $Hg^0$ ) and mercuric chloride ( $HgCl_2$ ) feed system showed a high degree of accuracy and precision. In replicate tests of weight loss vs time, the variation from the amount of  $Hg^0$  or  $HgCl_2$  fed at a particular calibration condition was  $\pm 4\%$  or less for  $Hg^0$  and  $\pm 6\%$  for  $HgCl_2$ . Figure 2 shows the  $Hg^0$  calibration data. In these tests, the weight loss of several of the commercially available  $Hg^0$  permeation tubes was measured as a function of temperature. In these calibration tests, emphasis was placed on 110 and 114 °C, the typical temperatures of the  $Hg^0$  feed system pilot plant operations. Six calibration runs were made at each of these two temperatures. Similar precision was obtained in the calibration of the  $HgCl_2$  feed subsystem. Figure 3 shows the amount of  $HgCl_2$  evolved at three different calibration conditions. The data represent four to six replicate tests at each calibration condition.

### Flue Gas Sampling and Analysis

Several preliminary tests were made in which  $Hg^0$  and/or  $HgCl_2$  were added to the pilot plant flue gas, and the gas sampled using EPA Method 29, followed by cold vapor atomic absorption (CVAA) analysis of the impingers solutions.<sup>14</sup> The flue-gas mercury concentration in these tests was 4 to 24  $\mu g/m^3$ , typical of concentrations found downstream of a coal-fired boiler. Figure 4 shows that in tests with only  $Hg^0$  addition, there was very good agreement between the Method 29 gas sampling/analysis results and the amount of  $Hg^0$  fed to the flue gas via the feed system. The mercury concentration in the flue gas based on Method 29 results was 10 to 12.5  $\mu g/m^3$ , compared to 9 to 9.5  $\mu g/m^3$  based on feed system calibration. In the  $HgCl_2$  tests, the flue gas mercury concentration based on sampling/analysis was, on average, 30% lower than that based on the feed system calibration (Figure 4 and Table 1). It appears that the ionic mercury present in the pilot plant flue gas was not entirely recovered and/or detected by the Method 29 sampling train and analytical procedures. The accuracy of the mercury feed rates were further confirmed by injecting a large excess of activated carbon at low temperature (<93 °C or 200 °F), and measuring the mercury captured by analysis of the sorbent recovered from the baghouse.

Table 1 shows that the ionic mercury ( $HgCl_2$ ) was in general evenly distributed between the front impingers containing nitric acid and peroxide and the back set of impingers containing permanganate and sulfuric acid. This was true in several tests in which the mercury concentration in the flue gas was varied. These results are contrary to reported assumptions that ionic mercury is primarily captured in the front impingers.<sup>4,6,11</sup> All the elemental mercury was captured in the back set of impingers (permanganate), which agrees with reported assumptions.<sup>4,6,11</sup> Additional testing will be done to further investigate mercury capture and speciation by Method 29.

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TABLE 1. CAPTURE OF ELEMENTAL AND IONIC MERCURY IN METHOD 29 SAMPLING TRAIN

Test	Species Fed	Mercury Recovered in Impingers, % of Total Mercury Fed	
		HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	KMnO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub>
A	HgCl <sub>2</sub>	48	39
B	HgCl <sub>2</sub>	34	42
C	HgCl <sub>2</sub>	38	24
D	HgCl <sub>2</sub>	10	31
E	HgCl <sub>2</sub>	38	29
F	Hg <sup>0</sup>	<4	134
G	Hg <sup>0</sup>	<4	106

