B. Krishnakumar, S. Niksa, and N. Fujiwara, “Predicting selenium emissions from utility gas cleaning systems,” Int. Conf. on Air Quality IX, UND EERC, Arlington, VA, Oct. 2013.

PREDICTING SELENIUM EMISSIONS FROM UTILITY GAS CLEANING SYSTEMS

Balaji Krishnakumar, Stephen Niksa
Niksa Energy Associates, LLC; Belmont, CA 94002 USA; neasteve@gmail.com

Naoki Fujiwara
Coal and Environment Research Laboratory, Idemitsu Kosan Co., Ltd., Chiba 299-0267 Japan

ABSTRACT

NEA’s Se transformation mechanism contains six chemical reactions: irreversible scavenging of SeO_2 and SO_2 by molten Fe-aluminosilicates upstream of the furnace exit; competitive, irreversible chemisorption of both species on CaO at temperatures below 800°C, where $CaSeO_3$ becomes stable as the sorption product; and reversible physical adsorption of both species on whole flyash. The first two reaction processes are also mediated by film transport resistances. All three reaction processes are applied to both SeO_2 and SO_2, based on the very similar chemistry expected from their common grouping in the periodic table. Physical adsorption is responsible for the bulk of the Se capture on flyash, and is usually responsible for 40 -50 % capture for typical ash contents. Its contribution shifts in proportion to the coal ash content for T- and wall-fired furnaces, which have very similar splits between bottom ash and flyash. But cyclone firing gives substantially less flyash, so the contribution from physical adsorption is reduced accordingly. We have not yet found any coal ash that contains enough Fe-aluminosilicates to scavenge an appreciable portion of the vaporized Se. The competition for available CaO sites by SO_2 and SeO_2 is an essential aspect of the greater Se capture on flyash from low rank coals, which contains much more CaO than ash from bituminous coals, and more of it tends to be dispersed as CaO aerosol. This distinctive ash component introduces a fairly strong dependence on the coal-S level into Se capture which is compounded by the relatively low S levels in low rank coals, and the very high S levels in some bituminous coals.

Our simulation results have been validated with a database from twelve full-scale cleaning systems in the U.S., Europe, and China. The predicted Se capture levels on flyash are within 10 % of the measured values in nine of those cases. Across the database, the measured captures vary from 30 to 110 %, while the predicted captures vary from 35 to 85 %, so the analysis clearly delivers Se captures on flyash within useful quantitative tolerances. Moreover, the predicted captures closely track important variations in the measured Se captures due to different firing configurations, coal ash contents, ash CaO levels, coal-S, and the thermal histories across the PCDs.

INTRODUCTION

Selenium (Se) is an essential trace element in human physiology but is toxic in large doses, and is classified as a hazardous air pollutant under the Clean Air Act. Under EPA’s Mercury and Air Toxics Standards for new coal-fired electric power generation stations, Se emissions must be less than 0.05 lb/GWh. Whereas this threshold is not expected to trigger dedicated controls on Se emissions, it is an unmistakeable signal to the utility industry to develop an awareness of the magnitudes and operating characteristics for Se emissions in utility gas cleaning systems. Our goal in this paper is to use simulations based on realistic chemical reaction mechanisms that have been thoroughly validated with field test data to identify (i) the main Se transformations along utility gas cleaning systems; (ii) the operating conditions that most strongly affect these transformations; and (iii) the primary means of inherent Se removal for the range of coal quality of commercial interest.

SE TRANSFORMATIONS

A series of studies in lab- and pilot-scale systems clearly establishes the basic phenomenology of Se transformations under utility gas cleaning conditions. Se contents in as-fired samples of coal typically vary between 0.5 and 1.5 ppmw with some coals having values as high as 77 ppmw. Either Se vaporization is nearly complete with most coals, or it is complete and some small fraction can be scavenged from the vapor phase into molten mineral phases before the flue gas passes through the furnace exit. Either way, the portion that remains in char is typically 10 to 20 % of coal-Se, and never more than 30 %. Iron aluminosilicates are the most likely Se scavenger at high temperatures. Otherwise, Se vapors are fairly refractory and do not interact with halogens. There is no evidence of any gas phase chemistry involving Se and flue gas constituents other than the oxidation of Se by O_2 to form SeO_2. The formation of SeO_2 is based on thermochemical equilibrium because no direct Se speciation measurements have been reported.

