Partitioning of Mercury, Arsenic, Selenium, Boron, and Chloride in a Full-Scale Coal Combustion Process Equipped with Selective Catalytic Reduction, Electrostatic Precipitation, and Flue Gas Desulfurization Systems[†]

Chin-Min Cheng,*[,‡] Pauline Hack,[‡] Paul Chu,[§] Yung-Nan Chang, Ting-Yu Lin, Chih-Sheng Ko, Po-Han Chiang, Cheng-Chun He, Yuan-Min Lai, and Wei-Ping Pan[‡]

[‡]*Institute for Combustion Science and Environmental Technology, Department of Chemistry, Western Kentucky University, 2413 Nashville Road, Bowling Green, Kentucky 42101,* [§]*Electric Power Research Institute, 3420 Hillview Avenue, Palo Alto, California 94304, and* [∥]*Department of Chemical Engineering, Ming-Chi University of Technology, 84 Gungjuan RD., Taishan, Taipei, Taiwan 243 R.O.C*

A full-scale field study was carried out at a 795 MWe coal-fired power plant equipped with selective catalytic reduction (SCR), an electrostatic precipitator (ESP), and wet flue gas desulfurization (FGD) systems to investigate the distribution of selected trace elements (i.e., mercury, arsenic, selenium, boron, and chloride) from coal, FGD reagent slurry, makeup water to flue gas, solid byproduct, and wastewater streams. Flue gases were collected from the SCR outlet, ESP inlet, FGD inlet, and stack. Concurrent with flue gas sampling, coal, bottom ash, economizer ash, and samples from the FGD process were also collected for elemental analysis. By combining plant operation parameters, the overall material balances of selected elements were established. The removal efficiencies of As, Se, Hg, and B by the ESP unit were 88, 56, 17, and 8%, respectively. Only about 2.5% of Cl was condensed and removed from flue gas by fly ash. The FGD process removed over 90% of Cl, 77% of B, 76% of Hg, 30% of Se, and 5% of As. About 90% and 99% of the FGD-removed Hg and Se were associated with gypsum. For B and Cl, over 99% were discharged from the coal combustion process with the wastewater. Mineral trona (trisodium hydrogendicarbonate dehydrate, $Na_3H(CO_3)_2 \cdot 2H_2O$) was injected before the ESP unit to control the emission of sulfur trioxide (SO_3). By comparing the trace elements compositions in the fly ash samples collected from the locations before and after the trona injection, the injection of trona did not show an observable effect on the partitioning behaviors of selenium and arsenic, but it significantly increased the adsorption of mercury onto fly ash. The stack emissions of mercury, boron, selenium, and chloride were for the most part in the gas phase.

Introduction

In response to the implementations of tightening federal (e.g., the Clean Air Interstate Rule (CAIR) and the Clean Air Visibility Rule (CAVR)) and state (e.g., Illinois Mercury Rule) air regulations, many emission control technologies (e.g., coal blending, selective catalytic reduction, flue gas desulfurization, and sorbent/additive injection) have been used increasingly through-out the coal-fired power industry to reduce the emissions of sulfur dioxide (SO_2), nitrogen oxide (NO_x), mercury (Hg), and particulate precursors (e.g., sulfur trioxide (SO_3)). The Energy Information Administration (EIA) estimated that the use of flue gas desulfurization (FGD) technologies will be increased to 141 Gigawatts during the next 20 years,[1] which will be about double the amount in 2001.[2] The increase in application of emission control technologies can significantly increase the production of coal combustion byproduct, for example, solid and wastewater streams from the FGD process and fly ash as a result of sorbent injection. During the combustion process, coal trace elements (i.e., concentrations of elements in the coal less than 100 $\mu g/g$) are released and redistributed to the bottom ash, fly ash, and the gaseous phase.[3] The application of emission control technologies can also affect the redistribution behaviors of coal trace elements and alter the concentrations of these metals (especially for volatile elements such as selenium, arsenic, and mercury) in certain coal combustion byproducts. The more stringent air pollution regulations become, the higher the piles of coal combustion byproduct and the greater the trace metal concentrations in coal combustion byproduct will be. As a result, the disposal (i.e., landfilling and impoundment) and utilization (e.g., construction and agricultural applications) of fly ash and FGD solid waste, as well as discharge of FGD wastewater, have merited great environmental, operational, and regulatory concerns.

New ash-handling requirements have been discussed in the Congress.[4] The US Environmental Protection Agency (EPA)

[†] Progress in Coal-Based Energy and Fuel Production.

*To whom correspondence should be addressed. Email: chin-min.cheng@wku.edu.

(1) Energy Information Administration (EIA), Department of Energy, *Annual Energy Outlook 2006 with Projections to 2030*, http://www.eia.doe.gov/oiaf/archive/aeo06/pdf/trend_5.pdf (accessed February 23, 2009).

(2) *NESCAUM Environmental Regulation and Technology Innovation: Controlling Mercury Emissions from Coal-Fired Boilers*, Northeast States for Coordinated Air Use Management: Boston, MA, 2000.

(3) Pavageau, M.; Pecheyran, C.; Krupp, E.; Morin, A.; Donard, O. *Environ. Sci. Technol.* **2002**, *36*, 1561.

(4) Johnson, J. F. The Foul Side of "Clean Coal", *Chem. Eng. News*, February 23, **2009**, p 44.

Table 1. Coal and Boiler Characteristics of the Tested Unit

			unit 1
boiler design	PC[a]		
load	795 MWe		
particle control	cold-side ESP[b]		
SO$_2$ control	limestone forced-oxidation FGD[c]		
NO$_x$ control	SCR[d] with anhydrous ammonia injection		
SO[c] control	trona injection		
coal rank	bituminous		
	heat value	Btu/lb	13200 ± 60
	moisture[d]	wt %	3.6 ± 1.2
	ash	wt %	12.2 ± 0.6
	vol. mat	wt %	33.6 ± 0.09
S	sulfur	wt %	2.09 ± 0.05
C	carbon	wt %	74.8 ± 0.10
H	hydrogen	wt %	5.11 ± 0.06
N	nitrogen	wt %	1.47 ± 0.11
O	oxygen	wt %	4.32 ± 0.7

[a] Pulverized coal. [b] Electrostatic precipitator. [c] Flue gas desulfurization. [d] Dry basis; moisture was determined as received.

is also in the process of determining whether to revise the effluent guidelines for the fossil fuel electric industry,[5] with the focus being on selenium[6,7] and other trace elements.[6] All these actions may result in more restrictive waste disposal and wastewater discharge regulations and have the potential to impact the design and operation of coal-fired power plants.[8] There is a need for the coal-fired power industry to start assessing the impact of these more stringent environmental regulations on their overall solid and wastewater management systems. To further this end, a better understanding of the behaviors of trace elements (i.e., partitioning profile of trace elements) in the coal combustion process (including FGD system) is the key, which will allow the utilities to develop a predictive relationship that can have more accurate estimates on the change of trace elements in coal combustion byproduct based on operational conditions.

The Institute for Combustion Science and Environmental Technology (ICSET) of Western Kentucky University (WKU) carried out a full-scale field investigation at a coal-fired power plant equipped with selective catalytic reduction (SCR), electrostatic precipitator (ESP), and FGD systems to investigate the fate of selected elements (i.e., mercury, arsenic, selenium, boron, and chloride) in the coal combustion process. The trace elements were selected because of environmental concerns as well as different partitioning behaviors in a coal combustion process. The objectives of this study are (1) to collect gas samples from various locations along the flue gas path for trace elements, halogens and halogen halides, and particulate matter (PM) measurements; (2) to collect coal, bottom ash, fly ash, and solid and liquid samples from FGD streams for trace elements and halogens analyses; and (3) to calculate the partitioning of Hg, As, Se, B, and Cl in the coal combustion process.

(5) *EPRI Treatment Technology summary for Critical Pollutants of Concerns in Power Plant Wastewaters*, EPRI Technical Update 1012549; Electric Power Research Institute: Palo Alto, CA, 2007.

(6) US Environmental Protection Agency. *Fed. Regist.* 2007, *72* (29),61342. http://bulk.resource.org/gpo/register/2007/2007_61342.pdf (accessed March 1, 2009).

(7) Chu, P.; Goodman, N.; Fink, D., Higgins, T.; Wallschlager, D.; Orr, D.; Behrens, G.; Braman, C.; Park, B. In *Evaluation and Management of the Impact of FGDs on Wastewater*, Paper No. 105; Proceedings of MEGA Symposium: Baltimore, MD, 2008.

(8) *USEPA Users Guide to the Docket for the 2008 Annual Review and the Final Effluent Guidelines Program Plan*, Docket Number EPA-HQ-OW-2006−0771; United States Environmental Protection Agency: Washington, DC, 2008.

