

MULTI-MEDIA EMISSIONS OF SELENIUM FROM COAL-FIRED ELECTRIC UTILITY BOILERS

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ABSTRACT

Eleven coal-fired boilers were sampled for process streams while carrying out stack measurements of trace metals using Method 29 for the 2010 EPA ICR. Samples were taken of: coal (a split of the ICR sample, if possible), bottom ash (if available), economizer ash (if available), and ash from the particulate control device hopper. For plants with flue gas desulfurization (FGD), samples of limestone, make-up water, gypsum product, and the scrubber chloride purge stream were collected. Partitioning of selenium (Se) in the boiler, particulate control device and scrubber were calculated for the eleven plants sampled in detail. Overall removal of selenium across the power plant ranged from 72% to 99.3%. For the bituminous plants with cold-side ESPs, less than 40% of the selenium input ended up in the fly ash. For the subbituminous plants, most of the selenium was captured in the fly ash in the ESP or fabric filter. Even in boilers where selenium capture in the scrubber was highest (80% to 95%), the selenium capture did not approach the level of SO₂ capture (92% to 99%). Other plants appeared to only capture 50% of the selenium in the scrubber. The selenium that was removed from the scrubber predominantly (greater than 80%) ended up in the gypsum product. The scrubber design and operation conditions did not appear to be a factor in selenium removal in the scrubber. The firing system and NO_x control subsystem did not appear to play a factor in selenium behavior at one plant with two boilers that had different configurations but fired the same coal.

INTRODUCTION

In December 2004, the U.S. Environmental Protection Agency (EPA) proposed revised water quality criteria recommending safe levels for short-term and long-term selenium exposure in both freshwater and saltwater environments. EPA released a draft ambient water quality criterion for selenium in October, 2008. The criteria recommendations were intended to protect aquatic life under the Clean Water Act.¹ EPA is in the process of revising the Effluent Guidelines² for the electric utility industry, which may include limits on the discharge of trace metals, including Se, from FGD wastewater.

Selenium is also listed as a hazardous air pollutant under the Clean Air Act. Currently there are no limits on air emissions of selenium from combustion sources. However, EPA is in the process of setting maximum achievable control technology (MACT) standards for coal-fired power plants, which could include standards for air emissions of selenium.³

Selenium is found in coals in trace concentrations. USGS has reported concentrations in coal as high as 150 µg/g,³ but 0.5 to 10 µg/g is a more typical range for US coals. The mode of occurrence of selenium in coal can be assayed using selective leaching (chemical fractionation).⁴ Selenium has two principal modes of occurrence: association with pyrite and association with the organic matter. Minor amounts of selenium are sometimes associated with HCl-soluble sulfides and silicates. The minerals in bituminous coals from the Eastern U.S. can contain significant amounts of pyrite, and selenium is often mostly associated with pyrite. In subbituminous coals from the Powder River Basin (PRB), selenium is mostly associated with the organic matrix.

Selenium is a volatile element and vaporizes to a great extent during coal combustion. High-temperature equilibrium calculations show that under flame conditions (>2400°F, oxidizing atmosphere) the most thermodynamically stable species of selenium is SeO₂(g). Selenium is soluble in silicate glasses, and is used in the glass industry to “de-colorize” glass, by reacting with iron to form a Fe-Se compound. Fang and Lynch⁵ measured the solubility of selenium in silicate slags in equilibrium with Cu-Se alloy. As the amount of Fe²⁺ increased in the slag (relative to Fe³⁺), the solubility of Se increased in the slag. They reported 0.2 wt% to 3 wt% Se in the slags at temperatures of 1185°C and 1250°C (2165°F and 2280°F). Their results were consistent with a model that had been proposed, in which selenium was postulated to exist in both a neutral state and as a Fe-Se complex in the slag.

Thus, in a coal-fired boiler, some portion of selenium might dissolve in molten silicate particles in the flame. However, the greatest part of selenium is expected to exit the high-temperature combustion zone of the boiler as

SeO₂(g). Gaseous selenium might react with the surface of fly ash particles as the flue gas passes through the heat exchange region of the boiler.

Based on fundamental studies,⁷⁻⁹ calcium oxide is capable of capturing of selenium between 400°C and 600°C (750°F and 1100°F), which is to say at the economizer inlet or outlet. The reaction rate of SeO₂ will be higher than that of SO₂ in this temperature range, but the concentrations of SO₂ are much higher. SeO₂ should react with the CaO in this temperature range until a product layer builds up from sulfation and reduces the number of sites for reaction.