A few dozen full-scale field tests clearly resolve the coal quality impacts and indicate where in the cleaning system Se can be collected. Low rank coals give consistently greater Se capture in particle collection devices (PCDs), due to stronger partitioning onto flyash. There is no evidence for enhanced Se capture on unburned carbon (UBC) in flyash, despite its markedly greater surface area. The most likely explanation for the enhanced Se capture is an association between Se and Ca mineral phases that acts in parallel to SeO_2 condensation (described shortly); it could also be that CaO stabilizes adsorbed SeO_2 in such a way that the stabilization frees up sites for additional adsorption. Calcium selenite is the most likely condensed phase on CaO because it is unstable above about 800°C, consistent with the absence of particulate-Se above 550°C in the lab-scale database. It is also important to note that the onset of Se/Ca interactions occurs after the flue gas traverses the temperature window for inherent SO_2 capture on CaO. And while lab-tests indicated that sulfation inhibits Se adsorption on CaO, the full-scale test data suggests that sufficient sites remain to capture appreciable portions of coal-Se. This is not too surprising because Se/Ca ratios are as much as four orders of magnitude smaller than S/Ca ratios, so only a small portion of CaO must remain to adsorb the available Se vapors.

At some temperature below about 550°C, a slow, physical adsorption accumulates Se on flyash as an as-yet unidentified Se(IV) compound. With most bituminous coals, 40 – 50 % of coal-Se will be bound to flyash at the PCD, and with low rank coals, the particulate-Se will be significantly greater. The bound Se is distributed across the entire ash PSD, and Se concentrations are strongly enriched in the fumes. We suspect that the enrichment is due only to the greater specific external surface areas of smaller particles, because the Se concentrations do not correlate well with the levels of Ca, Fe, or any other mineral species across the flyash PSD.

Hence, the most important factor in predicting Se emissions from stacks is an accurate partitioning of Se in flue gas and onto flyash. Equilibrium predictions of completely condensed Se species at stack conditions are contradicted by the wide range of Se vapor emissions seen in field tests. We believe that the partitioning into particulate-Se is determined by a physical condensation onto the full flyash PSD because Se does not preferentially concentrate in either the submicron or supermicron mode. Presumably, SeO_2 is the condensing species although the adsorbed form is, as yet, unknown. Ash composition is important because SeO_2 may be scavenged at furnace temperatures by Fe-aluminosilicates, and SeO_2 competes with SO_2 for CaO sites during quenching in a gas cleaning system.

Unlike Hg compounds, Se partitioning in flyash does not show any correlation with UBC levels in the flyash. ESPs and fabric filters (FFs) capture particulate-bound Se as expected. The flyash size at which the capture efficiency is at a minimum coincides with the modes of fumes, which may carry adsorbed Se. Notwithstanding, it is unlikely that appreciable amounts of Se are released from the stack on submicron fumes because such fumes typically constitute an insignificant fraction of flyash. The partitioning and removal of Se associated with flyash is the predominant factor in determining Se stack emissions in gas cleaning systems with only PCDs. Se capture on fabric filters (FFs) is somewhat greater than on ESPs, notwithstanding a contrary observation in one field test. This has not yet been explained, although we think that the contact within FF filtercakes is sufficiently favorable to achieve adsorption equilibrium with the flue gas composition, and the equilibrium capture level is the highest that can be attained. In any case, the vast majority of Se downstream of a PCD will be in the vapor phase. Wet FGDs retain essentially all the Se vapor at the inlet, notwithstanding a few contradictory observations in the full-scale database. Most Se is retained in the gypsum product, and much less persists in the FGD wastewater.

Unfortunately, we did not find any qualified tests on Se transformations across SCRs, so these units cannot yet be factored into any quantitative analysis of Se transformations. We also did not find any determinations of Se speciation, except that Se(IV) compounds predominate in particulate-Se, and that Se(IV) species in wet FGDs may be oxidized to Se(VI) species by $S_2O_8^{2-}$. But there is no good reason to suppose that SeO_2 does not predominate among the vapor species throughout entire gas cleaning systems.