Experimental Section

Testing Sites and Sampling Setup. The study was carried out at a coal combustion utility with a 795 MWe gross load pulverized coal (PC) boiler, which burned eastern bituminous coal. The coal and boiler parameters can be seen in Table 1. The unit SCR to reduce nitrogen oxide emissions with the assistance of anhydrous ammonia injection. Both SCR and ammonia injection were in operation during the testing period. A cold-side ESP was used for particulates collection. Mineral trona (trisodium hydrogendicarbonate dehydrate, Na$_3$H(CO$_3$)$_2 \cdot$ 2H$_2$O) was injected before the ESP unit to control sulfur trioxide (SO$_3$) levels in the flue gas. A wet forced oxidation FGD process was operated using limestone as reagent.

Depending on testing purposes, while carrying out flue gas measurements, gas samples were collected from as many as four locations along the flue gas path, that is, SCR outlet, ESP inlet, FGD inlet, and stack. The ESP inlet sampling location was upstream of trona injection. After leaving the boiler, the flue gas was divided into two streams before entering the SCR unit. The divided streams flowed into a common duct after the air heater. At a given sampling location, flue gas samples were collected from all available ducts. The port(s) located at the center of each duct was selected for sampling. At the stack, flue gas samples were collected from both south and north ports. A schematic description of the sampling setup can be seen in Figure 1. As shown, trace elements (including gas phase and particulate-bound) and filterable particulate matters (FPMs) were measured at all available sampling locations. Halogen and hydrogen halide measurements were carried out at the ESP inlet, FGD inlet, and stack. Condensable PM and sulfuric acid mist (including sulfuric acid (H$_2$SO$_4$) and sulfuric trioxide (SO$_3$)) were measured at the FGD inlet and stack.

Flue Gas Sampling. During each flue gas measurement, a sampling run was started simultaneously at all applicable sampling locations. For a given sampling location, flue gas samples were collected using isokinetic sampling systems provided by Apex Instruments (Raleigh, NC). A complete set of the flue gas sampling system included either a probe with glass linear or/and inertial type sampling device, a heated filter box (when EPA Method 5[9] was employed), a set of glass impingers, umbilical cord, and a metering console.

The probe equipped with type S pitot tubes and a thermocouple sensor for measuring gas velocity and stack temperature, respectively, was used at the low ash load area. While the probe was used, a glass fiber filter assembly was enclosed in a holder placed in a temperature-controlled heated sample box (EPA Method 5[9]) at 120 $\pm$ 10 °C or in the stack (EPA Method 17[10]). The nozzle, probe linear, connecting glassware, and filter are referred to as the "front-half" of the sample train. The "back-half" of the sample train consists of the sampling glass impingers, which are cooled in an ice bath and kept at a temperature below 20 °C. At the high ash load sampling location an inertial probe was used.

(9) *USEPA Method 5-Determination of Particulate Matter Emissions from Stationary Sources*; United States Environmental Protection Agency Promulgated Method: Washington, DC, 2000.

(10) *USEPA Method 17-Determination of Particulate Matter Emissions from Stationary Sources*; United States Environmental Protection Agency Promulgated Method: Washington, DC, 2000.
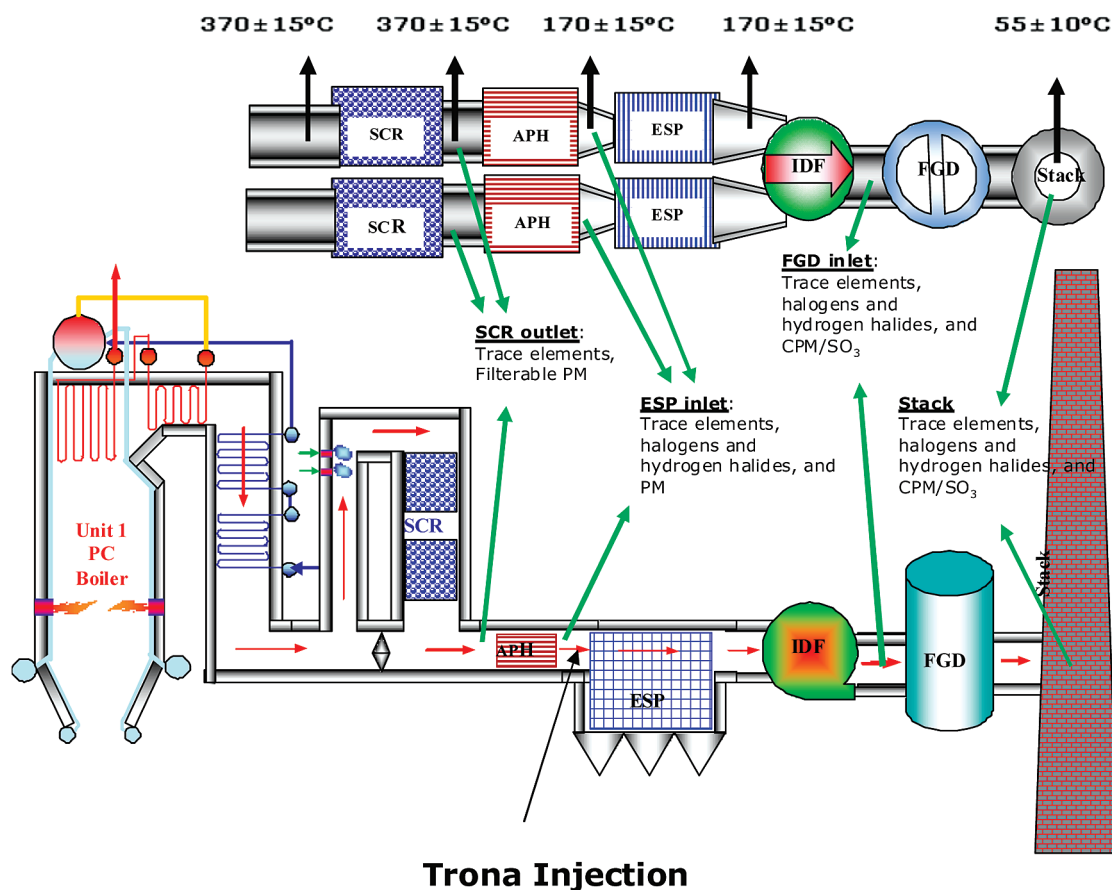
Trona Injection

Figure 1. Configuration of test unit.

The umbilical cord, used to connect the sample train to a control box, contains a vacuum hose, pitot lines, thermocouple wires, and a four-wire electrical cord. The control box maintains the stack gas sampling rate and provides gas volume, sampling velocity, pressure, and temperature readings with respect to sampling conditions through the flow meter, manometer, vacuum gauge, and digital display, respectively.

Trace Element Sampling and Analysis. The emissions of trace elements were determined by the EPA method 29.[11] This method, sometimes referred to as the "multi-metals" method, has historically been the most commonly used method for quantifying mercury and a long list of metals including the eight total selected metals (TSM) defined in the Boiler MACT in stack gas.

Detailed setup of the sampling train has been described in the method. In summary, seven ice-bath-chilled impingers were connected in a series with leak-free ground glass fittings for collecting gaseous emissions. The first impinger was empty and was used as a moisture trap. The second and third impingers, which contained 100 mL of 5% (v/v) HNO_3/10% (v/v) H_2O_2, absorbed and retained trace elements in the gaseous phase. The fourth and fifth impingers contained $KMnO_4$ for elemental Hg capture. The seventh impinger contained 200−300 g of dried and preweighed silica gel, which was employed to determine the moisture gain and prevent moisture condensation in the pump and the metering device.

An inertial-type flue gas sampling probe was used at the SCR outlet and ESP inlet locations to reduce the sampling difficulty caused by a high load of "in-flight" ash. At the FGD inlet and stack, the EPA Methods 17[10] and 5B[12] were used, respectively. Each sampling run was carried out for about 2.5 h. After each sampling, solution samples recovered from the back-half of the sampling trains were analyzed for mercury using cold-vapor atomic absorption spectroscopy (CVAAS, Leeman Lab Hydra, Teledyne Leeman Laboratories, Hudson, NH); low-level arsenic using cold-vapor atomic fluorescence spectroscopy (CVAFS, PSA 10.055 Millennium Excalibur system, PS Analytical, Deerfield Beech, FL); and other trace elements using inductively coupled plasma atomic emission spectroscopy (Prodigy ICP-AES, Teledyne Leeman Lab, Hudson, NH). Before mercury analysis was carried out, samples were digested using an automated mercury preparation system (Leeman Lab Hydra Prep, Teledyne Leeman Laboratories, NH). A 4 mL aliquot of each recovered sample were transferred to a 15 mL digestion tube, in which 0.2 mL of concentrated H_2SO_4, 0.1 mL of concentrated HNO_3, 1.2 mL of 5% $KMnO_4$, and 0.32 mL of 5% $K_2S_2O_8$ were added automatically to each tube through a dispenser. The tubes were heated in a water bath at a constant temperature of 95 °C for two hours. After cooling, 1.333 mL of a reagent solution with 12% of NaCl and 12% of hydroxylamine sulfate was added before the sample was analyzed for mercury.