In pilot-scale coal combustion experiments carried out at the University of Arizona,^{10,11} the Se distribution in the fly ash of bituminous coals appeared to track the iron distribution. In the bituminous coal experiments, Se was observed in the submicron particles at temperatures greater than 1830°F to 2010°F (1000 to 1100°C), suggesting reaction with iron in the submicron ash at high temperatures. Adding iron or calcium to the bituminous coals increased the concentration of Se in fly ash. Iron had the larger effect on Se concentration in the fly ash. The temperature of the lower furnace sampling location might have been too high to see significant Se-Ca reaction.

There was evidence for reaction between Se and calcium in a Wyodak subbituminous coal at temperatures less than 1830°F (1000°C), which was consistent with the laboratory observation that the reaction product between calcium and selenium was not stable above 800°C. Adding Se to the Wyodak coal increased Se concentration in all particle sizes. Adding supermicron iron to the Wyodak combustion experiment resulted in a modest increase in Se in the supermicron ash particles. Perhaps this reflected mass transfer limitations, because the Se content of the Wyodak coal was low.

With sufficient calcium in fly ash, selenium might be expected to form a calcium selenite/selenate at temperatures below about 930°F (500°C). In a coal-fired boiler, this temperature corresponds roughly to the inlet of the economizer. For coals with low sulfur, but moderately high iron, iron selenite might form at temperatures below 570°F (300°C) (that is, in the air preheater or downstream). Without sufficient calcium or iron (or in the presence of relatively high concentrations of SO₂), selenium might be expected to condense as SeO₂ at temperatures below about 290°F (200°C). Partial condensation would lead to selenium leaving the particulate control device as a gas (SeO₂), which is observed in bituminous-fired plants. Laboratory work has suggested the selenium interacts with unburned carbon or activated carbon at low temperatures (250-480°F).¹²⁻¹³

EPA is in the process of setting MACT standards for coal-fired and oil-fired power plants, which could include standards for air emissions of hazardous air pollutant (HAP) metals, including selenium.³ At the end of 2009, EPA issued an information collection request (ICR) to the electric utility industry, requesting information on emissions of HAPs from electricity generating units (EGUs) firing coal or oil. A subset of EGUs were required to conduct measurements of non-mercury HAP metals (antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, nickel, and selenium) in the boiler stack using EPA Method 29 during 2010. These metals were also measured in a coal sample taken concurrently with each stack test.

EPA chose 175 EGUs with the newest particulate control devices; this was intended to represent EPA's best guess of the top 15% lowest emitting units. EPA also chose 50 boilers at random. This data set represents a range of fuel types and air pollution control device (APCD) types. However, since the ICR data set includes only stack measurements, it is not possible to discern from these data the effect of multiple APCDs on selenium emissions. When a boiler has a combination of an ESP and a wet flue gas desulfurization (FGD) scrubber, for example, one cannot determine the fate of selenium in that system. Whether selenium ends up primarily in fly ash, in the scrubber solid byproduct, in the scrubber purge stream, or in stack emissions is important, because the fate of selenium in the environment is affected by the form in which it is emitted.

The objective of this work was to provide supplemental information on the fate of selenium in coal-fired boilers as a complement to the 2010 Utility Information Collection Request (ICR) data set. Eleven coal-fired boilers, which were carrying out stack measurements of trace metals using Method 29 during 2010, were sampled. At each plant, samples were taken during stack testing: coal (a split of the ICR sample, if possible), bottom ash (if available), economizer ash (if available), ash from the particulate control device hopper. For plants with flue gas desulfurization (FGD), samples of limestone, make-up water, gypsum product, and scrubber purge stream were collected.

EXPERIMENTAL

Site Descriptions

Eleven EGU boilers at seven coal-fired power plants were selected for measurement, after discussion with EPRI, URS, and various utilities. Table 1 describes the boilers in terms of combustion system, capacity, fuel, and APCD configuration. All of the FGD systems used limestone reagent and produced gypsum, and all except at Boiler F Unit 1 operated with forced oxidation; the FGD on Boiler F Unit 1 operated with high natural oxidation.

Table 1. Description of power plants tested.