SIMULATIONS FOR INHERENT SE REMOVAL

NEA's implementation of the main Se transformations in a mathematical analysis for quantitative simulations shares several elements in common with a previous modelling study on Se emissions[1], although the relative importance of certain mechanisms differs between these two efforts. NEA's mechanism contains six chemical reactions: irreversible scavenging of SeO_2 and SO_2 by molten Fe-aluminosilicates upstream of the furnace exit; competitive, irreversible chemisorption of both species on CaO at temperatures below 800°C, where $CaSeO_3$ becomes stable as the sorption product; and reversible physical adsorption of both species on whole flyash. The first two reaction processes are also mediated by film transport resistances, although intraparticle transport resistances are deemed to be negligible because flyash has no internal pore system. All three reaction processes are applied to both SeO_2 and SO_2, based on the very similar chemistry expected from their common grouping in the periodic table. The rate parameters for physical adsorption were specified by interpreting a single lab-scale dataset[2] that closely regulated the collection temperatures and transit times over broad ranges. The activation energies for both the SeO_2 adsorption and desorption reactions were set to 0.5 kcal/mol, which is firmly within the range of expected values for physical adsorption. The other model parameters were taken from literature or set in the course of our validation work. Once these values were established, they were not adjusted further, so that none of the validations in this report reflect unrestrained tuning of rate parameters to achieve better agreement with the measured values.

Physical adsorption is responsible for the bulk of the Se capture on flyash, and is usually responsible for 40 -50 % capture for typical ash contents. Its contribution shifts in proportion to the coal ash content for T- and wall-fired furnaces, which have very similar splits between bottom ash and flyash. But cyclone firing gives substantially less flyash, so the contribution from physical adsorption is reduced accordingly. Although physical adsorption is applied to both SeO_2 and SO_2, no more than a few percent of the SO_2 in flue gas is collected this way, as expected.

High temperature scavenging by Fe-aluminosilicates was implemented with the rate constants reported in the literature from similar work on Se transformations. In contrast to the role for this scavenging described by Senior et al.[1], we have not yet found any coal ash that contains enough Fe-aluminosilicates to scavenge an appreciable portion of the vaporized Se. So our analysis imposes complete Se vaporization without any significant reduction in the SeO_2 vapor concentration upstream of the furnace exit.

The competition for available CaO sites by SO_2 and SeO_2 is an essential aspect of the greater Se capture on flyash from low rank coals. Flyash from low rank coals contains much more CaO than ash from bituminous coals, and more of it tends to be dispersed as CaO aerosol. This distinctive ash component introduces a fairly strong dependence on the coal-S level into Se capture which is compounded by the relatively low S levels in low rank coals, and the very high S levels in some bituminous coals. One might have expected the much greater concentration of SO_2 than SeO_2 to overwhelm any potential for SeO_2 capture on CaO; in fact, the rate parameters for SO_2 capture on CaO from limestone under isothermal conditions at moderate temperatures predict this outcome. But flame-processed CaO has no internal surface area and probably much lower active site densities than limestone sorbents, and gas cleaning systems impose fairly fast gas quench rates that often render isothermal behavior irrelevant. We have demonstrated that SeO_2 adsorption on CaO will be mediated by competitive SO_2 adsorption under typical gas cleaning conditions, but not necessarily shut down altogether. Indeed, our field test database contains numerous instances where the extents of Se capture on flyash shift according to the behavior of our competitive adsorption model.

These reaction mechanisms have been implemented into a simulator for applications in utility gas cleaning systems with the following calculation sequence:

(1) Assign flue gas compositions leaving the furnace zone from fuel properties and firing conditions and an equilibrium calculation.
(2) Lay out the specified gas cleaning system for detailed simulations based on the thermal history and sequence of APCDs.
(3) Solve the simultaneous differential equations describing Se partitioning between flue gas and flyash and the competition with SO_2 for CaO as the flue gas moves from the furnace into an ESP.
(4) Sequence through each unit in the gas cleaning system with updated temperatures and flow cross sections, as necessary.

Table 1. Input Data Requirements.