(11) *USEPA Method 29-Determination of Metal Emissions from Stationary Sources*; United States Environmental Protection Agency Promulgated Method: Washington, DC, 2000.

(12) *USEPA Method 5B-Determination of Nonsulfuric Acid Particulate Matter Emissions from Stationary Sources*; United States Environmental Protection Agency Promulgated Method: Washington, DC, 2000.

Filterable and Condensable Particulate Matter Measurements. Filterable PMs were measured using either EPA Method 17[10] or Method 5B.[12] While a sampling run was carried out, a flue gas sample was withdrawn isokinetically from the duct or stack. The particulate was then separated from the flue gas using a glass fiber filter. The temperature of the filter was maintained the same way as that of the flue gas temperature or at 160 ± 14 °C to prevent water condensation. The samples collected from Method 5B[12] were heated in an oven at 160 °C for 6 h to volatilize any condensed sulfuric acid that may have been collected. The mass of the particulate matter was determined gravimetrically.

Condensable PMs were tested using the EPA Other Test Method (OTM) 28.[13] In this method, the gas sample was drawn through an 11 cm water-jacketed coil condenser, a moisture dropout impinger, a modified open-tube impinger, and finally, through a Teflon filter. Each sampling run was carried out for at least 2.5 h. Upon completion of each measurement, the sampling train was purged with ultra high purity (UHP) grade nitrogen immediately for 1 h in the mobile chemistry lab at ICSET, which was set up on site. After the nitrogen purge, the organic and inorganic fractions of CPM were extracted from the sampling train using $MeCl_2$ and deionized water, respectively. Each PM fraction was determined gravimetrically after drying. The total of all fractions represents the CPM. An aliquot of the inorganic solution was measured for anions (i.e., Cl^-, F^-, SO_4^{-2}, and PO_4^{-3}) and cations (i.e., Ca^{2+}, Na^+, K^+) using ion chromatography (ICS-1000, Dionex, Sunnyvale, CA).

To reduce the concern that the dry impinger method might not reduce artifact bias sufficiently, a controlled condensate method, that is, EPA CTM-13,[14] was carried out concurrently with the method 5B/dry impinger sampling. Results obtained from the CCS measurement provide a less biased value for sulfuric acid. The CPM was then determined by the following equation.

$$\text{Inorganic } CPM_{calculated} = \text{Inorganic } CPM_{OTM\ 28}$$
$$- \text{Sulfate}_{OTM\ 28} + \text{Sulfate}_{CCM} \quad (1)$$

Sulfuric Acid Mist (Including H_2SO_4 and SO_3). In summary, this method used a temperature-controlled ($T = 270$ °C) quartz in-line filter to remove particulate matter from the gas stream prior to capturing SO_3. In addition, the use of a controlled condensation technique eliminated the potential for interference from sulfur dioxide, which has been reported when EPA Method 8 is applied.[15] Before sampling, the condenser assembly was filled with water and the temperature was maintained between 75 and 85 °C using a rod-shape electric heating metal. While sampling was carried out, the flue gas sample passed through a modified Graham condenser, whose coil length (20 cm) was about twice as long as a regular condenser. A thermocouple was installed to directly measure the flue gas temperature at the outlet of the condenser. Glass wool is loosely packed at the outlet of the glass coil to adsorb sulfur trioxide (SO_3) present in water vapor that was selectively condensed. The flue gas then passed a series of impingers, which were similar to those used in EPA Method 6; the first two were filled with 20 mL of 3% (v/v) hydrogen peroxide to capture the SO_2. These impingers were followed by one empty impinger and another silica gel-filled impinger.

Halogens and Hydrogen Halides. Detailed sampling procedures for halogen and hydrogen halide measurements applied in this study can be seen in EPA Method 26A.[16] After particulates were removed by filtering, the flue gas sample was extracted and pulled through a series of glass impingers containing dilute sulfuric acid and dilute sodium hydroxide solutions. The hydrogen chloride and fluoride were dissolved in the acidic solution and formed chloride (Cl^-) and fluoride (F^-) ions. Chlorine and fluorine have a very low solubility in the acidic solution and passed through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate was also added in excess to the alkaline solution. The halide ions in the separate solutions were measured by an ion chromatography (IC) system (ICS-1000, Dionex Co., CA).

Solid and Liquid Samples Collection and Analyses. Coal, bottom ash, fly ash, and FGD slurry samples were collected for mercury, trace elements, and halogen analyses. During the testing period, one composite coal sample was collected every day by plant personnel. Equal amounts of coals were collected from all available coal feeders to prepare the composite coal samples. In addition to coal, one composite ash sample was also collected daily from the four ESP hoppers at the center of the first two rows of the ESP unit. The FGD liquid and slurry samples, including service water, reclaimed water, reagent slurry, and chloride purge were collected from the appropriate locations after each flue gas measurement was carried out for about an hour. Due to the operation setup, FGD gypsum samples were collected each day during the testing period when the dewatering system was in operation. A schematic of FGD slurry sampling locations can be seen in Figure 2.

Detailed analytical methods and instruments employed for the solid and liquid analyses are summarized in Table 2. For the FGD slurry sample, the solid and liquid portions

(13) *USEPA OTM 28-Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources*; United States Environmental Protection Agency Other Testing Method: Washington, DC, 2009

(14) *USEPA CTM 13-Determination of Sulfuric Acid Vapor or Mist and Sulfur Dioxide Emissions from Kraft Recovery Furnaces*; United States Environmental Protection Agency Conditional Testing Method: Washington, DC, 1996.

(15) Andracsek, R.; Gaige, D. In *Particulate Emissions-Combustion Source Emissions Dependent on Test Method*, Proceedings of the 14th International Emission Inventory Conference, Las Vegas, NV, April 11–14, 2005.

(16) *USEPA Method 26A-Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Isokinetic Method*; United States Environmental Protection Agency Promulgated Method: Washington, DC, 2000.

(17) *ASTM D3176 − 89 Standard Practice for Ultimate Analysis of Coal and Coke*; ASTM International: West Conshohocken, PA, 2002; DOI: 10.1520/D3176-89R02.

(18) *ASTM D4239 - 08 Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods*; ASTM International: West Conshohocken, PA, 2008; DOI: 10.1520/D4239-08.

(19) *ASTM D6722 - 01 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis*; ASTM International: West Conshohocken, PA, 2006; DOI: 10.1520/D6722-01R06.

(20) *ASTM D5142 - 09 Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures*; ASTM International: West Conshohocken, PA, 2009; DOI: 10.1520/D5142-09.

(21) *ASTM D5865 - 07a Standard Test Method for Gross Calorific Value of Coal and Coke*; ASTM International: West Conshohocken, PA, 2007; DOI: 10.1520/D5865-07A.
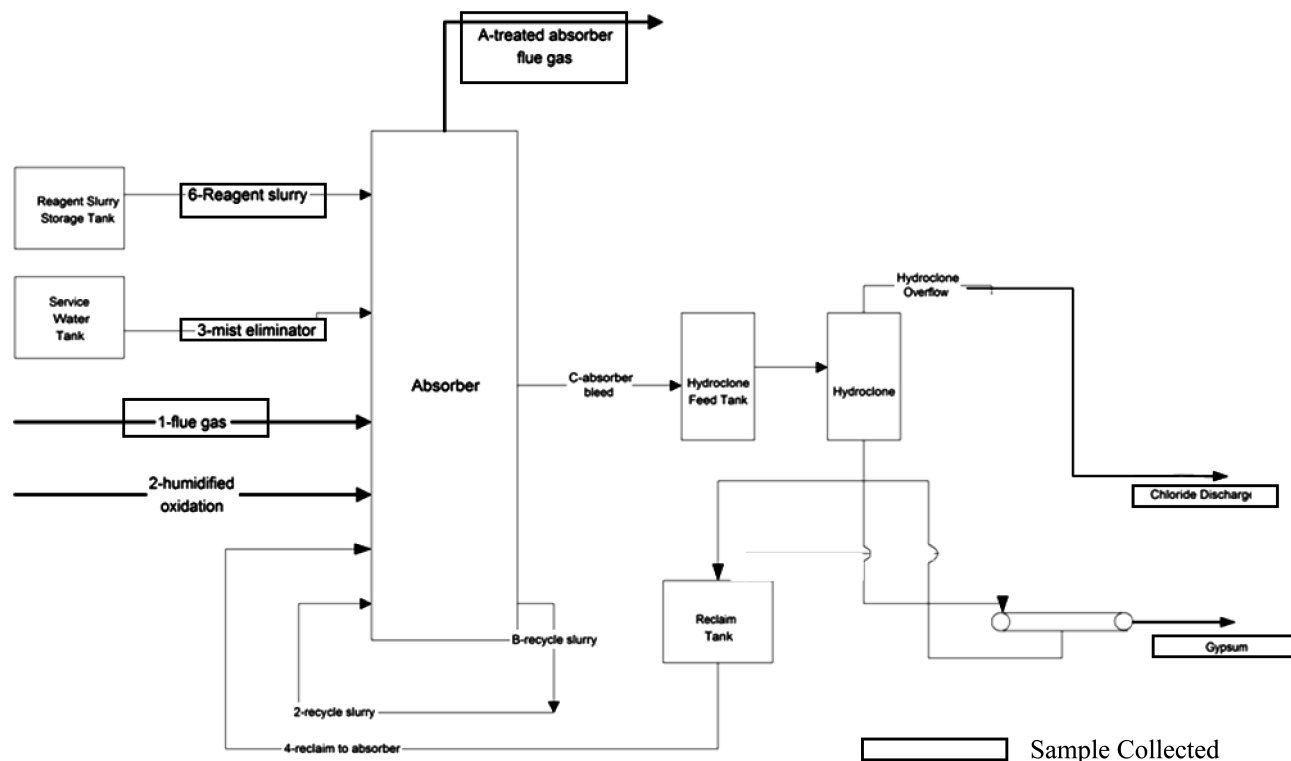
Figure 2. Schematic description of the FGD process and the sampling locations.

