Elucidating Arsenic and Selenium Speciation in Coal Fly Ashes

Final Report

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Executive Summary

Coal fly ash (CFA) is produced during the coal combustion process and contains trace elements (<100 ppm) including selenium (Se) and arsenic (As), both detrimental for environmental and human health. Existing management strategies for CFAs involve disposal in landfills and ash ponds, as well as beneficial usage in other applications such as in concrete. Both the direct disposal and beneficial usage of CFA raise concerns for environmental hazards due to the potential leaching of Se and As. CFAs were classified as reusable material by the U.S. Environmental Protection Agency (EPA) with the first federal regulation (Disposal of Coal Combustion Residuals from Electric Utilities, CCR) for its disposal established six years ago.

During coal combustion process, parameters such as furnace firing type, emissions controls, coal rank, use of additives, and particulate matter controls, could contribute to significant variability in As/Se concentrations and their speciation. Although there have been a handful of studies on As/Se speciation on small sets of samples, they do not fully represent the current state of coal-fired electrical generating units. Little information exists on the detailed speciation (e.g. oxidation state, complexation state) of As/Se in large set of fly ash samples. To better investigate the role of the potential contributing parameters, a large-scale survey study with representative samples of typical coal source and combustion conditions is highly desired.

The overall goal of this research is to systematically characterize As and Se speciation of representative coal fly ash samples using state-of-the-art synchrotron based spectroscopic and microscopic techniques, in order to develop a correlation between coal source/type, operation condition, As/Se speciation, and As/Se mobility. A detailed survey study was conducted documenting the current state-of-knowledge on fossil power generating units as a function of coal type/source, operating conditions, environmental control systems, additive use, and fly ash handling methods. Based on this survey, a matrix of fly ash samples representing a range of conditions were chosen and collected. The collected ash samples were analyzed for bulk characteristics such as elemental composition, microstructure, chemical and mineralogical composition, surface area, and particle size distribution. State-of-the-art synchrotron X-ray microscopy and spectroscopy techniques were applied to reveal the molecular scale speciation information of As and Se, such as oxidation state, association with other elements/minerals, and complexation states.

Introduction

Coal fly ashes (CFAs) are byproducts of the coal combustion process. CFAs are heterogeneous materials comprised of major elements (>1000 mg/kg) including Al, Ca, Fe, and Si, as well as trace elements (<1000 mg/kg), such as Se, As, and Hg. The exact composition of CFAs is directly influenced by coal source, coal rank, and combustion conditions. Recent EPA Coal Combustion Residuals (CCR) and Effluent Limitation Guidelines (ELG) regulations have set the first federal boundaries on the amount of toxic metals (e.g., Hg, Se, As, etc.) and other harmful pollutants that steam electric power plants are allowed to discharge to their waste streams. Addressing compliance with these regulations can present a significant financial and environmental burden to the coal industry.

During coal combustion process, As and Se may volatilize and condense onto fly ash particles. The actual concentrations of captured trace metals and their speciation (e.g., oxidation state, mineralogy, complexation state) can be governed by complex interactions among feedstock composition, furnace operation conditions, configurations of downstream environmental control systems, boiler additives, reagents, and/or sorbent injection for Mercury and Air Toxics Standards (MATS) control. It is well known that metal speciation determines their reactivity, fate, and transport. Speciation is defined as the chemical (e.g., oxidation state, complexation state, mineral phase) and physical states (e.g., association with other elements or mineral phases) of an element. In order to understand the fate of As and Se during beneficial usage or landfill disposal of coal fly ash, it is thus important to develop an in-depth understanding on the correlation among coal source/type, operation condition, and As/Se speciation.

The overall goal of this project is to systematically characterize As and Se speciation of a range of representative coal fly ash samples using state-of-the-art synchrotron-based spectroscopy and microscopy techniques. A detailed survey study was conducted documenting the current state-of-knowledge on fossil power generating units as a function of coal type/source, operating conditions, environmental control systems, additive use, and fly ash handling methods. Based on this survey, a matrix of fly ash samples representing a range of conditions were chosen and collected. The collected ash samples were analyzed for bulk characteristics, including elemental composition, mineralogy, density, microstructure, surface area, particle morphology, and particle size distribution. Synchrotron X-ray microscopy and spectroscopy techniques were applied to reveal the molecular scale speciation of As and Se, such as oxidation state, mineralogy, association with other elements/phases, and complexation states.