Plant	Unit	Unit Type	MWe	Fuel	PM Control	NO _x Control	SO ₂ Control	Hg Ctrl	SO ₃ Ctrl
Plant A	Unit 1 ¹	PC, front wall	48.3	bit.	C-ESP, w/o FGC	--	--	--	--
Plant A	Unit 2 ¹	PC, front wall	48.3	bit.	C-ESP, w/o FGC	--	--	--	--
Plant B	Unit 1	PC, front wall	207.9	bit.	C-ESP, w/o FGC	SCR	Wet FGD (Spray and Tray)	--	--
Plant B	Unit 2	PC, front wall	203.2	bit.	C-ESP, w/o FGC	SCR	Wet FGD (Spray and Tray)	--	--
Boiler C	Unit 4	PC, wall	175.0	bit.	FF (pulse)	SCR	Wet FGD (Spray and Tray)	--	Wet ESP
Plant D	Unit 1 ²	Cyclone	150.7	bit., petcoke	C-ESP, w/o FGC	SCR	Wet FGD (Spray type)	--	--
Plant D	Unit 2 ²	PC, tangential	260.7	bit., petcoke	C-ESP, w/o FGC	SNCR	Wet FGD (Spray type)	--	--
Boiler E	Unit 4	PC, opposed wall	707.7	subbit.	C-ESP, w/o FGC	SCR	Wet FGD (Spray type) ³	--	--
Boiler F	Unit 1	PC, tangential	566.0	subbit.	FF (reverse gas)	--	Wet FGD (Spray type)	--	--
Plant G	Unit 1	PC, opposed wall	448.5	subbit.	FF (pulse)	--	Wet FGD (Spray type)	--	--
Plant G	Unit 2	PC, opposed wall	440.0	subbit.	FF (pulse)	--	Wet FGD (Spray type)	--	--

¹Unit 1 and 2 had combined stack

²Unit 1 and 2 shared scrubber and stack

³Scrubber was off-line during metals testing

Sampling Protocols

The following samples were collected for analysis during the period when ICR stack sampling was being conducted.

- **Coal samples** – One split of the ICR coal composite per day of Method 29 sampling for each unit. A minimum of a gallon of crushed coal was collected.
- **Fly ash samples** – An ash sample from the unit being sampled on the day of each Method 29 run was collected from a representative hopper in the first field of the ESP or from one of the FF hoppers. Approximately one gallon of fly ash was collected. At Plant B, entrained fly ash was collected directly from the duct upstream of the ESP.

- **Bottom ash (and/or economizer ash) samples** – These were collected on the day of the Method 29 sampling. Wet (sluiced) bottom ash samples were dried before analysis.
- **Limestone samples** – Samples were collected on the day of the Method 29 runs. The preferred method of collection was to take several samples from the weigh belt feeding the mill and mix them in a clean bucket. If it was difficult to collect a sample from the weigh belt, a slurry sample from the reagent feed tank could be collected in a bottle.
- **Scrubber make-up water** – Samples were collected in bottles on the day of the Method 29 run.
- **FGD blowdown or chloride purge stream** – Samples were collected on the day of the Method 29 run. These were collected from the thickener overflow, secondary (or sometimes primary) hydrocyclone overflow, belt or drum filtrate, or centrifuge centrate.
- **Gypsum product** - Samples were collected on the day of the Method 29 run. The preferred method was to collect several pieces from the vacuum filter; catch several pieces at various points along the belt or drum and composite them in a gallon Zip-loc bag. For some plants with multiple-unit secondary dewatering, hydrocyclone or thickener underflow slurry was sampled to provide unit-specific gypsum samples.

Additional operational information was collected from the plant, which included the following.

- Load, MW
- Firing Rate, lb/hr
- Economizer O₂ %
- Economizer Outlet or air preheater (APH) Inlet Temperature
- APH Outlet Temperature
- APH Outlet O₂ %
- Stack O₂ %

Analytical Methods

Short proximate analyses (ash, moisture, sulfur, heating value) were conducted on the coal samples by SGS, North America (Denver, CO). Moisture and carbon content analyses were conducted on the ash samples at SGS as well. Some of the bottom ash samples were sampled in slurry form. These were dried, and subsequently sent out for trace metal analysis as dry samples.

All coal and ash samples were analyzed for a range of elements by Instrumental Neutron Activation Analysis (INAA) at the Jožef Stefan Institute, Department of Environmental Sciences (Ljubljana, Slovenia). A selected number of coal and ash samples were analyzed for total selenium by Inductively Coupled Plasma-Dynamic Reaction Cell-Mass Spectrometry (ICP-DRC-MS) at Brooks Rand Labs (Seattle, WA).