Coal Properties	Proximate: Moisture, Ash Ultimate: C, H, O, N, S, Se Available CaO and Fe-aluminosilicates HHV
Furnace Conditions	Rating, Load, S.R. or Economizer O_2, Bottom ash (% total ash)
Gas Cleaning Configuration	Flow diagram from furnace exit to stack, including all heat exchangers and APCDs
Thermal History	Temperatures and residence times along the gas cleaning system
ESP	Ash collection efficiency, modes in the flyash PSD and flyash density

All the input specifications for simulating Se partitioning onto entrained flyash are collected in Table 1. The coal's proximate and ultimate analyses are required, along with the mass fractions of CaO and Fe-aluminosilicates in flyash. The only addition to these standard properties is the Se-content in the ultimate analyses. The furnace firing conditions are also very standard. The coal and air flowrates can be obtained from the furnace rating, load, S.R. and gross thermal efficiency, if these values are not directly provided. The bottom ash fraction is required to determine the entrained flyash flow rate. The configuration of the units in the gas cleaning system will be known; however, the complete thermal history is rarely available because the residence times along the gas cleaning system are almost never reported. Flow areas and lengths may be used to assign the thermal history but such measurements are generally unavailable. Consequently, it is simpler to assign nominal transit times through the gas cleaning system based on typical plant operating conditions. The flow geometry is then assigned from typical gas velocities to reproduce the nominal residence time at the specified operating temperature. With regard to ESP specifications, in addition to operating temperature and the ash collection efficiency, the modes in the flyash PSD and density must be specified. The model implements typical values for these parameters by default; however, since Se partitioning and emissions would certainly be affected by atypical conditions in the ESP, unusual conditions should be specified by the user.

The model includes reactions between the available CaO and Fe-aluminosilicates in the flyash and the gas species. The high temperature ash composition gives a basis to estimate these quantities, although the calculation procedure is somewhat involved. We first use a normative analysis to estimate the levels of illite, kaolinite, pyrite, and quartz from the high temperature ash chemistry analysis, and then estimate the levels of Na, Ca, and Mg from the partitioning of K into illite. This procedure gives total CaO. As an initial approximation, the free CaO is assigned in proportion to its fraction in the total ash. For bituminous coals, this is typically negligible since they have very little CaO and greater levels of aluminosilicates. Based on the examination of a Pittsburgh #8 bituminous coal by Helble et al.[3], the amount of Fe incorporated into aluminosilicates and therefore available for high-temperature scavenging of Se was assigned equal to 30 % of the total iron oxide in the ash from any coal type.

VALIDATION DATABASE

The qualified database for model validations appears in Table 2. Although all these datasets are suitable for model validation work, many of them do not report even the most basic coal property data. These cases can only be simulated with assumed nominal values, which inevitably introduce uncertainties into the validations. At the outset it is worth noting the most important input parameters that affect Se partitioning: ash content, coal-S and Se, flyash CaO, flyash sizes, and the mass fractions of flyash in the submicron and supermicron modes. Complete coal analyses were reported only for four test cases: the pilot-scale tests of Noda et al.; the full-scale tests of Huang et al.; and for Plants Yates and Hammond. Coal ash contents were available for all plants except the one from Chu et al. Whereas, the ash contents reported for the Chinese and Spanish plants by Huang et al. and Cordoba et al., respectively, exceed 30 % and represent the highest ash levels in this database, the subbituminous at the ICR-F site had the lowest ash level of 5.5 wt. %, as seen in Table 2. The partitioning between flyash and bottom ash was not reported for any of the test sites; instead, it was estimated from the reported furnace firing configurations. The bottom ash/flyash splits were 25/75 except for the cyclone furnace in site ICR-D, which has a 65/35 split between bottom ash and flyash.

Table 2. Field-test data on Se transformations.