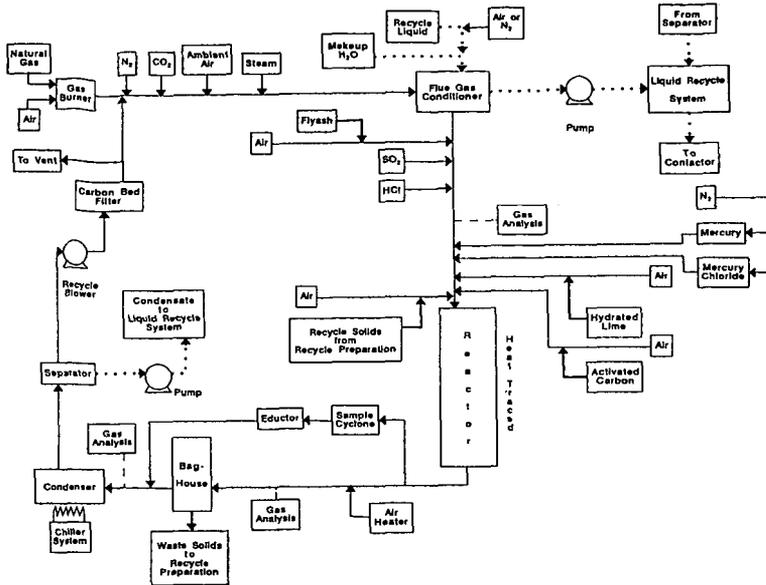


Figure 1. Schematic of CONSOL Sorbent Injection Pilot Plant

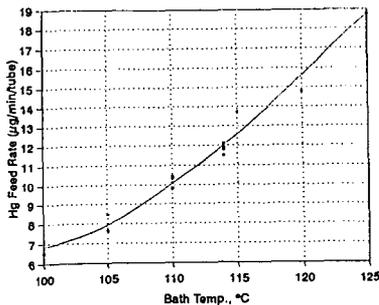


Figure 2. Calibration of Elemental Mercury Feed System.

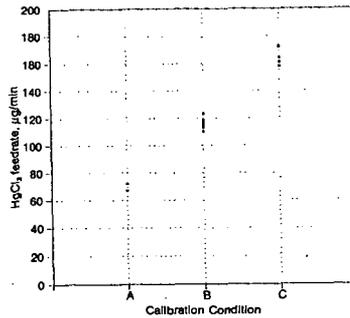


Figure 3. Calibration of Mercuric Chloride Feed System.

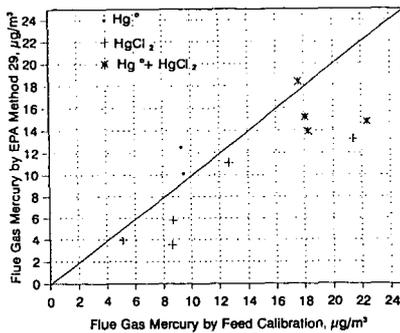


Figure 4. Comparison of Flue Gas Mercury Concentration Based on Method 29, with Concentration Based on Mercury Feed System Calibration.

## DEVELOPMENT OF MERCURY CONTROL TECHNOLOGY FOR COAL-FIRED SYSTEMS

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**Keywords:** Toxics, Mercury Control, Coal

### INTRODUCTION

The emission of hazardous air pollutants (air toxics) from various industrial processes has emerged as a major environmental issue that was singled out for particular attention in the Clean Air Act Amendments of 1990. In particular, mercury emissions are the subject of several current EPA studies because of concerns over possible serious effects on human health. Some of these emissions originate in the combustion of coal, which contains trace amounts of mercury, and are likely to be the subject of control requirements in the relatively near future. Data collected by the Department of Energy (DOE) and the Electric Power Research Institute (EPRI) at operating electric-power plants have shown that conventional flue-gas cleanup (FGC) technologies are not very effective in controlling emissions of mercury in general, and are particularly poor at controlling emissions of elemental mercury. This paper gives an overview of research being conducted at Argonne National Laboratory on improving the capture of mercury in flue gas through the use of dry sorbents and/or wet scrubbers.