The INAA analysis can detect a range of elements based on the radioactive decay of elements after the sample is exposed to a neutron beam. The irradiation of samples was carried out at the TRIGA Mark II reactor at the Jožef Stefan Institute using the k₀-method of INAA, which is an accredited method for environmental samples (soil, sediments, sewage sludge, biological materials) according Accreditation Certificate LP-090 dated on 18.5.2010 for 31 elements: Ag, As, Au, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, Yb, Zn and Zr. An additional four elements can be determined, but are not accredited: Ba, Cd, Ga, W. For the determination of these 35 elements, k₀-INAA long irradiation is used, in which 0.16-0.20 g of material are sealed in an ampoule and combined with a standard (Al-0.1%Au). The sample is irradiated for 14 hours. After irradiation, the sample is measured after 2 to 4 days and 8 to 14 days using HPGe detectors. With an additional short irradiation by k₀-INAA the following elements can be determined: Al, Cl, Cu, Dy, Mg, Mn, Ti and V. For these elements k₀-INAA is not accredited. For determination of short-lived radionuclides, 0.16-0.20 g of sample are irradiated together with a standard (Al-0.1%Au) for 3 minutes. After irradiation, the sample is measured after 6 minutes and 30 minutes. Standard procedures are used to determine the elemental concentrations.

Additional measurements of Se in coal and ash samples were carried out by ICP-DRC-MS. Conventional ICP-MS can over report concentrations of Se because of the formation of polyatomic ions that have the same mass as the Se isotope of interest. These interfering ions are counted by the detector as Se, which results in Se concentrations that are biased high. Interferences with Se can come from ions that are common to the measurement system (Ar) and elements that are common in coal and ash samples (H, C, O, S, Cl, Ca). In order to eliminate interfering ions before the sample gas reaches the mass analyzer, a dynamic reaction cell is employed. Reactive gases are injected into this chamber; these gases react with the specific interfering ions so that they are not measured by the mass analyzer.

URS analyzed wet FGD samples for a number of analytes, including wt% suspended solids in slurry samples, dissolved chloride in blowdown samples, and various solid-phase analyses to determine limestone utilization and gypsum byproduct purity (EPRI Methods F1, H1, I2, N4). These results were used to estimate gypsum product and chloride purge stream flow rates for the plant selenium balances. ¹⁶Results and Discussion

Mass Balances

The coal compositions are summarized in Table 2. Se, Cl, and Br concentrations are from INAA and are reported on an as-received basis. The bituminous coals (Plant B, Boiler C, Plant D) have higher Se contents than the low-rank coals (Boiler E, Boiler F, and Plant G). (Note that the Plant G fuel appears to be on the border between subbituminous and bituminous ranks, based on higher heating value.) The Se contents are consistent among multiple samples from a given plant, although the two samples from Boiler F have a relatively high deviation from one another in terms of Se content. Boiler C coal has the highest concentrations of chlorine and bromine with average values of 1956 µg/g and 12 µg/g, respectively. Plant B has an average Cl content of 667µg/g and an average Br content of 9 µg/g. The other bituminous coal, from Plant D, has a very low chlorine content for a bituminous coal, 115 µg/g, with a bromine content that is also low, 1.8 µg/g. The low-rank coals have chlorine contents that are typical of Western fuels, in the range of 8 to 19 µg/g, with correspondingly low bromine contents. Fly ash was also analyzed (results not shown) for unburned carbon content, major, minor and trace elements.

FGD samples were analyzed as shown in Table 3. . Other FGD operating data were collected (or estimated) in order to calculate a selenium mass balance around the scrubber. At some plants a make-up water sample was not collected. However, the concentration of selenium in the make-up water was never very high.

In the case of Plant D, which had a wet ESP (WESP) following the FGD, effluent was collected from the WESP, although there was not enough information about the operation of the WESP to determine a flow rate of effluent. The concentration of Se in the effluent from the WESP was significantly higher than that in the make-up water, but lower than the Se concentration in the FGD blowdown liquid. There did seem to be some selenium being captured in the WESP, but the flow rate could not be quantified. The wet ESP blowdown was used as makeup water to the FGD system, so this uncertainty did not impact the overall selenium balance.

Based on the boiler and FGD operating parameters and the measured concentrations of Se, URS calculated the selenium content of the FGD input and output streams. In order to calculate the selenium flow rates around the FGD, simplifying assumptions were made. In particular, the scrubber was assumed to be at steady state with respect to chloride: that is, the chloride purge rate was assumed to be equal to the input rate of chloride from coal. For boilers B-1, B-2, C, G-1, and G-2, most of the selenium left the scrubber in the gypsum. Only Plant D (boilers D-1 and D-2 with a combined scrubber) had more selenium leaving the scrubber in the stack than in the gypsum. The flow rate of selenium in the chloride purge stream was always less than the flow rate out in the gypsum.