were separated on site in the ICSET's mobile chemical laboratory within 24 h after sampling. The analyses were carried out in ICSET's analytical lab in Bowling Green, Kentucky on the WKU campus. The chloride purge samples collected in this study represent the inflow for the wastewater treatment process.

All liquid samples (including the liquid portion of the FGD slurry samples) were separated into three containers and preserved separately, based on the type of analyses to be performed. For mercury analysis, 0.05−0.1 g of ACS certi-fied $KMnO_4$ was added into the solution to stabilize mer-cury.[24] For trace element analysis, the solution was preserved in 5% (v/v) nitric acid to prevent precipitation.[24] No filtra-tion was applied to any of the liquid sample. Therefore, results from the trace element analysis represent the "total" concentrations.

Results and Discussion

Concentration Profiles of Trace Elements, Halogens, and Particulate Matter in Flue Gas. Results from trace elements emission measurements are summarized in Table 3, in which the concentrations of both vapor phase and particulate-bound trace elements are listed. As shown, the partitioning

of selected trace elements in the flue gas during the post-combustion process can be generalized into three groups. Group I consists of elements, that is, As, Be, Cd, Co, Cr, Mn, Ni, and Pb, which predominantly present in the particulate phase. Most of these elements in the vapor phase are close-to or lower-than the detection limits. For those detected group I elements, the gas phase concentrations are approximately 2 orders of magnitude less than what were observed in the particulate phase before the ESP unit. These elements are categorized as least-volatile (e.g., Mn) or semivolatile (As, Be, Cd, Co, Cr, Ni, and Pb) elements.[25] Group II is made up of Se and B, whose concentrations are similar (within 1 order of magnitude) to the vapor and particulate phases before the particulate precipitators. The volatility of these two elements is higher than the previous group.[26] Both Se and B are soluble and were effectively removed from the flue gas by the FGD unit. Group III is mercury, which is the most volatile element. The vapor-phase mercury concentration is 1 order of magnitude higher than the concentrations in the particulate phase.

In general, the concentrations of particulate-bound trace elements decreased to the levels that are close-to or lower-than the analytical detection limits after the ESP unit. Because only small amounts of particulates were collected at the FGD inlet and stack, whole thimbles or filters were digested using microwave-assisted extraction methods (as listed in Table 2) to determine the concentrations of particulate-bound trace elements at these locations. The contents of selected trace elements in the blank filters were used to calculate the detection limits if the results from sampled filters were not able to be differentiated from the blank filter.

(22) *ASTM D4208 - 02 Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method*; ASTM International: West Conshohocken, PA, 2007; DOI: 10.1520/D4208-02R07.
(23) *ASTM D6357 - 04 Test Methods for Determination of Trace Elements in Coal, Coke, & Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, & Graphite Furnace Atomic Absorption Spectro-metry*; ASTM International: West Conshohocken, PA, 2004; DOI: 10.1520/D6357-04.
(24) *EPRI FGD Chemistry and Analytical Methods Handbook; Vo-lume 2-Chemical and Physical Test Methods*, Rev. 2, Final Report 1012247; Electric Power Research Institute: Palo Alto, CA 2007.

(25) Swaine, D. L. *Fuel Process. Technol.* **2000**, *65*, 21.
(26) Xu, M.; Yan, R.; Zheng, C. G.; Qiao, Y.; Han, J; Sheng, C. *Fuel Process. Technol.* **2004**, *85*, 215.

Table 2. Analytical Methods and Instruments Used for Coal, Ash, and FGD Slurry Samples

method/substance	analysis	sample type	sample matrix	method	instrument utilized
coal	carbon, hydrogen, and nitrogen	solid	coal	ASTM D3176[17]	LECO TruSpec CHN
	sulfur			ASTM D4239[18]	LECO TruSpec S
	mercury			ASTM D6722[19]	Ohio Lumex or Leeman Hydra C
	moisture, ash, and volatile matter			ASTM D5142[20]	LECO TGA 701
	BTU			ASTM D5865[21]	LECO AC 600
	chlorine, fluorine, bromine			ASTM D4208[22]	LECO AC 600/Dionex ICS-1000
	total selected metals (TSM)			ASTM D6357[23]	Milestone Microwave/Leeman ICP
ash	chlorine, fluorine, bromine	solid	economizer ash, ESP ash, "in-flight" ash	ASTM D4208[22]	Dionex ICS-1000
	TSM			ASTM D6357[23]	Milestone Microwave/Leeman ICP
	Mercury			ASTM D6722[19]	Ohio Lumex or Leeman Hydra C
FGD Material	chlorine, fluorine, bromine	solid	slurry cake	ASTM D4208[22]	Dionex ICS-1000
	TSM			EPRI H1[24]	Milestone Microwave/Leeman ICP
	mercury				Ohio Lumex or Leeman Hydra C
	chlorine, fluorine, bromine	liquid	FGD liquid, water (stabilized by adding $KMnO_4$ and HNO_3)	EPRI I2[24]	Dionex ICS-1000
	TSM			EPRI H1[24]	Milestone Microwave/Leeman ICP
	mercury				Leeman CVAA
bottom ash	chlorine, fluorine, bromine	solid	bottom ash	ASTM D4208[22]	Dionex ICS-1000
	TSM			ASTM D6357[23]	Milestone Microwave/Leeman ICP
	mercury				Ohio Lumex or Leeman Hydra C
limestone	chlorine, fluorine, bromine	solid	$CaCO_3$	ASTM D4208[22]	Dionex ICS-1000
	TSM			EPRI H1[24]	Milestone Microwave/Leeman ICP
	mercury				Ohio Lumex or Leeman Hydra C
gypsum	chlorine, fluorine, bromine	solid	$CaSO_4$	ASTM D4208[22]	Dionex ICS-1000
	TSM			EPRI H1[24]	Milestone Microwave/Leeman ICP
	mercury				Ohio Lumex or Leeman Hydra C

The flue gas measurement results suggest that, for group II and III elements, the gaseous form was predominant in the stack emissions. From values reported in Table 3, 98.8% and 99.7% of mercury and boron, respectively, were emitted into the atmosphere in the gas phase. No detectable particulate selenium was found. This observation is similar to what was reported by other researchers for coal-fired power plants, in which no FGD process was employed.[27−29] For group I elements, no particular form can be concluded. Less than 43% of arsenic stack emissions was in the particulate phase. However, the gas phase was predominant in the stack emissions for manganese.

High variation was observed in the concentrations of several trace elements in the vapor phase (e.g., As and Se) between the three measurements carried out at one sampling location. The low concentration levels of group I elements (e.g., As, Mn, Ni, and Pb) in the flue gas might have resulted in the observed high variation. In the case of Se, the high variation might be due to the variation of Se in the coal, stratification in the flue gas, and/or ineffectiveness of the applied sampling method on capturing Se. Due to the increasing concerns on the emission of Se from the coal combustion process, further investigation on the flue gas selenium measurement is needed.

Table 4 summarizes the results from the halogen and hydrogen halide measurements in the flue gas across the ESP and FGD units. The concentrations of HF, F_2, and HCl decreased 30, 36, and 10%, respectively, after the flue gas passed the ESP unit. The decrease was likely due to the condensation of halogen vapors on fly ash. Such condensation was less significant for Cl_2 and HBr as the concentrations of these compounds in the fly ash remain relatively constant across the ESP unit. The change of Cl and F in fly ash along the flue gas path is discussed in a later section. All halogen and halogen halide concentrations decreased to levels close to the analytical detection limits after the FGD process.