Survey Study and Sample Selection

The first objective of this project is to conduct a comprehensive survey of operating U.S. coal-fired electrical generating units (EGUs) that produce fly ash as a combustion byproduct. This task was performed by EPRI. Several public and internal databases were searched, including EPA's Emissions & Generation Resource Integrated Database, the S&P Global Power Plant Book and Screener Tool 2020, as well as EPRI's own internal collections of databases on plant systems. The criteria used to search the databases included generating nameplate capacity (gross capacity in megawatts; MWg), boiler firing configurations, coal ranks, and installed emission controls for nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter (PM), and Hg. The databases were actualized up to December 2019. Units with a capacity of less than 90 MWg were excluded.

The results of the survey were used to select a sample subset of EGUs, which provided a wide array of representative operating units that fire various coal ranks and have different pollution control configurations. Fly ash samples were collected from seven EGUs in this group.

The results of the survey were recently published as a Technical Report by EPRI:

> **Survey of Coal-Fired Power Plants and Analysis of Selected Fly Ashes: A Task Toward Elucidating Arsenic and Selenium Speciation**
> Report number: 3002025163
> Date published: Jul 29, 2022
> URL: https://www.epri.com/research/products/000000003002025163

Following the survey study, sixteen representative samples from seven EGUs were selected and collected by EPRI. Two additional CFA samples were ordered from the National Institute of Standards and Technology. One additional sample was collected from a coal-fired powerplant from the southeast U.S. region.

Bulk Characterization

Morphological and elemental distribution analysis of CFA samples were performed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX), while mineralogical analysis was conducted by X-ray powder diffraction (XRD). For SEM-EDX analysis, thin section glass slides were prepared for each sample. SEM images and EDX spectra were obtained using a Hitachi SU 8230 field emission FE-SEM/EDX, and XRD patterns were collected using a Malvern PANalytical Empyrean XRD. Elemental analysis for major elements and loss on ignition tests (LOI) were performed using a ThermoARL X-ray Fluorescence Spectrometer (XRF) for elemental analysis. To determine the concentrations of As and Se, total digestion was performed and solutions were analyzed by ICP-MS (Agilent 7500a). In addition, density and particle size were tested using ASTM C188-17 and laser diffraction.

A summary of overall composition, average particle size, and bulk density is presented in Table 1. According to ASTM C-618, CFAs are classified into class C or F based on major elemental composition (wt%), including Fe_2O_3, SiO_2, and Al_2O_3. Class C contains a minimum of 50% Fe_2O_3, SiO_2, and Al_2O_3; while class F contains a minimum of 70% Fe_2O_3, SiO_2, and Al_2O. This ASTM provides specifications for fly ashes used in concrete including maximums for LOI and SO_3, respectively with values of 6 and 5 wt%. Based on this, 11 samples were classified as C while 8 samples belong to class F.

Crystalline mineral phases were identified by XRD, as shown in Figure 1. All class F samples (10–14, 1B, 90, and F) contain quartz (SiO_2), hematite (Fe_2O_3), and magnetite (Fe_3O_4). All samples except sample 10 contain mullite ($3Al_2O_3 \cdot 2SiO_2$). All class F samples except samples 13, 14, 90, and F contain portlandite ($Ca(OH)_2$), while anhydrite ($CaSO_4$) is also found in all class F samples except samples 11 and 90. Lime (CaO) is also present in class F samples, except for samples 10, 90 and F. Periclase (MgO) is present in all class F samples, except samples 90, 1B, 13, and 14. Mineral phases found in all class C CFAs (samples 1–9, 2S, and 91) include quartz, hematite, and magnetite. All class C samples except samples 2S and 91 contain thenardite (Na_2SO_4), calcite

($CaCO_3$), and gehlenite ($Ca_2Al(SiAl)O_7$). All class C samples except samples 9 and 91 contain periclase (MgO). Sample 91 contains mullite, anhydrite, and tricalcium aluminate (C_3A).

SEM-EDX revealed an abundance of aluminosilicates, as shown in Figure 2. SEM images revealed particles have irregular or spherical morphology, including plerospheres, and particle sizes were as small as 1 µm (Figure 3). Cenospheres which are characterized by their hollow nature were also present (Figure 4). Physical properties measured included particle size and density. A particle sizes range at around 10–100 µm, with samples 10 and 11 corresponding to the lowest and highest sizes.

Table 1. Composition, particle size, and bulk density of CFA samples. NM: not measured.