### BACKGROUND

Mercury emissions from coal combustion have been shown to vary considerably from site to site. Those emissions depend not only on the composition of the coal, but also upon the type of boiler, the operating conditions, and the FGC system. Mercury belongs to a group of elements/compounds denoted as Class III, which remain primarily in the vapor phase within the boiler and subsequent FGC system. However, that state can be influenced by reactions with other elements, such as chlorine, and by fly-ash characteristics that affect adsorption processes. The concentration of mercury in the flue gas from typical coal combustors ranges from less than 10 to more than 50  $\mu\text{g}/\text{Nm}^3$ .

Few reliable data on mercury control have been available for FGC technologies used on coal-fired systems. Large variations in reported removals have been typical, due both to differences in coal and operating characteristics and to inaccuracies in sampling/analytical procedures.<sup>1</sup> Particulate-matter collectors, such as electrostatic precipitators (ESPs) and baghouses, can be effective for mercury control to the extent that mercury is adsorbed on the fine particulate matter (fly ash) in the gas stream or is converted to another chemical form that can be collected as particulate matter. Recent data on mercury removals for ESPs range from about 15 to 75%, while very limited removal data for baghouses range from 10 up to 70%. Mercury removal in wet flue-gas desulfurization (FGD) systems is also quite variable, with values ranging from near zero to about 50%.<sup>2</sup> Much of that variation may be caused by differences in the chemical form of the mercury, inasmuch as the chloride is much more easily captured than the elemental form. Most available information on mercury control technologies for combustion sources has originated in work with waste incinerators. In such cases, activated carbon has been shown to be an effective sorbent for mercury. However, flue-gas conditions at incinerators are much different in temperature and composition than those found at coal-fired utility boilers, and the performance/economics of activated carbon can be expected to vary as well. In addition, the presence of wet FGD systems at many utility boilers presents a considerably different set of conditions and problems/opportunities that need to be evaluated.

### RESEARCH PROGRAM

Based on an initial survey of published information, a number of chemical additives and sorbents with the potential for enhancing the capture of elemental mercury in dry or wet/dry FGC systems were selected for laboratory investigation. The study of dry sorbents was chosen for several reasons. Many existing coal-fired plants have only particulate-matter control, usually in the form of ESPs, and these could be well suited to duct- or furnace-injection of mercury sorbents. Also, European experience with the addition of sorbents/chemicals to spray-dryer systems on municipal waste incinerators has indicated that greatly enhanced mercury removals are possible. A more extensive discussion of this research can be found in Reference 3. The research program also includes investigation of mercury removal in wet scrubbing. The initial study found very little information regarding potential performance enhancements for scrubbers operating on coal-fired systems, although some work has been done for applications in other industries.<sup>4</sup> To date, the research has focused on physical modifications designed to improve the absorption of mercury

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by the scrubber liquid, on the testing of chemical agents selected for their potential to react with mercury, and on process modifications designed to combine gas-phase and liquid-phase reactions.

## EXPERIMENTAL FACILITIES

Argonne's FGC-laboratory facilities include a fixed-bed reactor system for studying dry sorbents, a complete wet scrubber system, and a spray-dryer/fabric-filter system. Supporting facilities include a system that can provide known concentrations of elemental mercury in a gas stream, a gas-supply system capable of blending synthetic flue gas from bottled gases, on-line gas-analysis packages, and data loggers. The following sections briefly describe the key systems. More detailed descriptions of all of the systems can be found in References 5 and 6.

### Mercury Supply and Analysis

The feed-gas preparation system consists of a mercury-containing permeation tube, a constant-temperature water bath, and a carrier-gas supply. The design capacity of the system is 20 L/min of gas with mercury concentrations of up to 100  $\mu\text{g}/\text{m}^3$ . Mercury measurements are made using a gold-film mercury-vapor analyzer. The range of the instrument is 0 to 999  $\mu\text{g}/\text{m}^3$  with a sensitivity of 3  $\mu\text{g}/\text{m}^3$  and an accuracy of  $\pm 5\%$  at 100  $\mu\text{g}/\text{m}^3$ .