Unit	Firing Configuration	Coal	Cleaning Configuration	Se Balance (%)
Coal Creek[a]	T	lignite	ESP+FGD	88
Yates[b]	T	bit.	ESP+FGD	80 overall; ~100 for ESP
Hammond[b]	Wall	bit.	ESP	86
Chu et al.	Wall	bit	ESP+FGD	100
Noda et al.	-	bit.	-	-
Huang et al.	-	bit.	ESP	-
Alvarez-Ayuso et al.	-	blend	ESP+FGD	100 – 120
Cordoba et al.	-	blend	ESP+FGD	118
ICR-A[c]	Wall	bit.	ESP	85
ICR-B[c]	Wall	bit.	SCR+ESP+FGD	110
ICR-D[c]	Cyclone	bit.	SCR+ESP+FGD	90
ICR-F[c]	T	subbit.	FF+FGD	110
ICR-G[c]	Wall	subbit.	FF+FGD	85

[a]Battelle Corp. (1994), [b]Radziwon et al. 1996, [c]Senior et al. (2011).

Coal-S levels were reported for all sites. The daf coal-S loadings at ICR-F site were the lowest at 0.47 wt. % whereas ICR-D and the Spanish site tested by Alvarez-Ayuso showed coal-S in excess of 5 wt. %. Coal-Se loadings were reported for all coals, except by Chu et al., and generally varied between 0.6 to 5.4 daf ppmw. The major omissions in the database were flyash PSDs, including the weight fractions in both size modes; and the flyash compositions. We assumed mode sizes of 0.5 and 10 μm with 3 wt. % in the submicron mode. Only Cordoba et al. and Alvarez-Ayuso et al. reported ash compositions and these values were used without modification. For the rest of the cases, we assumed typical ash compositions based on the coal rank.

RESULTS AND DISCUSSION

We review the simulation results for each field test in Table 2 in turn. Under a U.S. DoE study[4], trace metal emissions were reported from Plant Coal Creek which has two identical units rated at 550 MW each firing North Dakota lignites. Each unit has a T-fired dry bottom furnace and the gas cleaning systems have an ESP and a Mg/lime WFGD. The plant contains two ESPs in parallel whose flue gas combines at the exit. Then a portion of the flue gas exiting the ESP is bypassed directly to the stack. Flue gas was sampled at all inlet and outlet locations along the gas cleaning system, and Se balances were reported. The Se balance closure across the furnace/ESP at Coal Creek was 97 % and the overall Se balance closure was approximately 88 %. About 21 % of the coal-Se was removed on the bottom and economizer ash and 57 % was removed in the flyash. Another 10 % was emitted as stack gas. Of the 21 % Se removed in the bottom and economizer ash, 75 % was removed in the bottom ash, which represents approximately 15 % of the coal-Se. The Se in the stack gas was attributed to the flue gas bypass from the ESP outlet and the data suggest that essentially all of the Se in the flue gas entering the WFGD was captured, although the Se balance closure across the scrubber was less than 60 %.

The predictions for this plant are compared with measured values in Fig. 1. The predicted Se partitioning onto flyash of 64 % compares very well with the 63.1 % measured at this plant. The bottom ash partitioning of Se at this plant appears to be relatively high at 15 %; perhaps this high value reflects unvaporized Se from relatively large ash particles, due to their moderate temperatures. Plant-specific factors may also be responsible since none of the other tests reported nearly as much Se in bottom ash.

Yates is a 100 MW, T-fired boiler equipped with an ESP and WFGD[5]. The plant fires an Illinois bituminous coal containing 11 % ash and 2.5 daf ppmw Se. Even though Plant Yates contains a FGD, the