Sample ID	Major elements (wt%)				Trace elements		Average particle size (µm)	Bulk density (mg/cc)	LOI
	Fe_2O_3	Al_2O_3	SiO_2	CaO	As	Se			
1	5.27	19.42	36.92	18.70	18.88	0.23	13.2	2.63	1.75
2	5.26	19.25	39.27	17.90	16.82	0.24	12.7	2.56	0.91
3	6.73	16.26	47.29	15.02	10.39	0.18	51.4	2.53	0.86
4	5.44	19.09	38.39	18.33	17.68	0.25	11.5	2.59	1.05
5	5.69	19.98	39.29	16.75	19.01	0.27	14.0	2.59	0.76
6	5.66	20.15	39.05	16.96	20.23	0.27	13.5	2.57	0.71
7	5.27	19.48	37.05	18.84	18.94	0.22	10.1	2.61	0.95
8	5.68	19.97	39.33	16.74	19.29	0.28	13.7	2.56	0.66
9	4.81	20.84	42.41	16.28	24.44	0.37	21.2	2.56	3.41
10	10.00	7.60	16.34	35.68	93.75	1.83	8.3	2.53	9.72
11	30.30	16.94	40.95	8.26	8.08	0.25	107.5	2.41	1.66
12	15.88	18.26	44.22	12.69	24.01	0.27	17.4	2.48	2.43
13	24.13	20.74	38.87	6.77	26.19	0.25	41.3	2.56	8.86
14	28.37	20.53	39.11	7.16	22.57	0.25	42.6	2.69	3.96
1B	17.48	21.71	49.10	4.75	45.09	0.31	30.2	2.37	0.42
2S	6.22	16.60	36.59	27.79	12.31	0.35	23.9	2.69	3.07
90	5.11	23.30	55.30	8.00	26	0.8	NM	NM	0.53
91	6.32	18.53	36.00	25.81	30	17	NM	NM	0.23
F	11.90	25.20	54.30	1.60	53.6	7.3	NM	NM	NM

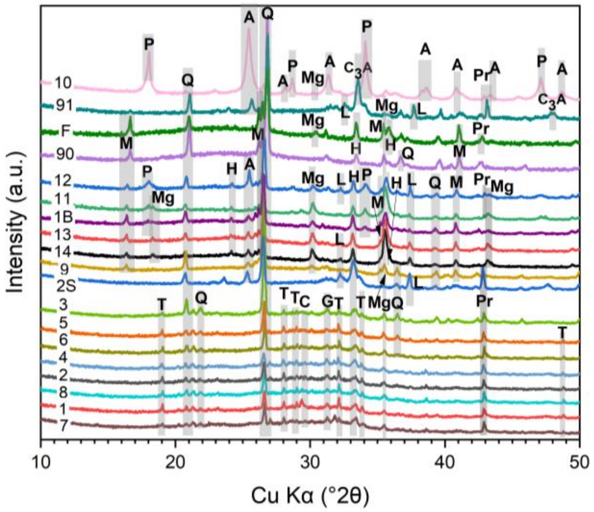

Figure 1. XRD spectra of CFA samples. Sample IDs are shown on the left and peak assignments are represented as gray bars. Minerals are shown as: Mullite (M), Portlandite (P), Magnetite (Mg), Thenardite (T), Quartz (Q), Hematite (H), Anhydrite (A), Calcite (C), Gehlenite (G), Lime (L), Hematite (H), and tricalcium aluminate (C_3A).

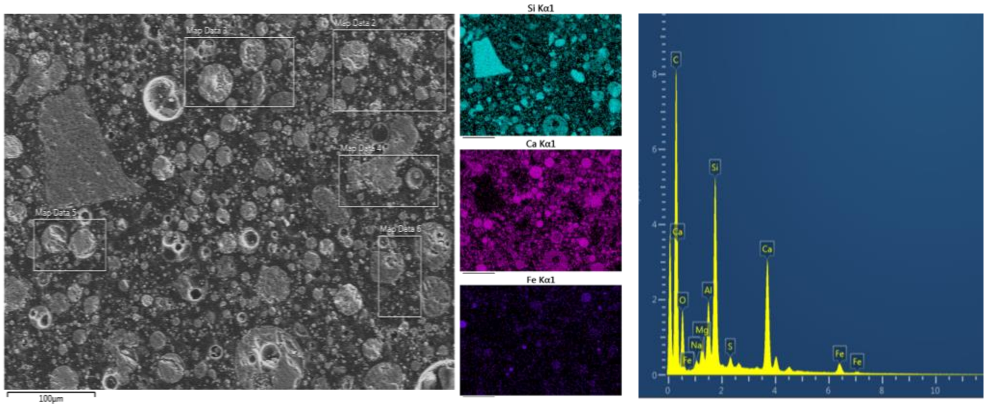

Figure 2. SEM image, elemental maps, and EDX spectrum of sample 2S.