### Fixed-Bed Reactor

The fixed-bed reactor vessel, which is constructed of glass, is 4 cm in diameter and 14 cm in height. A glass frit is positioned in the lower section to support materials placed inside the reactor. To avoid fluidization of the bed materials, the feed gas enters the reactor from the top and exits at the bottom. During shakedown and baseline tests, the reactor was packed with either silica sand (120 g) or a mixture of silica sand and hydrated lime ( $\text{Ca}(\text{OH})_2$ ) in a weight ratio of 40:1. The  $\text{Ca}(\text{OH})_2$  has been employed because it is a common sorbent for  $\text{SO}_2$  in FGC systems. The large amount of sand is used to avoid channeling caused by lime agglomeration. For additive/sorbent testing, small amounts of material being studied are added to the sand/ $\text{Ca}(\text{OH})_2$  bed material. To maintain a uniform temperature during experiments, the reactor is immersed in a fluidized-bed, constant-temperature sand bath. To preheat the incoming feed gas to a temperature equal to that maintained in the fixed-bed reactor, the gas-transfer line is wrapped with heating tapes.

### Wet Scrubber

All of the principal vessels in the wet-scrubber system are constructed of glass. The scrubber column has an inside diameter of 7.6 cm and an active height of nearly 53 cm. It is normally operated in a countercurrent mode with the flue gas entering at the bottom. The scrubber is constructed of several interchangeable sections so that it can be configured as a flooded column (no internals), a four-stage disc and donut column, or an intermediate combination. For most of the experiments described here, the combination mode was used with the lower part of the column left open to accommodate packing. The scrubber liquor drains into a holding tank from which it is recirculated to the top of the scrubber. The temperature of the liquor can be adjusted by heating the holding tank with heat tapes. The pH of the liquid in the tank is sampled continuously and can be adjusted either manually or automatically by adding reagent from a chemical feed tank.

## EXPERIMENTAL RESULTS

### Experiments with Dry Sorbents/Additives

Following initial shakedown tests that verified that neither the sand nor the lime in the fixed bed gave any measurable mercury removal, a variety of dry sorbents were studied. Various sorbents and chemical additives for mercury removal have been reported in the literature. These include activated carbon, activated carbon impregnated with various chemicals (notably sulfur and iodine), modified zeolites, glass fibers coated with special chemicals, and pure chemicals (such as sulfur, selenium, and ferrous sulfide and sulfate). In addition to comparing the performance of different types of sorbents/additives, the research program has included investigation of the effects of varying process parameters, such as sorbent particle size, sorbent loading in the reactor, reactor/gas temperature, and mercury concentration.<sup>3</sup> For most of the tests, the amounts of sorbent added ranged from 1 to 10 wt% (relative to the lime). Three fixed-bed reactor temperatures were evaluated: 55, 70, and 90°C. Target mercury concentrations in the nitrogen feed gas of either 44 or 96  $\mu\text{g}/\text{m}^3$  were used, and the feed-gas flow rate was fixed at 10 L/min.

By far the best removal results in the initial tests were obtained with an activated carbon that was commercially treated with about 15 wt% sulfur. The success of the sulfur-treated carbon is thought to be based on a combination of physical adsorption and chemical reactions that produce mercury sulfide. This suggests that chemical additives producing other compounds, such as mercury chloride, might also be beneficial for removals. To explore this possibility, another carbon sample that previously gave essentially no removal was treated with calcium chloride ( $\text{CaCl}_2$ ) in the ratio of about 6:1 by weight. The treated carbon gave excellent removals and actually performed better than the sulfur-treated carbon.