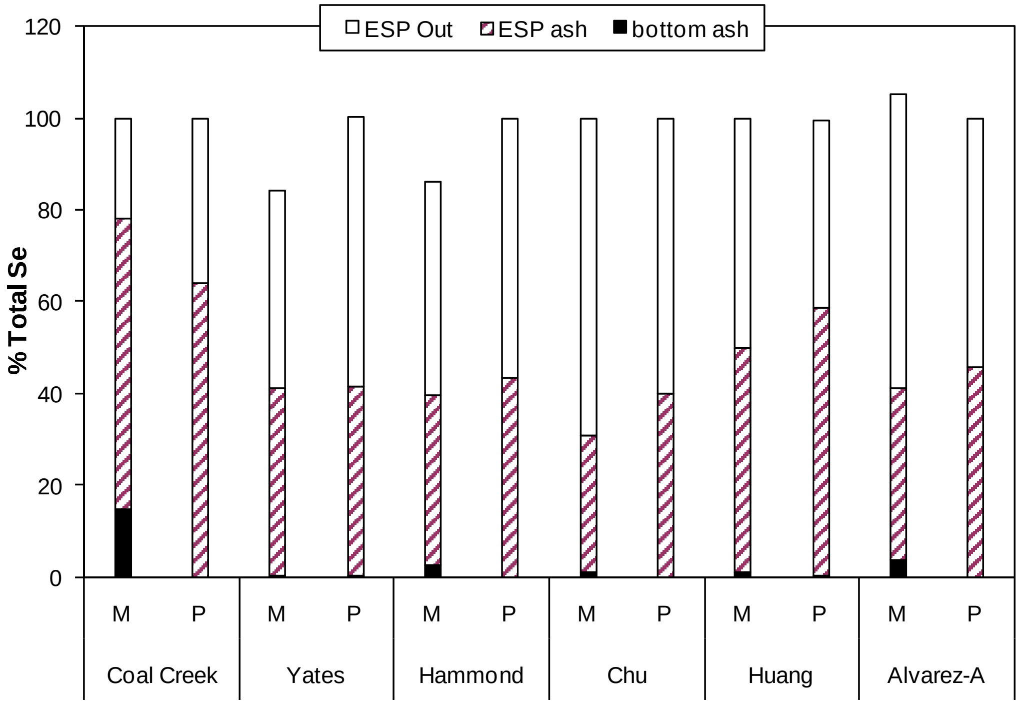

Fig. 1. Measured (M) and predicted (P) Se partitioning among the exit streams of full-scale plants as a percentage of coal-Se.

focus of the current modeling work is on the ESP alone. Field measurements were performed at all inlet and exit streams of the individual APCDs. The reported Se balance closure for the overall plant is approximately 80 % whereas for the exit streams across the ESP alone, the Se balance improved to approximately 100 %. The test data at Yates is simulated with a default thermal history from the furnace exit through the back-end heat exchangers, and reported temperatures and default residence times for the remainder of the cleaning system. The ash composition for a bituminous coal was assigned for this case.

The model prediction for Se partitioning is compared with the measured values in Fig. 1. The predicted Se in flyash of 41 % compares very well with the measured value. It is instructive to compare the predicted partitioning at Yates with the value predicted for the lignite at Coal Creek. While the ash loading at the two plants is similar, the assigned ash composition for the low rank coal has approximately 20 % CaO and a lower coal-S. Consequently, the capture on both the bulk flyash and on CaO is greater for the low rank coal by approximately 10 % for each difference. The Se capture in lignite ash is approximately 64 % v. 41 % for the bituminous ash, in accord with the data.

Hammond is a 500 MW opposed-wall fired boiler firing a bituminous coal with an ash content of 10 wt % and a coal–Se of 3.6 ppmw daf. The plant is equipped with an ESP[5]. Field test measurements were performed at all inlet and exit streams of the individual APCDs. The reported Se balance closure in the exit streams at Hammond based on coal-Se is approximately 86 %. The test data at Hammond is simulated with a default thermal history from the furnace exit to the back-end heat exchangers and with the reported temperatures and default transit times for the remainder of the cleaning system. The bituminous ash composition applied for Plant Yates was also used for this case.

The predicted Se partitioning at Hammond is compared with the measured values in Fig. 1. The predicted 43.5 % Se in flyash is approximately 7 % greater than the measured values but since the reported Se balance closure is only 86 %, the discrepancy is perhaps even lower. While Plants Hammond and Yates have similar ash compositions and loadings, the coal-S in Hammond is half of that at Yates, yet these plants show similar levels of Se capture. This is because of the lower ESP temperatures at Plant Hammond that result in slightly longer residence times and, therefore, greater Se adsorption, albeit by less than 10 % capture.