Results from the condensable particulate matters measurements are summarized in Table 5. As can be seen in the table, more CPMs were in the inorganic form. At the FGD inlet and stack, approximately 97 and 82%, respectively, of the total condensable particulate matter (CPM) were found to be inorganic. More than 80% of the inorganic CPM was removed from the flue gas in the scrubbing process, compared to 40% for the organic portion. No detectable CPM was observed on reagent blanks.

(27) Miller, B. B.; Dugwell, D. R.; Kandiyoti, R. *Fuel* **2002**, *81*, 159.
(28) Otero-Rey, R.; Lopez-Vilarino, M.; Moreda-Pineiro, J.; Alonso-Rodriguez, E.; Muniategui-Lorenzo, S.; Lopez-Mahia, P.; Prada-Rodriguez, D. *Environ. Sci. Technol.* **2003**, *37*, 5262.
(29) Yokoyama, T.; Asakura, K.; Matsuda, H.; Ito, S.; Noda, N. *Sci. Total Environ.* **2000**, *259*, 97.

Table 3. Concentrations of Trace Elements along the Flue Gas Path

		μg/dscm[a]		mg/dscm[b]									
		Hg[a]	As[a]	Se[b]	Be[b]	B[b]	Cd[b]	Co[b]	Cr[b]	Mn[b]	Ni[b]	Pb[b]	Sb[b]
						Vapor Phase							
SCR out	average	13	0.9	0.15	0.003	3.7	<0.003	0.007	0.04	0.018	0.017	0.011	0.060
	std. dev.	2	0.6	0.04		0.5		0.001	0.04	0.009	0.009	0.002	0.006
ESP in	average	11.6	NA	0.081	<0.003	3.3	<0.003	0.004	0.019	0.027	0.010	0.006	0.038
	std. dev.	0.7		0.036	<0.003	0.2		0.002	0.004	0.013	0.007		0.010
FGD in	average	9.9	0.18	0.12	<0.003	3.1	<0.003	<0.003	<0.002	0.04	0.005	<0.003	0.012
	std. dev.	0.5	0.18	0.08		0.5				0.03			0.003
stack	average	0.48	0.12	0.04	<0.002	0.28		<0.003	<0.002	0.008	<0.003	<0.003	0.004
	std. dev.	0.14	0.13	0.02		0.06				0.009			0.001
						Particulate Bound[c]							
SCR out	average	1.03	1300	0.34	0.159	2.4	0.075	3.0	3.0	1.96	1.20	1.8	0.087
	std. dev.	0.14	300	0.06	0.007	0.4	0.006	0.2	0.2	0.08	0.07	1.4	0.016
ESP in	average	0.87	600	0.30	0.14	2.0	0.065	3.0	2.4	1.9	1.08	2.1	0.054
	std. dev.	0.12	400	0.19	0.02	0.5	0.009	0.3	0.3	0.3	0.12	0.2	0.012
FGD in	average	0.009	7	<0.002	0.029	<0.012	<0.002	<0.003	<0.003	0.07	0.006	<0.002	<0.007
	std. dev.	0.005	4							0.10			
stack	average	0.006	0.9	<0.001	0.0010	0.0009	<0.0003	0.0004	<0.02	0.005	<0.0001	<0.2	<0.001
	std. dev.	0.002	0.8		0.0008	0.0008		0.0002		0.005			

[a] μg/dscm: microgram per dry standard cubic meter. [b] mg/dscm: milligram per dry standard cubic meter. [c] Results have been corrected for blank filter.

Table 4. Halogens and Hydrogen Halides Monitoring Results Using EPA Method 26A

3% (v/v) O_2, 20 °C, dry	mg/dscm[a]					
	HF	F_2	HCl	Cl_2	HBr	Br_2
ESP inlet	14.6 ± 0.8	0.39 ± 0.10	154 ± 4	3.0 ± 1.2	1.78 ± 0.06	<0.1
FGD inlet	9.8 ± 0.6	0.23 ± 0.8	136 ± 0.8	0.98 ± 0.8	2.00 ± 0.8	<0.1
stack	0.30 ± 0.1	0.15 ± 0.8	0.82 ± 0.8	0.75 ± 0.8	<0.1	<0.1

[a] mg/dscm: milligram per dry standard cubic meter.

Table 5. Filterable and Condensable Particulate Matter Monitoring Results

			mg/dscm[e]						
			condensable particulate matter						
			inorganic						
		filterable[a]	from OTM 28	OTM sulfate[b]	CCM sulfate[c]	calculated[c]	organic	calculated CPM[d]	total particulate matter
ESP inlet	average	13700	NA	NA	NA	NA	NA	NA	13700
	std. dev.	1700							1700
FGD inlet	average	44	27.1	6.3	7.2	27.9	1.7	29.6	74
	std. dev.	7	1.6	1.3	1.0	1.1	0.9	0.7	6
stack	average	1.0	6	5.5	4.2	4.8	1.0	5.8	6.8
	std. dev.	0.2	3	1.8	1.8	0.8	0.5	1.2	1.0

[a] Filterable PM at the ESP inlet location was measured using EPA Method 17; EPA Method 5B was used at the FGD inlet and stack. [b] From condensable particulate matter measurement (dry impinger method), including sulfate from ambient filter. [c] From Control Condensation Method. [d] Inorganic $CPM_{calculated}$ = Inorganic $CPM_{OTM\ 28}$ − $Sulfate_{OTM\ 28}$ + $Sulfate_{CCM}$. [e] mg/dscm: milligram per dry standard cubic meter.

At the FGD inlet, the sulfate content in the sampling train was much lower than the total CPM results, suggesting sulfate is not the main source for CPM at this location. By analyzing the anion concentrations (Table 6) in the CPM sampling solution, substantial amounts of chloride and fluoride were observed, indicating the composition of CPM at the FGD inlet might include chloride and fluoride salts. However, at the stack, sulfate compounds are likely the main composition of CPM. The study demonstrates that no measurable artifacts were observed using the dry impinger method.

According to results from Method 17 and Method 5B, the ESP unit removed over 99.7% of particulates from the flue gas. Fine particles with suggested particle size of less than 0.1−1.0 μm[25,30] passed through the ESP unit, and an additional 98% were further removed by the FGD wet scrubbers. These fine particles are the major source of semivolatile elements (e.g., arsenic) in the FGD process.

Elemental Analysis of Solid and Liquid Samples. Results obtained from proximate and ultimate analyses of the composite coal can be seen in Table 1. The mean value ($N = 3$) of each measurement results (in dry basis) is shown with a standard deviation of 95% confidence internal. As shown in the table, the concentrations of the trace elements in coal are in agreement with the ranges of concentrations reported by several authors for eastern bituminous coals.[31,32]

(30) Senior, C.; Helble, J.; Sarofim, A. *Fuel Process. Technol.* **2000**, *65−66*, 263.

(31) Ratafia-Brown, J. A. *Fuel Process. Technol.* **1994**, *39*, 139.
(32) Yudovich, Ya.E.; Ketris, M. P. *Int. J. Coal Geology* **2005**, *62*, 135.

Table 6. Anion Compositions Observed from the Sampling Train

location and run No.	F⁻		Cl⁻		Br⁻		NO₃⁻		HPO₄²⁻		SO₄²⁻		total anions
	μg/g	mg	μg/g	mg	μg/g	mg	μg/g	mg	μg/g	mg	μg/g	mg	mg
FGD inlet, No. 1	10.2	5.08	14.8	7.40	1.53	0.76	1.00	0.50	< 0.1	< 0.05	8.12	4.06	17.8
FGD inlet, No. 2	10.1	5.04	11.5	5.75	1.60	0.80	2.22	1.11	0.86	0.43	6.28	3.14	16.3
FGD inlet, No. 3	12.1	6.06	12.9	6.45	1.67	0.84	1.91	0.95	1.09	0.54	9.69	4.84	19.7
stack, No. 1	0.43	0.21	0.70	0.35	0.03	0.01	2.53	1.26	3.79	1.89	15.75	7.88	11.6
stack, No. 2	0.48	0.24	1.70	0.85	0.04	0.02	0.68	0.34	0.51	0.25	10.23	5.11	6.8
stack, No. 3	0.66	0.33	0.86	0.43	0.04	0.02	1.46	0.73	< 0.1	< 0.05	10.38	5.19	6.7
reagent blank	< 0.1	< 0.05	< 0.1	< 0.05	< 0.1	< 0.05	< 0.1	< 0.05	< 0.1	< 0.05	< 0.1	< 0.05	ND