Recently, the research has been focused on the development and testing of lower-cost alternatives to activated carbon. Several high-surface-area or low-cost mineral substrates have been identified and samples have been obtained. Tests of the materials in the as-received condition gave moderate mercury removals for a molecular sieve sorbent and essentially no removals for pumice and vermiculite samples. In current research, the samples are being treated with chemical additives shown to be effective with activated carbon and tests are being run at various additive concentrations, mercury concentrations, and flue-gas temperatures. Figure 1 gives the results of experiments with volcanic pumice treated with

potassium iodide,  $\text{CaCl}_2$ , or sulfur. The untreated pumice was ineffective for mercury removal, but the sulfur-treated sorbent gave 100% removal for over an hour, while the iodide-impregnated sorbent gave 100% removal for a few minutes followed by a decrease in removal that appeared to level out at about 30%. In order to explore the effects of temperature on the treated sorbents, additional tests were run at a temperature of 150°C. As shown in Figure 2, the iodide-impregnated sample behaved very similarly at the two temperatures. However, the sulfur treatment that was so effective at the lower temperature was found to be totally ineffective at the higher temperature. This may be due to a change in the form of the sulfur, but this issue is still under study and has not yet been resolved.

#### Experiments with Wet Scrubbing

Preliminary data from field-sampling campaigns have indicated that elemental mercury is not appreciably removed in typical wet-scrubber systems. This is not surprising given the very low solubility of mercury in the elemental form. Initial experiments were conducted using the scrubber as described above, no packing, and various degrees of "flooding" in the lower part of the column to promote gas-liquid contact. The scrubbing liquors tested were distilled water, a saturated  $\text{Ca(OH)}_2$  solution, and a  $\text{Ca(OH)}_2$  solution with 1000 ppm of potassium polysulfide. The polysulfide has been claimed to promote mercury removal in other research.<sup>4</sup> The mercury inlet concentration was about 40  $\mu\text{g}/\text{m}^3$ , the liquid height in the column was varied up to 43 cm, and the temperature was varied between 22 and 50°C. No mercury removal was detected under any of these conditions.

The addition of ceramic-saddle packing to the column produced removals of 3 to 5% with distilled water at 22°C, and removals of 6 to 7% were obtained when the temperature was raised to 55°C. However, tests involving polysulfide addition had to be terminated when reactions with the ceramic saddles produced hydrogen sulfide ( $\text{H}_2\text{S}$ ) that interfered with the operation of the mercury analyzer.

In earlier research on mercury capture, stainless steel packing was found to promote mercury capture.<sup>4</sup> Therefore, the ceramic saddles were replaced by 0.61-cm stainless-steel packing, which gave the rather unexpected result of 11% removal with no liquid in the column. Removals with water in the column ranged from 15 to 20%. Addition of polysulfide to the scrubber produced a noticeable increase in removal up to about 40%. It appears that there is a positive synergistic effect on removal involving the combination of polysulfide and stainless steel. It should be noted that this additive requires a very high pH to maintain its stability and this may preclude its use in most FGD systems.

In an effort to promote greater mercury capture through changing its chemical form, tests were conducted with several additives that combine strong oxidizing properties with relatively high vapor pressures. Tests with minimal gas-liquid contacting yielded mercury removals as high as 100%, and indicated that the removal reactions were occurring in the gas phase above the scrubber liquor. However, tests with the addition of  $\text{SO}_2$  to the gas stream showed the additives to be very reactive with that species as well, which could result in excessively high additive consumption in order to realize effective mercury control. Recently, tests with a new combination of oxidizing chemicals, NOXSORB™, which is a product of the Olin Corporation, have indicated promise for integrated removal of several flue-gas species including mercury. Preliminary data from those tests are shown in Figure 3. Further tests are exploring the effects of different additive concentrations, the relationship between  $\text{NO}/\text{SO}_2$  removal and mercury removal, and possible process configurations and economics.

#### CONCLUSIONS

The results and conclusions to date from the Argonne research on dry sorbents can be summarized as follows:

- Lime hydrates, either regular or high-surface-area, are not effective in removing elemental mercury.
- Mercury removals are enhanced by the addition of activated carbon.
- Mercury removals with activated carbon decrease with increasing temperature, larger particle size, and decreasing mercury concentration in the gas.
- Chemical pretreatment (e.g., with sulfur or  $\text{CaCl}_2$ ) can greatly increase the removal capacity of activated carbon.
- Chemically treated mineral substrates have the potential to be developed into effective and economical mercury sorbents.
- Sorbents treated with different chemicals respond in significantly different ways to changes in flue-gas temperature.