Table 2. Coal analyses, as-received basis.

Plant	Unit	Proximate analysis						
		%Moisture	%Ash	%S	Se, µg/g	Cl, µg/g	Br, µg/g	HHV, Btu/lb
Plant A	1&2	5.98%	11.13%	0.89%	4.48	1158	14.6	12,208
Plant A	1&2	7.05%	12.26%	0.97%	4.39	1142	13.9	11,771
Plant A	1&2	7.34%	11.98%	0.89%	4.71	1144	14.1	11,873
Plant B	1	5.61%	11.32%	1.48%	3.95	993	11.6	12,338
Plant B	1	5.40%	13.69%	1.56%	4.5	505	8.16	12,213
Plant B	2	4.70%	13.77%	0.98%	4.16	656	8.83	12,262
Plant B	2	4.06%	12.28%	1.22%	4.08	516	7.9	12,825
Plant C	4	16.29%	9.87%	3.29%	1.57	1889	11.3	10,512
Plant C	4	17.61%	10.30%	3.39%	1.73	2022	11.7	10,265
Plant D	1	11.21%	11.12%	3.96%	3.68	141	2.19	10,887
Plant D	1	10.91%	9.96%	4.13%	3.45	91.3	1.45	11,311
Plant D	1	11.12%	10.78%	4.60%	3.96	83.4	1.48	11,110
Plant D	2	11.51%	11.28%	4.15%	3.4	154	1.93	11,003
Plant D	2	12.01%	11.82%	3.90%	3.71	114	1.76	10,780
Plant D	2	11.41%	10.41%	3.86%	3.26	109	2.02	11,102
Plant E	4	27.94%	4.69%	0.22%	0.41	7.63	0.73	8,600
Plant E	4	26.05%	4.62%	0.21%	0.4	10.4	0.67	8,757
Plant E	4	27.33%	4.78%	0.23%	0.42	8.78	0.72	8,676
Plant F	1	30.27%	5.53%	0.30%	1.325	17.5	0.655	8,306
Plant F	1	30.07%	5.13%	0.78%	0.96	8.4	0.65	8,300
Plant G	1	19.62%	7.14%	0.52%	0.51	10.6	0.67	9,622
Plant G	1	19.29%	8.04%	0.52%	0.56	19.1	0.67	9,456
Plant G	2	18.70%	6.27%	0.38%	0.47	11.6	0.55	10,057
Plant G	2	18.56%	6.46%	0.41%	0.49	11.2	0.54	10,078

In calculating the overall boiler mass balances (coal to stack), the fly ash/bottom ash split from the boiler was assumed to be 80%/20% for pulverized coal (PC) units and 50%/50% for the cyclone unit (D-2). The collection efficiencies for the particulate control devices were taken from the NETL power plant database.¹⁵ If collection efficiencies were not available for a given plant in this database, typical values for the device were used.

Figure 1 summarizes the selenium mass balance results. The data points for scrubbed units are limited to those tests for which scrubber samples were analyzed. For Plant D, in which two boilers shared a common scrubber and stack, the scrubber flow rates of selenium were proportioned by heat input to compute balances for the separate units.

The mass balance is low for Boiler C. This plant has a wet ESP and the selenium concentration in the wet ESP effluent water was measured to be about sixteen times the level of selenium in the make-up water, so the wet ESP appeared to have removed selenium from the gas leaving the scrubber. However, the wet ESP effluent water is used as a source of FGD makeup water, so the selenium captured in the wet ESP should be reflected in the wet FGD byproduct streams. Thus, the low mass balance closure is not likely caused by selenium capture in the wet ESP. Other possibilities include a high bias in the coal sample or its selenium analysis, a low bias in the fly ash sample or its selenium analysis, a low bias in the selenium concentrations in the gypsum or in the Method 29 results, etc.

Table 3. FGD analyses and parameters.