Table 8 summarizes the concentrations of selected elements in the bottom ash, economizer ash, ESP ash, and "in-flight" ash collected at the SCR outlet and ESP inlet. The fluoride content in the coal was close to the detection limit (50 μg/g) of the method employed in this study. Only one coal sample was observed to have a detectable flouride concentration (87 μg/g). Since no flue gas measurement was carried out at the SCR outlet for halogens and halogen halides, the in-flight ash collected at the SCR outlet was not analyzed for Cl and F. Concentration levels of selected elements are lower in the bottom ash when compared to what are observed in the ash collected in the postcombustion process (i.e., economizer ash and ESP ash). These partially (i.e., As, Se, B) or fully (i.e., Hg) vaporized elements further went trough adsorption, condensation, and chemical transformation as the flue gas cools down in the postcombustion process.[26,33] For example, no detectable mercury was found in the bottom ash and economizer ash as a result of a high flue gas temperature at these two locations. As the temperature decreased from 350 °C to less than 180 °C after the air heater, the flue gas environment was more favorable for condensation and adsorption, which resulted in a detectable mercury concentration level found on the in-flight ash collected at the ESP inlet. No significant difference between the mercury concentrations of in-flight fly ash samples collected at the SCR outlet and ESP inlet were observed. The mercury content of ESP ash was substantially higher than the in-flight ashes. The injection of trona might have promoted the adsorption/condensation of mercury onto the fly ash by reducing the presence of elements or compounds (e.g., SO₃) in the flue gas that compete with mercury for the active site on the fly ash surface.[34] It has been shown that the concentration of sulfur in the coal has a negative effect on mercury's adsorption of fly ash.[35]

For arsenic, the concentration level in the ash, in general, increased as the flue gas flowed downstream to the stack. The observation is likely due to a strong affiliation of arsenic with smaller particles.[29] No difference in the concentrations of arsenic are found between ESP fly ash and in-flight ash collected at the ESP inlet. For selenium, no significant difference was observed between bottom ash, economizer ash, ESP ash, and the in-flight fly ash. Selenium is expected to behave like boron and arsenic with no enrichment in the bottom ash[30] due to its low boiling point. However, it is

(33) Meij, R.; Janssen, L. H. J. M.; Van der Kooij, J. *Air Pollutant Emissions from Coal-Fired Power Stations*; Kema Scientific & Technical Reports: 1986; Vol 4, p 51.
(34) Dunham, E.; Hill-Brandt, K. L.; Olson, E. S.; Pavlish, J. H. In *The Effects of SO₃ on Mercury Capture by Activated Carbon Sorbents*. Proceedings of the 31st International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, May 21–26, 2006; pp 1051.
(35) Li, S; Cheng, C.-M.; Chen, B.; Cao, Y.; Vervynckt, J.; Adebambo, A.; Pan, W.-P. *Energy Fuels* **2007**, *21*, 3292.
(36) Yan, R.; Gauthier, D.; Flamant, G.; Peraudeau, G. *Environ. Sci. Technol.* **2001**, *35*, 1406.

Table 7. SO₃ and SO₂ Monitoring Results Using EPA CTM-13

	SO₃/H₂SO₄		SO₂	
	mg/dscm[a]	ppmv[b]	mg/dscm	ppmv
FGD inlet	6.0 ± 0.8	1.8 ± 0.3	2100 ± 500	790 ± 180
stack	3.5 ± 1.5	1.1 ± 0.5	33 ± 3	12.7 ± 1.0

[a] mg/dscm: milligram per dry standard cubic meter. [b] ppmv: part per million by volume.

plausible that the selenium in the coal might have affected the diffusion of vaporized selenium within the molten inclusion.[36] Table 9 summarizes the concentrations of selected elements in the liquid and liquid portion of the slurry samples collected from the FGD process.

Partitioning of Hg, As, Se, B, and Cl in Coal Combustion Process. By reviewing the mechanisms governing the fate of trace elements during coal combustion, Linak and Wendt[37] proposed possible routes along which trace elements partitioned into vapor and submicrometer and supermicrometer particles. Along the flue gas path, these particles are collected as bottom ash, economizer ash, and ESP ash. The supermicrometer particles might be washed out in the FGD wet scrubbers or be emitted into the atmosphere. Trace elements partitioned in the vapor phase redistribute into liquid, solid, and gaseous phases in the FGD process. All forms of coal combustion byproduct are therefore considered in this study for overall material balance calculation. A recovery index (RI) was calculated based on the following equation:

$$\text{RI} = \frac{M_{\text{out}}}{M_{\text{in}}} \qquad (2)$$

where M_{in} is the amount of a selected element that is added into the coal combustion process when one unit of coal is burned. In this study, coal; makeup water used in the FGD system; and FGD reagent slurry are the considered sources for the selected element. M_{out} is the overall output for the selected element, which includes stack gas (M_{stack}), bottom ash (M_{ba}), economizer ash (M_{econ}), precipitator ash (M_{fa}), and the FGD process (M_{FGD}).

$$M_{\text{out}} = M_{\text{stack}} + M_{\text{fa}} + M_{\text{ba}} + M_{\text{econ}} + M_{\text{FGD}} \qquad (3)$$

where

$$M_{\text{stack}} = V_{\text{DF,3\%}} C_{\text{stack}} \qquad (4)$$

$$M_{\text{ba}} = y_{\text{ba}} A C_{\text{mba}} \qquad (5)$$

$$M_{\text{econ}} = y_{\text{econ}} A C_{\text{mecon}} \qquad (6)$$

$$M_{\text{fa}} = y_{\text{fa}} A C_{\text{mfa}} h_{\text{ESP}} \qquad (7)$$

(37) Linak, W. P.; Wendt, J. O. L. *Fuel Process. Technol.* **1994**, *39*, 173.

Table 8. Chemical Properties of Solid[a]

	analyst		composite coal	bottom ash	economizer ash	in-flight ash collected by Thimble at ESP inlet	composite ESP Ash	reagent slurry	FGD gypsum
	sample number	*N*	3	3	3	3	3	6	6
Cl	chloride	μg/g	940 ± 120	120 ± 40	620 ± 180	420 ± 30	400 ± 100	170 ± 8	210 ± 30
Hg	mercury	μg/g	0.11 ± 0.02	< 0.01	< 0.01	0.064 ± 0.013	0.18 ± 0.07	0.06 ± 0.05	0.64 ± 0.04
As	arsenic	μg/g	6 ± 2	10.2 ± 0.5	26 ± 8	59 ± 4	58 ± 3	0.005 ± 0.003	4 ± 2
B	boron	μg/g	61 ± 5	< 1.5	73 ± 10	141 ± 23	89 ± 11	5.0 ± 1.7	5.7 ± 1.1
Se	selenium	μg/g	8 ± 2	24 ± 3	25 ± 2	30 ± 3	32 ± 9	23 ± 3	19.5 ± 0.3

[a] The F content in the coal was only detected in 1 sample and was less than 50 μg/g in the other 2 samples. [b] Dry basis; moisture was determined as received. [c] Not analyzed.

Table 9. Chemical Properties of Liquid

	analyst		service water	reagent slurry	chloride purge
			liquid samples		
Cl	chloride	mg/L	34.8 ± 0.5	116 ± 9	5560 ± 298
Hg	mercury	μg/L	0.05 ± 0.04	0.5 ± 0.4	39 ± 15
As	arsenic	μg/L	0.61 ± 0.04	0.11 ± 0.04	1.08 ± 0.04
B	boron	mg/L	1.3 ± 0.3	2.2 ± 1.1	180 ± 20
Se	selenium	mg/L	0.04 ± 0.02	0.07 ± 0.02	0.36 ± 0.05

$$M_{\text{FGD}} = C_{\text{m,blowdown}} \times m_{\text{blowdown}} + C_{\text{m, gypsum}} \times m_{\text{gypsum}} - C_{\text{m, makeup}} \times m_{\text{makeup}} - C_{\text{m, reagent}} \times m_{\text{reagent}} \quad (8)$$

$V_{\text{DF,3\%}}$ in eq 4 is calculated dry flue gas volume (at 3% and 20 °C) produced when one unit of coal is burned. Also in eq 4, C_{stack} is the concentration of the selected element in the stack gas (including vapor and particulate phases). Take Hg as an example, it is 0.48 μg/dscm. The parameters y_{ba}, y_{econ}, and y_{fa} are the mass ratios of bottom ash, economizer ash, and precipitator ash, respectively, to the mineral fraction of coal. According to plant information (PI) data and measurement, the values of these parameters are summarized in Table 10. *A* is the mass ratio of mineral fraction to the coal, which is determined by the ash content in the coal (Table 1). C_{mba}, C_{mecon}, C_{mfa}, $C_{\text{m,blowdown}}$, $C_{\text{m,gypsum}}$, $C_{\text{m,makeup}}$, and $C_{\text{m,reagent}}$ are the element concentrations in bottom ash, mechanical ash, precipitator ash, FGD blowdown, gypsum, makeup water, and FGD reagent, respectively. Because no detectable mercury concentration was observed in the bottom ash and economizer ash, the C_{mba} and C_{mecon} values are set to be 0 in the calcualtion. The values of C_{mfa}, $C_{\text{m,blowdown}}$, $C_{\text{m,gypsum}}$, and $C_{\text{m,makeup}}$ are shown in Tables 8 and 9. The solid content (i.e., 0.2145) of FGD reagent slurry was used to calculate $C_{\text{m,reagent}}$ for Hg, which is 41.7 μg/kg. The parameters, m_{blowdown}, m_{gypsum}, m_{makeup}, and m_{reagent}, which are the amounts of chloride purge, FGD gypsum, makeup water, and FGD reagent that were produced or consumed when one unit of coal was burned, are listed in Table 10.