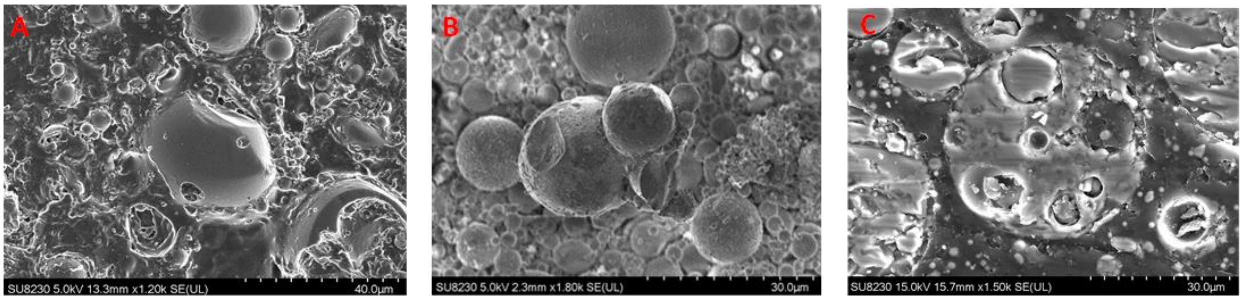

Figure 3. SEM images for samples 90 and 2S, showing A) irregular morphology; B) spherical morphology; and C) plerosphere.

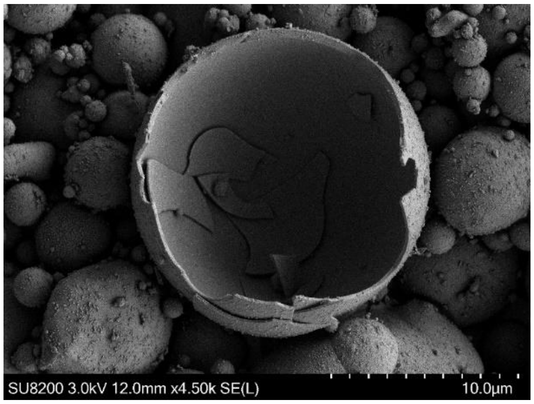

Figure 4. SEM image of a cenosphere in sample 9.

Characterization of As and Se Speciation Using Synchrotron Techniques

Bulk speciation characterization using X-ray absorption spectroscopy

As and Se K-edge bulk X-ray absorption spectroscopy analyses were conducted at Beamline 12-BM at the Advanced Photon Source (APS, Lemont, IL, USA). X-ray absorption near edge structure (XANES) spectra were collected for samples and model compounds (Table 2). Model compounds for As include $Ca_3(AsO_3)_2$, $Ca_3(AsO_4)_2$, Na_3AsO_4, Na_3AsO_3, As_2O_5, As_2O_3, As(V) adsorbed/doped ferrihydrite, and As(III) adsorbed/doped ferrihydrite. Se model compounds include Se(0) foil, Na_2SeO_4, $CaSeO_3$, SeO_2, Se(IV) adsorbed on lime, Se(IV) adsorbed/doped ferrihydrite, and Se(VI) adsorbed/doped ferrihydrite. Samples were finely ground with a mortar and pestle, placed in a sample holder, and covered with Kapton tape. Energy calibration for As and Se was performed with Au and Se foil, with 3-6 scans collected for each sample. The software Athena was used for XAS data analysis. Principle component analysis and linear combination fitting (LCF) was conducted to identify the relative percentage of contributing species.