Plant	SO ₂ Removal	Limestone Utilization	Gypsum Purity	Blowdown Solids	Gypsum Se	Blowdown Liquid Se	Blowdown Solids Se	Limestone Se	Make-up Water Se	WESP Effluent Se
	%	%	%	wt%	µg/g	µg/L	µg/g	µg/g	µg/L	µg/L
B-1	97.8%	96.8	98.2	0.91	10.1	2059	45.4	<0.57	0.448	--
B-2	95.4%	96.9	96.4	0.70	11.4	1690	23.9	<0.57	0.448	--
C	95% ¹	97 ¹	95 ¹	0.051	1.3	96.5	8.64	<0.62	2.22	36.5
D	92% ¹	97 ¹	95 ¹	0.2535	3.5	1210	294	<0.62	--	--
F	92.6%	98.0	99.2	0.0013	<0.60	7.81	4.79	<0.57	0.396	--
G-1	92% ¹	97 ¹	95 ¹	4.1	2.01	942	65.5	1.22	--	--
G-2	92% ¹	97 ¹	95 ¹	3.85	1.9	861	59.5	1.23	--	--

¹Estimated

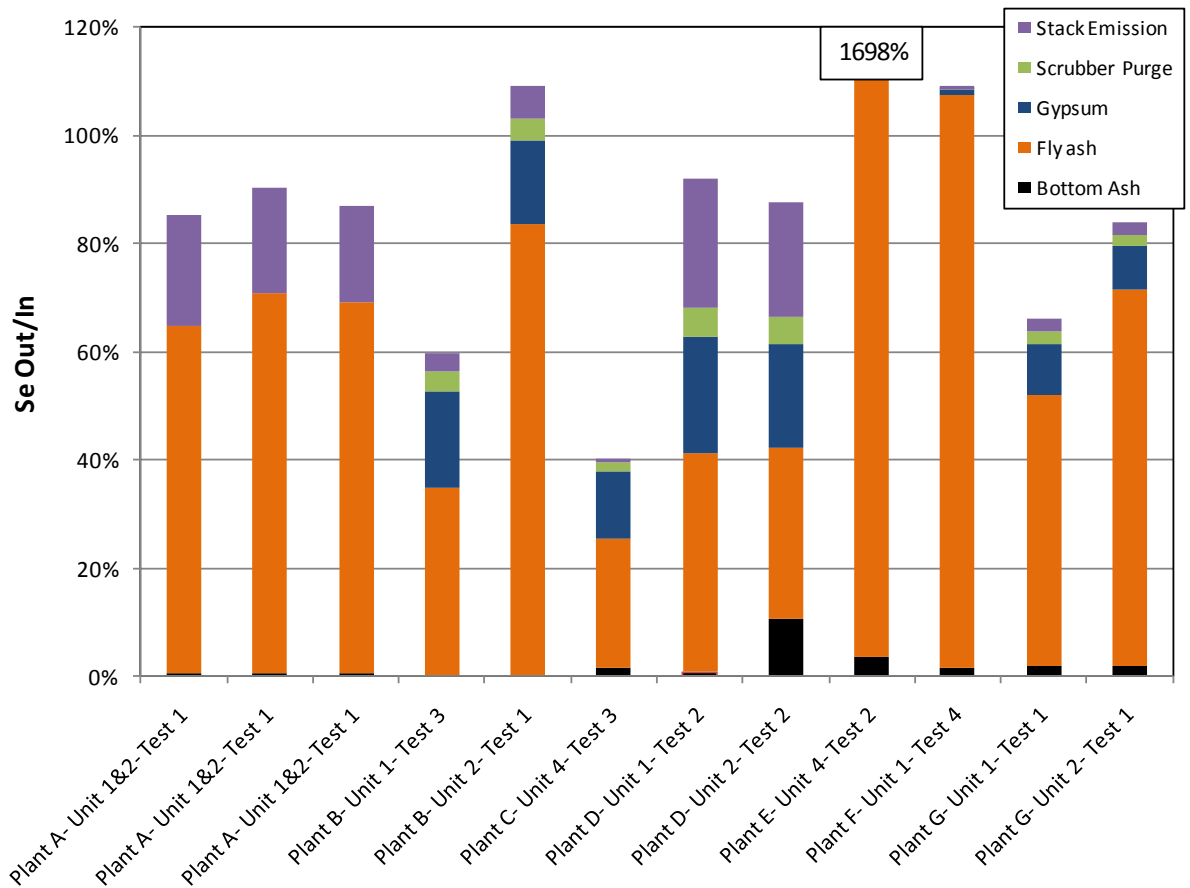


Figure 1. Selenium mass balance around the boiler (out/in).