Chu et al. reported total Se measurements for a conventional PC boiler under EPRI's PISCES program[6]. The plant was a 690 MW wall-fired boiler equipped with an ESP and a limestone WFGD. No ash PSD, complete coal properties or Se contents were reported. The plant fired a bituminous coal with 2.8 wt. % sulfur. The Se balance between the inlet and the outlet streams is close to 100 %. Approximately 30 % of the Se was captured in the flyash while 55 % was captured in the FGD outlet streams. The remaining 25 % exited the stack. The simulations for this plant involved the greatest level of uncertainties since virtually all parameters had to be estimated as nominal values, including coal moisture and ash levels. For the nominal assignments, the predicted Se partitioning was approximately 40 % vs. a measured value of 33 %, as shown in Fig. 1. As expected, this value is similar to that at plant Yates since the input conditions for the two cases are nearly identical.

Huang et al. examined Se contents in coal, bottom ash, and flyash from a Chinese power plant whose cleaning system contained only an ESP that removed 99 % of the particulates[7]. The plant fires a Chinese bituminous coal at 220 tons/h at a furnace S.R. of 1.35. The coal has an ash content exceeding 30 % and a Se content of 5.4 ppmw daf, which is also higher than the other tests in this report. The test case was simulated with a default thermal history for typical U.S. boilers. The predicted Se distribution between the flue gas and flyash streams are within 10 % of the measured values, as shown in Fig. 1. The predicted level of adsorbed Se at this plant of about 60 % is about 20 % higher than those at Plants Yates and Hammond due to both a lower coal-S and a higher ash loading. Note, however, that the flue gas Se was not monitored but was instead assigned based on the difference between the input coal-Se and the Se-contents in bottom and flyash.

Alvarez-Ayuso et al. reported Se and other trace metal measurements from a Spanish power plant firing a blend of several subbituminous coals with an ESP+WFGD configuration[8]. In these tests, 40 % of the coal–Se was captured in ash (5 % in bottom ash) and all Se entering the FGD was in the vapor phase, of which more than 98 % was captured in the WFGD solids. The measurements included Se balances across the ESP and WFGD which closured between 100 and 120 %. Unfortunately, no coal properties or cleaning conditions were reported for these tests. However, the coal-S and Se and the ash composition including CaO were reported. To simulate this test case, coal ultimate analyses from another Spanish coal reported by Cordoba et al. were used with 23 % ash, similar to the ash contents in other Spanish plants. The ash CaO for this blend was only 3.5 %, which appears low for a subbituminous coal; however, this is similar to the values reported in other Spanish coals by Cordoba et al.[9] and Otero-Rey et al.[10]

As shown in Fig. 1, the measured and predicted partitionings of Se onto flyash are within a few percent at approximately 40 %. The flyash Se capture for the lignite-fired unit at Coal Creek and for the bituminous fired Chinese plant reported by Huang et al. exceed 60 %. The lignite coal shows higher Se capture due to lower S and higher Ca whereas the Chinese plant exhibits a higher Se capture due to lower S and higher ash content. While the ash content at the plant tested by Alvarez-Ayuso is high at 23 %, the Se capture is restricted to 40 % due to two factors: the lower CaO in Spanish subbituminous coal ash and a very high coal-S of approximately 5.7 daf wt. %. This high SO_2 competes effectively for the ash surfaces to effectively reduce the amount of sorbed Se. This effect of coal-S variation on Se capture is evident in the parametric evaluations presented later. These comparisons clearly reveal the importance of the competition of SO_2 for the flyash surface sites that capture SeO_2, and also demonstrate the model's quantitative performance for different ash contents and compositions.

Cordoba et al. reported measurements of several trace metals at a 337 MW Spanish power plant firing a blend of several native subbituminous and imported bituminous coals[9]. The native coals have very high ash levels in comparison to U.S. utility fuels, varying between 26 and 47 dry wt. %. The gas cleaning system at this plant consisted of an ESP and a limestone WFGD. Metals sampling and chemical analyses were performed using several European and ASTM standards. All solid and liquid streams were sampled for trace metal concentrations and the flue gas was sampled at the outlet of the ESP and the WFGD. The trace metal measurements included total Se concentrations but did not include any speciation. Mass balances were performed across the ESP and the WFGD and also for the whole plant. The Se balance closures across the ESP and the WFGD were 110 and 109 %, respectively. For the complete power plant, the total Se in all the outlet streams was 118 % of the inlet streams.