LCF of As bulk XANES revealed As(V) to be the dominant oxidation state (≥89%) for all CFAs. CFAs were best fitted by $Ca_3(AsO_4)_2$ and As_2O_5, with the exceptions of samples 13, 14, 1B, and 2S. Sample 1B was best fitted by As(V) species as 85.8% $Ca_3(AsO_4)_2$ and 11.1% Na_3AsO_4. In contrast, samples 13, 14, and 2S contain ≥19% of As(III), noticeably sample 14 contains ≥40% and sample 13 ≥51% of As(III). In contrast to LCF results for As bulk XANES, LCF results for Se bulk XANES indicate a wider distribution of oxidation states including Se(0), Se(IV), and Se(VI). All CFAs, with the exception of samples 13 and 14, were best fitted by some percentage of Se(VI) adsorbed on Fe oxide (ferrihydrite). Notably, samples 13 and 14 contain ≥89% Se(0), while samples 11 and 12 contain ≥45% Se(0) and samples 5, 8, 10, and 2S were best fitted by ≥11% Se(0). All CFA samples were best fitted by a Se model compound containing Fe, Ca, or an oxide; in addition, based on LCF results all CFAs were found to contain Se associated with Fe oxides (≥13.9%).

Table 2. Information on model compounds and sources.

Oxidation State	Model Compound	Source
As(III)	As_2O_3	Purchased
	Na_3AsO_3	Purchased
	As(III) adsorbed on FeOx	Synthetic
As(V)	$Ca_3(AsO_3)_2$	Synthetic
	As_2O_5	Purchased
	Na_3AsO_4	Purchased
	As(V) adsorbed on FeOx	Synthetic
	As(V) doped in FeOx	Synthetic
	$Ca_3(AsO_4)_2$	Synthetic
Se(0)	Se foil	Beamline
Se(IV)	$CaSeO_3$	Purchased
	SeO_2	Purchased
	Se(IV) doped in FeOx	Synthetic
	Se(IV) adsorbed on lime	Synthetic
	Se(IV) adsorbed on FeOx	Synthetic
Se(VI)	Se(VI) adsorbed on FeOx	Synthetic
	Se(VI) doped in FeOx	Synthetic
	Na_2SeO_4	Purchased

Microscale speciation using micro-X-ray fluorescence spectromicroscopy

Micro X-ray fluorescence (µXRF) microscopy combined with micro-XANES (µXANES) were performed on selected fly ash samples prepared as petrographic thin sections. Data collection was conducted at the beamline 2-3 at Stanford Synchrotron Radiation Lightsource (SSRL, Menlo Park, CA). Thin-sections were mounted on a sample stage, and selected areas were mapped with a spatial resolution of 2 µm × 2 µm and dwell time of 100 ms. µXRF images were collected at 13 keV. µXRF data analysis used the Sam's Microanalysis Toolkit (SMAK). Multiple µXANES spectra were collected at µXRF-determined As/Se hot spots. LCF of µXANES spectra was performed following the same procedure as bulk XANES spectra. Results for As µXANES showed strong associations with Ca and Fe, and a dominant presence of As(V), with lower amounts of As(III) for some particles, consistent with bulk XANES analysis. Se results revealed Se co-localization with Fe, Ca, and Na. Oxidation states of Se(IV) and Se(VI) were observed.

Conclusion

Overall CFA has been widely investigated in terms of As/Se total concentration, mineralogy, morphology, and trace metal concentrations. However, most studies are limited to a small sample group with no or limited information on coal combustion conditions. Results from this study indicate samples have spherical morphology including cenospheres and plerospheres, as well as irregular morphology. XRD revealed the presence of amorphous phase and mineral phases magnetite, hematite, quartz, mullite, portlandite, anhydrite, thenardite, lime, periclase, and calcite.

Bulk As K-edge XANES analysis showed the dominant As species to be As(V) and As(III), and they exist as oxides, Ca/Na arsenate/arsenite salts, and Fe oxide doped species. Bulk Se K-edge XANES analysis showed the presence of Se(0), Se(IV), and Se(VI). They dominantly exist as Se(0), SeO_2, selenite adsorbed/doped Fe oxide, selenite adsorbed on lime, Ca selenite salt, and selenite adsorbed/doped Fe oxide. µXRF analysis combined with µXANES confirmed the bulk speciation results. For example, based on bulk XANES sample 8 contained 14.6% Se(0), 22.0% Se(IV) doped in FeOx, and 65.7% Se(VI) adsorbed on FeOx while µ-XANES of a small spot within the sample showed 30.9% Se(0) and 69.1% Na_2SeO_4.

Samples that contain >10% As(III) had SCR as an NO_x control, compared to the other samples that used combustion controls (low NO_x burner) to limit NO_x. Since CFA is collected after NO_x controls, this may suggest that SCR may influence the oxidation state of arsenic.