The material balance results of selected elements (i.e., Hg, As, Se, B, and Cl) in the coal combustion process can, therefore, be established and the results can be seen in Table 11. Also included in the table are the values that were converted into g/h (grams per hour). As shown, the RI values are 0.79 ± 0.15, 0.73 ± 0.17, 1.0 ± 0.4, 0.74 ± 0.5, and 0.99 ± 0.09 for Hg, Se, As, B, and Cl, respectively. A RI value of 1 represents a perfect recovery.

With carefully executed sampling steps, high quality analytical results, and well-defined calculation domain, to obtain high RI value, collecting representative samples is the key, especially when only relatively small portions of the solid, liquid, and slurry samples can be collected from the

Table 10. Parameters Used for Material Distribution Calculation

parameter	unit	value
$V_{\text{DF,3\%}}$ [a]	dscm/kg coal	8.62
y_{ba} [a]		0.1
Y_{econ} [a]		0.05
Y_{fa} [a]		0.85
h_{esp} [a]	%	99.7
m_{blowdown} [a]	kg/kg coal	0.235
m_{gypsum} [a]	kg/kg coal	0.10
m_{makeup} [a]	kg/kg coal	0.15
m_{reagent} [a]	kg/kg coal	0.22

[a] Obtained from either facility operation data or empirical values

sampling locations through preinstalled valves or discharge pipes. In addition, only a small aliquot of each collected sample was analyzed. Therefore, the homogeneity of the selected elements in the collected samples plays an important role in the outcomes of RI values, which might contribute to the low RI values observed in Hg, Se, and B, as well as the greater standard deviation observed in As. Also, due to the operation setup, the FGD gypsum samples were collected only when the dewatering process was in operation. As a result, the samples were not collected concurrently with flue gas sampling. Because, for both Hg and Se, significant portions were distributed in the FGD gypsum, it is plausible that the collected FGD gypsum samples might not fully represent the samples generated during the flue gas sampling.

Figure 3 demonstrates the partitioning of selected elements in the coal combustion process based on the output results summarized in Table 11. As shown, the selected elements demonstrate different partitioning behaviors in the tested coal combustion process. Mercury and boron have similar behaviors in the flue gas. About 15 and 80% of these two elements were removed by the particulate precipitator and FGD process, respectively. The high removal efficiency of mercury by the ESP unit was due to the injection of trona. Detailed discussion is provided in a later section. However, in the FGD process, more mercury was affiliated with the solid portion of the FGD slurry and was later removed from the coal combustion process with FGD gypsum. Boron is more soluble. As a result, more than 80% of boron was discharged into the chloride purge wastewater stream. Approximately 5% of mercury and boron were emitted into atmosphere.

About 88% of arsenic was collected by the particulate precipitators. On the basis of the flue gas measurement results, most arsenic (over 98%) in the flue gas was particulate-bound. By combining the particulate removal efficiency by the ESP unit, which was determined by the particulate matter measurements carried out in this study, it was expected that the arsenic removal efficiency of the ESP unit should be about 97%. In the work carried out by Sandelin

Table 11. Partitioning of Selected Elements in the Coal Combustion Process

| | mass balance | | | | | | | | |
| | Hg | | Se | | As | | B | | Cl | |
	μg/kg coal[a]	g/h	μg/kg coal	g/h	μg/kg coal	g/h	mg/kg coal	kg/h	mg/kg coal	kg/h
	Input									
coal	110 ± 20	58 ± 11	8000 ± 2000	4000 ± 1000	6000 ± 2000	3200 ± 1100	61 ± 5	32 ± 3	940 ± 120	500 ± 60
mist eliminator water	0.023 ± 0.019	0.012 ± 0.010	14 ± 5	8 ± 3	0.25 ± 0.01	0.13 ± 0.01	0.49 ± 0.06	0.26 ± 0.03	14.3 ± 0.5	7.6 ± 0.3
reclaim to absorber (from service water)	0.7 ± 0.03	0.37 ± 0.02	160 ± 40	90 ± 20	10 ± 2	5.2 ± 1.1	15.0 ± 1.2	8.0 ± 0.6	450 ± 40	240 ± 20
reagent slurry	8.2 ± 1.2	4.3 ± 0.6	1100 ± 300	590 ± 160	180 ± 40	100 ± 20	0.43 ± 0.18	0.23 ± 0.10	21.5 ± 1.3	11.4 ± 0.7
total input	**119 ± 20**	**63 ± 11**	**9000 ± 2000**	**4700 ± 1000**	**6000 ± 2000**	**3300 ± 1100**	**77 ± 5**	**41 ± 3**	**1400 ± 130**	**760 ± 60**
	Output									
emission	4.09 ± 0.19	2.17 ± 0.10	340 ± 170	180 ± 40	1.0 ± 0.9	0.5 ± 0.5	2.5 ± 0.2	1.30 ± 0.11	17 ± 6	9 ± 3
bottom ash	<0.2	<0.1	290 ± 40	150 ± 20	240 ± 14	128 ± 7	<0.003	<0.002	1.7 ± 0.5	0.9 ± 0.3
economizer ash	<0.1	<0.1	164 ± 4	87 ± 2	143 ± 8	76 ± 4	0.35 ± 0.05	0.19 ± 0.03	4.3 ± 1.3	2.3 ± 0.7
esp ash	16 ± 6	10 ± 4	3700 ± 200	1980 ± 110	5300 ± 800	2800 ± 400	7.7 ± 1.0	4.1 ± 0.5	34 ± 8	18 ± 4
chloride purge	8 ± 4	4 ± 2	84 ± 5	45 ± 3	0.259 ± 0.002	0.142 ± 0.001	45.5 ± 1.9	24.2 ± 1.0	1325 ± 6	703 ± 3
gypsum	64 ± 6	34 ± 2	2000 ± 110	1060 ± 60	300 ± 140	160 ± 70	0.63 ± 0.15	0.34 ± 0.08	22.4 ± 0.5	11.9 ± 0.3
total output	**94 ± 9**	**50 ± 5**	**6600 ± 300**	**3500 ± 130**	**6000 ± 800**	**3200 ± 400**	**57 ± 2**	**30.1 ± 1.1**	**1380 ± 12**	**745 ± 6**
RI	**0.79 ± 0.15**		**0.73 ± 0.17**		**1.0 ± 0.40**		**0.74 ± 0.05**		**0.99 ± 0.09**	

[a] The amount of the element when 1 kg of coal is burned.

and Backman,[38] in which the distribution of trace elements in two coal-fired power plants were studied, they showed over 99% of arsenic was distributed in the fly ash. Similar high distribution ratio of arsenic in fly ash (97.6%) was also reported by Otero-Rey et al.,[28] who investigate the fate of several trace elements during the coal combustion process. The lower than expected partitioning of arsenic in the ESP fly ash observed in this study suggested that the particulate-bound arsenic was more concentrated on the finer fly ash particles in the flue gas. Those fine particulates, escaping from the ESP unit, were removed by the wet scrubbers (as shown in Table 5), which resulted in the additional 82% of arsenic removal by the FGD process. The particulate arsenic removed by the FGD process seems to be insoluble or easily incorporated into the solid portion of the slurry in the scrubber tanks. Only less than 0.5% of total arsenic was discharged into the wastewater stream.

As with arsenic, about 5 and 3% of total selenium was found in the bottom ash and economizer ash, respectively. The majority of selenium (56%) was collected by the particulate precipitators. Similar partition ratios of selenium in the bottom ash and ESP ash were also reported by Otero-Rey et al.[28] Most selenium removed by the FGD process was found in the FGD gypsum with a noticeable amount discharged into the wastewater stream. There are four possible selenium species in the environments; i.e., selenate (Se^{6+}), selenite (Se^{4+}), selenium (Se^0), and selenide (Se^{2-}). The investigation of selenium species in the FGD process was not in the scope of this study; however, the partitioning of selenium is likely associated with its forms of occurrence in the FGD system. Selenate and selenite have been reported to be the dominant species in the power plant matrix (i.e., fly ash, FGD gypsum, and wastewater).[39,40] Selenite (Se^{4+}) is
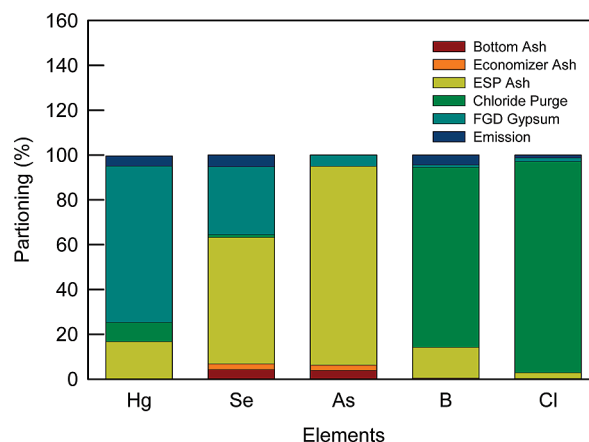
Figure 3. Partitioning of selected elements in coal combustion process.

less soluble and has been reported as the dominant species of selenium in FGD gypsum.[41]

In the case of chloride, over 95% was removed from the flue gas in the FGD process and discharged into the FGD wastewater stream. About 3% was condensed on the fly ash particle.