Preliminary results from the wet scrubbing research include:

- No removal of elemental mercury is obtained under normal scrubber operating conditions.
- Mercury removal is improved by the addition of packing or other techniques to increase the gas-liquid contact area.

- Stainless steel packing appears to have beneficial properties for mercury removal and should be investigated further. Beneficial synergisms with polysulfide solutions have been observed.
- Oxidizing additives may be used in conjunction with wet scrubbing to greatly enhance removals. Selectivity is required to avoid excessive additive consumption from competing reactions.

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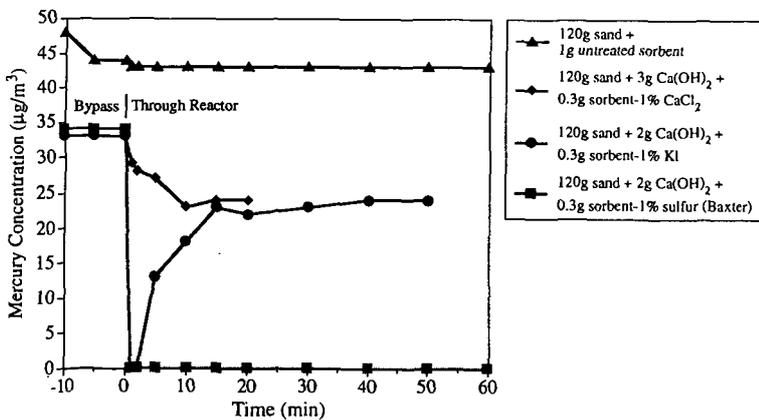


Figure 1. Effects of chemical pretreatment on an inert substrate at 70°C.

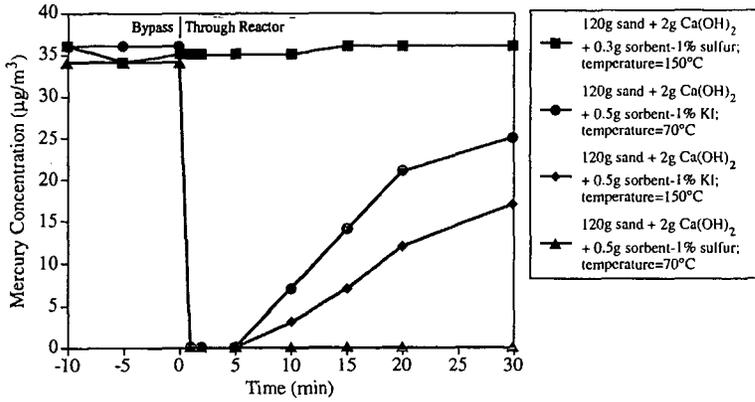


Figure 2. Effects of different temperatures on a chemically pretreated inert substrate.

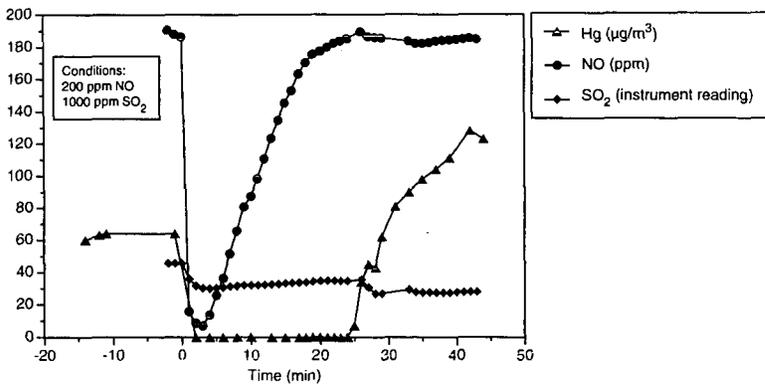


Figure 3. Removals of Hg, NO, and  $\text{SO}_2$  in the wet scrubber with a 4% NOXSORB™ solution.