At Plant D, Unit 1 had a cyclone boiler and Unit 2 had a tangentially fired, PC boiler. Unit 2 also had an SNCR system for NO_x control, while Unit 1 had an SCR. The distribution of selenium among the various output streams was essentially the same at the two boilers, with the exception of somewhat more selenium in the

bottom ash of Unit 2, the PC boiler. This is counter to expectations, since Unit 1, the cyclone boiler, was assumed to produce 2.5 times the amount of bottom ash compared to Unit 2. Overall, the firing system and NOx control subsystem did not appear to play a factor in selenium behavior at Plant D.

There was only one fly ash sample collected at Boiler E and the selenium concentration in that ash sample was very high – so high that the Se mass balance closure (out/in) was 1698%. The selenium concentration in this fly ash sample was measured by two different methods at two different labs. Results from the two labs were within 16% of one another. The sample appears to be anomalous, but the measurements appear to be correct. Volatile species such as selenium are sometimes observed to be enriched in smaller fly ash particles when compared to larger particles. It is possible that the fly ash sample from Boiler E was biased to include more small particles, such as are collected in the back fields of the ESP, and therefore not representative of the bulk fly ash.

Behavior of Selenium in the Boiler and Particulate Control Devices

Table 4 summarizes the inputs and outputs of selenium and the calculated removal. Most of the selenium into the plant was from the coal; less than 5% came from the FGD inputs (mostly limestone) in plants with FGDs. Removal of selenium across the boilers ranged from 72% to 99.4%. All the plants in Table 4 had scrubbers except Boiler A and Boiler E (where the scrubber was off-line during stack testing).

Table 4. Selenium inputs and outputs (lb/TBtu) and overall removals.

Plant	Se input (fuel)	Se input (FGD)	Se stack emission	Se removal
A-1&2	378.87	--	72.83	81%
B-1	368.46	2.37	12.60	97%
B-2	339.26	1.65	21.70	94%
C	168.53	6.78	1.15	99%
D-1	305.01	7.14	74.60	76%
D-2	344.16	7.14		79%
E	45.68	--	12.70	72%
F	115.66	0.60	0.76	99%
G-1	59.22	2.07	1.50	98%
G-2	46.73	1.50	1.28	97%

Plant A, Plant D, and Boiler E had lower (72-81%) removals than the other plants. Plant A burned a bituminous coal, had a cold-side ESP and no scrubber. Plant D also burned a bituminous coal and had a cold-side ESP, but it did have a wet FGD. Boiler E burned a subbituminous coal and only had a cold-side ESP on line during the sampling. The rest of the boilers had wet FGDs and showed greater than 90% selenium removals. The highest selenium removal observed (99.3%) was at Boilers C and F. Boiler C burned a bituminous coal and had the following APCDs: fabric filter, wet FGD and wet ESP. Of course, Boiler C also showed poor recovery of the input Se in the plant outputs, including the stack flue gas (Figure 1), so the high apparent Se removal is not well supported by the mass balances. However, it is otherwise not surprising that a unit with all three of these APCDs in series would achieve high selenium capture. Boiler F fired subbituminous coal and had a reverse-gas fabric filter followed by a wet FGD system for particulate control. As described below, Boiler F achieved a very high selenium capture efficiency in the fabric filter.

For the bituminous plants with ESPs (Plant B, Plant D), less than 40% of the selenium input ended up in the fly ash (with the exception of Plant B, Unit 2), as shown in Figure 1. For the subbituminous plants (Boiler E, Boiler F and Plant G), most of the selenium was captured in the fly ash in the particulate control device. Boiler F, in particular, had very little selenium captured in the scrubber or measured in the stack gas, because almost all the selenium was captured by the fly ash. This unit fired PRB coal, which produces an ash with a high calcium oxide content, and has a conservatively sized reverse-gas fabric filter particulate control device, both of which may favor selenium capture with the ash. Boiler E had an anomalously high measured concentration of selenium in the fly ash sample, which might have represented contamination or a non-representative sample. In

any case, the overall removal of selenium at Boiler E based on coal and stack flue gas analyses suggested that 72% of the selenium was captured by the fly ash

Previous full-scale data has shown that bituminous boilers with cold-side ESPs do not capture selenium with high efficiency in the particulate control device. Modeling and recent pilot-scale combustion results¹⁶ would suggest that in bituminous-fired boilers, only a portion of the selenium would be captured in the fly ash, while the rest would exit the particulate control device in the gas phase. In subbituminous-fired boilers, most of the selenium would be captured in the fly ash in the particulate control device, as observed in this study, because of the relatively high concentration of CaO in the fly ash.