Evaluation of Trona Injection on Fly Ash Trace Element Composition. Mineral trona (trisodium hydrogendicarbonate dehydrate, $Na_3H(CO_3)_2 \cdot 2H_2O$) was injected before the ESP unit to control the emission of sulfur trioxide (SO_3). The possible effect of trona injection on the concentration levels of trace elements might be from (1) the addition of trace element source as a result of the injection, (2) complex interactions between gaseous phase trace elements (e.g., Hg, Se, and As), sulfur compounds (e.g., sulfur trioxide), and trona. To evaluate the effect, in this study, the chemical compositions of trace elements in the fly ash samples collected from the locations before and after the trona injection were analyzed.

(38) Sandelin, K.; Backman, R. *Environ. Sci. Technol.* **2001**, *35*, 826.
(39) Shah, P.; Strezov, V.; Stevanov, C.; Nelson, P. *Energy Fuels* **2008**, *21*, 506.
(40) *EPRI Technical Manual: Guidance for Assessing Wastewater Impacts of FGD Scrubbers*, Final Report No. 1013313; Electric Power Research Institute: Palo Alto, CA 94304.

(41) Souhail, R.; Al-Abed, G. J.; Kirk, G. S.; Thabet, T. Speciation. *Environ. Sci. Technol.* **2008**, *42*, 1693.

The injection of trona during the testing period remained at a rate of approximately 500 kg/hour. Although no trona sample was collected during the testing period, according to the results from the chemical analysis of a trona sample collected from the previous study at the same test utility, no detectable mercury ($< 0.01\ \mu g/g$) and arsenic ($< 1.5\ \mu g/g$) was observed. The concentration levels of Se, B, and Cl were found to be about 5, 100, and 50 $\mu g/g$, respectively. On the basis of the elemental analysis results, the concentrations of Se, B, and Cl in the fly ash samples collected at the ESP inlet (before trona injection) by thimbles (i.e., composite ESP Ash in Table 8) were greater than those observed from the trona sample collected from previous study. In addition, considering 530 ton of coal was burned every hour during the testing period, which generated over 59 000 kg/h of fly ash, the amount of injected trona at the ESP inlet was only about 0.8% of the total fly ash. It can be conclude that the amounts of trace elements that were added into the flue gas as a result of the injection were not significant.

Except for Hg and B, the concentration levels of As, Se, and Cl in the fly ash samples collected at the ESP inlet (i.e., the in-flight ash collected by Thimble at ESP inlet in Table 8) and from the ESP hoppers (i.e., composite ESP Ash in Table 8) were very similar. Therefore, it is concluded that the injection of trona did not show an observable effect on changing the concentrations of selenium, arsenic, and chloride in the ESP fly ash. Pflughoeft-Hassett et al.[42] also found that the concentrations of trace elements (e.g., As) are similar for the baseline fly ash and fly ash with sodium injection. Currently, to the best of our knowledge, only calcium-based sorbents have shown effect on the adsorption of As[43] and Se[44] at temperatures higher than 400 °C or at a temperature at 120 °C.[45]

The concentration of mercury in the ESP fly ash was found to be much higher than the concentration observed in the in-flight fly ash collected right before the trona injection location. Sulfur trioxide has been shown to inhibit the adsorption of mercury on to activated carbon.[46] The promotion of mercury adsorption by fly ash was likely due to the removal of SO_3 as a result of trona injection. Results obtained from this study suggest that it is necessary to evaluate the mobility of mercury in the fly ash produced from trona injection, which might affect the utilization of the resulting ash as well as its disposal.

Conclusions

Volatile and semivolatile metals and metalloids (i.e., Hg, As, Se, and B) showed different distribution behaviors in the tested unit. It was found that 76% of the total Hg was removed from the flue gas by the FGD system, where 90% of the removed Hg was found in the gypsum. Approximately 17% of the total Hg was found in the ESP fly ash. About 8% of the total Hg was emitted into the atmosphere. In the case of As, according to Table 11, 88% of the total As output was found in the ESP fly ash. The amount of As in bottom ash, economizer ash, and gypsum accounted for 5.8, 2.4, and 5%, respectively, of the total As output. A negligible amount of As was found in the chloride purge and emission. It was found that 56% of Se was in the ESP fly ash and 30% was observed in the FGD gypsum. About 5% of Se was found to emit into the atmosphere. Unlike Hg and Se, most of the B (99%) was found in the chloride purge. Eight percent of B was removed by ESP. Less than 0.5% of the total B was emitted into the atmosphere. The material balance results of selected elements (i.e., Hg, As, Se, Cl, and F) were calculated to be in a range of 73−100%. A value of 100% represents a perfect balance between the input and output of the selected element within the coal combustion process.

The FGD unit greatly reduced the concentrations of HCl, Cl_2, HF and F_2 in the flue gas. Over 90% of total Cl (including HCl and Cl_2) was removed from the flue gas and discharged from the combustion process by the chloride purge. It has been suggested that the employed EPA Method 26A has difficulty in differentiating the chloride speciation at the concentration of F_2 and Cl_2 below 5 ppmv.[47] Therefore, it is plausible that the measurement results might be due to the artifact of the method applied.

Over 99.7% of filterable PM was removed by the ESP unit. About 95% of condensable PM at the FGD inlet was inorganic. After the flue gas passed the FGD process, over 70% of condensable PM was reduced. No significant difference was observed between sulfate concentration observed by the dry impinger method and control condensation method. The difference between the sulfate results from the two methods was within 10%, with an exception of the results from the first measurement at the stack. It was found that the composition of CPM at the FGD inlet and stack were different. Sulfate compounds might account for more than 90% of CPM at the stack, but only about 20% at the FGD inlet. Chloride and fluoride salts might be the other sources of the CPM observed at this location.

Nomenclature

ACS = American Chemical Society.
ASTM = American Society for Testing and Materials.
BTU = british thermal unit.
USEPA = US Environmental Protection Agency.
FGD = flue gas desulfurizaton.
CCS = controlled condensation system.
SCR = selective catalytic reduction.
ESP = electrostatic precipitator.
CPM = condensable particulate matter.
FPM = filterable particulate matter.
ICP-AES = inductively coupled plasma atomic emission spectroscopy.
IC = ion chromatography.
ICSET = Institute for Combustion Science and Environmental Technology.
TSM = total selected metal.
CVAAS = cold vapor atomic adsorption spectroscopy.

(42) Pflughoeft-Hassett, D.; Ladwid, K.; Hassett, D.; Dockter, B.; Heebink L., Eylands, K.; Hoffarth, J. *Characteristics and Performance of Fly Ash from Sodium Sorbent Scrubbing of SO₃ Emissions from Coal-Based Power Plants.* Proceedings of the 2009 World of Coal Ash Conference, Lexington, KY, May 4−7, 2009.
(43) Mahuli, S.; Agnihotri, S.; Chauk, A.; Chosh-Dastidar, A; Fan, L.-S. *Environ. Sci. Technol.* **1997**, *31*, 3226.
(44) Ghosh-Dastidar, A.; Mahuli, S.; Agnihotri, R.; Fan, L.-S. *Environ. Sci. Technol.* **1996**, *35*, 598.
(45) Lopez-Anton, M. A.; Diaz-Somoano, M.; Spears, D. A.; Martinez-Tarazona, M. R. *Environ. Sci. Technol.* **2006**, *40*, 3947.
(46) Brickett, L, Feeley, T., Granite, E., Presto, A., O'Palko, A., Jones, A., *DOE-NETL's Experience with Activated Carbon Injection in High SO3 Environments.* Presented at the Electric Utilities Environmental Conference, Tucson, AZ. Jan. 21−24, 2006.

(47) Johnson, L. *Stack Sampling Methods for Halogen and Halogen Acids.* Presented at EPA/A&WMA International Symposium Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC. May1996.

CVAFS = cold vapor atomic fluorescence spectroscopy.
PC = pulverized coal.
QA/QC = quality assurance and quality control.
WKU = Western Kentucky University.

PI = plant information.
ND = not detected.
NA = not available.
std. dev. = standard deviation.