Boiler C, which fired a bituminous coal and had a fabric filter, did not appear to have much selenium in the fly ash as a percent of the inputs compared to the other units. This is somewhat surprising, as Boiler F, which also had a fabric filter for particulate control, had the highest percentage capture of selenium with the fly ash of the units sampled. However, Boiler C fired bituminous coal rather than the high-calcium subbituminous coal fired by Boiler F. Also, mass balance closure for Boiler C was poor, which may indicate that the fly ash capture of selenium in the coal was under-represented in these results.

Behavior of Selenium in Wet FGDs

As described above, eight of the 11 units sampled had operating wet FGD systems, five that fired bituminous coal and three that fired subbituminous coal. The overall selenium balances showed that generally less selenium was captured with the fly ash in the bituminous coal units than in the subbituminous coal fired units. Correspondingly, more selenium penetrated the particulate control devices and was captured in the wet FGD systems in the bituminous coal units.

The percentage of input selenium accounted for in the byproduct gypsum ranged from 13 to 20% in the bituminous coal units, while the chloride purge streams accounted for 2 to 5%. In contrast, in the subbituminous coal units only 1 to 9% of the input selenium was accounted for in the gypsum and 0 to 2% was accounted for in the chloride purge streams.

There is no obvious relationship in the results on the effects of FGD design or operating conditions on FGD capture of selenium, although the number of data points for each coal type are limited. The lowest values for percentage of input selenium recovered in the FGD samples were from subbituminous Boiler F Unit 1, which as discussed above was measured to achieve very high selenium capture with the fly ash in its reverse-gas fabric filter and very high overall selenium capture efficiency.

In most of the units with FGD systems, selenium in the chloride purge stream accounted for 12 to 20% of the selenium leaving in the FGD byproduct streams. This percentage varied depending on the relative chloride purge rates from system to system, wt% solids in the chloride purge streams, and the relative concentrations of selenium found in the liquid and solid phases. The exception was subbituminous coal Boiler F, Unit 1, where only 3% of the FGD capture of selenium was accounted for in the chloride purge stream. This appears to be a result of the very small percentage capture of input selenium in the FGD system, and the correspondingly low selenium concentrations in the FGD liquor. Also, subbituminous coals tend to have low halogen contents, so chloride purge rates are typically lower than for bituminous coals.

For four of the FGD systems, samples were also available of the absorber slurry, which were analyzed separately for selenium concentrations in the slurry liquor and solids. Of the four absorber slurries analyzed, three were from units that fired bituminous coal (Plants B-1, B-2 and C). In these three samples the selenium concentrations in the absorber liquor ranged from 181 to 2080 µg/L, while the solids concentrations ranges from 1.27 to 11.4 µg/g. These values correspond with 36% to 49% of the selenium in the absorber slurry being found in the liquor phase. The fourth sample was from Boiler F, which fired subbituminous coal, and also had a reverse-gas fabric filter that removed most of the selenium in the flue gas. In that sample (actually samples from two absorbers in service), the average liquor concentration was 26 µg/L and the average solid-phase concentration was 0.61 µg/g. This corresponds with an average of 26% of the selenium being found in the liquor phase. Again, this is most likely influenced by the relatively small percentage of the coal selenium that penetrated the reverse-gas fabric filter at Boiler F.

CONCLUSIONS

Coal-to-stack removal of selenium across the boilers ranged from 72% to 99.4%. Eight out of 12 data sets had acceptable mass balance closure (80% to 100%). However, there is some uncertainty about the measurements as the Se mass balances need some improvement.

In the bituminous-fired boilers a significant portion of the selenium input (15% to 50%) exited the particulate control device, probably in the gas phase. In the subbituminous-fired boilers, most of the selenium entering the boiler was removed in the particulate control device. Removal of selenium across the wet scrubbers ranged from 53% to 95% of selenium entering the scrubber. Of the selenium entering the scrubber, most was removed in the gypsum, while only 10% to 15% was removed in the chloride purge stream. In this limited data set, there was no obvious relationship between the FGD design or operating conditions on FGD capture of selenium. Even though selenium is expected to be in the vapor phase at the inlet to the scrubber, the removal of selenium across the scrubbers was generally much lower than typical values for SO₂ removal.

The fate of Se is highly variable in coal-fired boilers, and the factors affecting the distribution of Se are not completely understood. The type of coal being burned and the air pollution control devices in use are key indicators of the fate of selenium in coal-fired boilers.

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