More than 60 % of the Se was captured on the flyash with approximately 15 and 25 % partitioning in the boiler slag and the flue gas, respectively. The only other plant in this database that showed such high partitioning of Se in boiler slag was Coal Creek with 15 % Se in bottom ash. For most of the other plants, this value rarely exceeds a few percent. The flyash CaO for the Spanish subbituminous coals is very low at about 2 %, and coal-S was moderate at 1.3 daf wt. %. This coal has the highest flyash loading in the

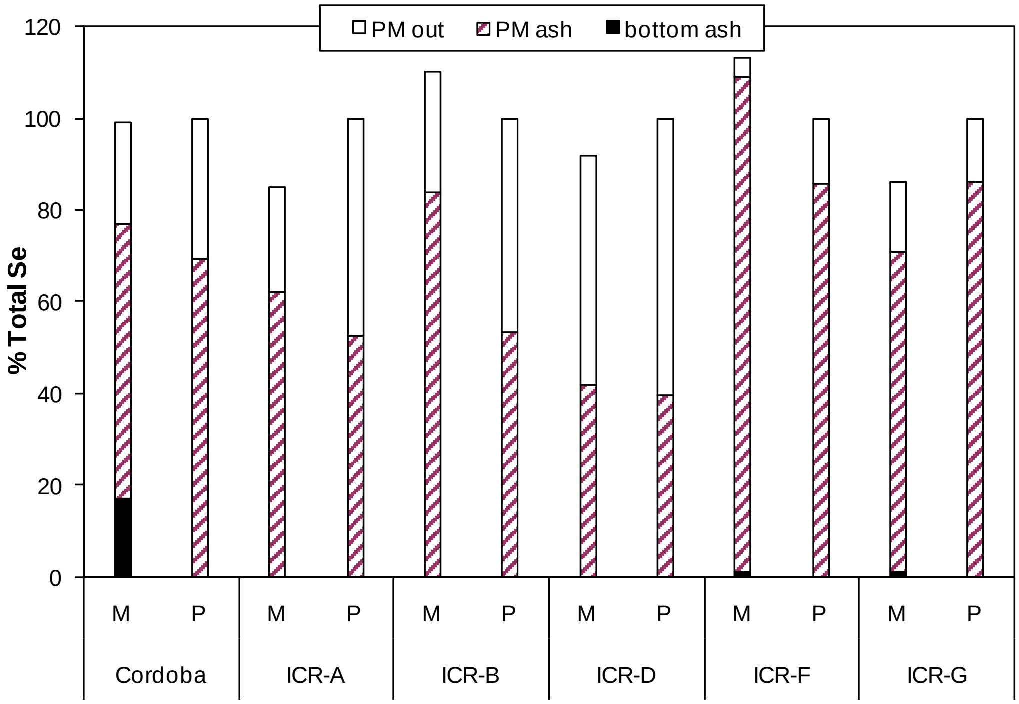

Figure 2. Measured (M) and predicted (P) Se partitioning among the exit streams of full-scale plants as a percentage of coal-Se.

current database and, consequently, the predicted Se capture in flyash is approximately 70 %, within 7 % of the measured value, as seen in Fig. 2. Comparing the predictions of the two Spanish plants, the model predictions quantitatively account for the variations in coal-S and flyash loading on Se capture for these subbituminous coals with low CaO and high ash contents.

In late 2009 the U.S. EPA issued an information collection request (ICR) to the electric utility industry requesting information on hazardous air pollutant (HAP) metals including Se. The ICR metals data on Se included only stack emissions and, in a few cases, the coal properties as well. Unfortunately, such measurements do not provide any insight into the transformation and capture of Se, particularly for plants with different gas cleaning configurations. To complement the ICR data, several testing teams measured Se concentrations along all inlet and outlet streams at several coal-fired power plants in the ICR test effort. Senior et al.[11] compile the reported measurements and the Se balance closures for all these plants. Of the seven plants, five plants report Se mass balance closures between 80 and 120 % and these are included in our validation work.

The configuration and operating conditions for these sites were already presented in Table 1. Plants A and B fire bituminous coals, Plant D fires a blend of blend of bituminous coal and petcoke while Plants F and G fire subbituminous coals. All plants are either wall-or T-fired furnaces with the exception of the cyclone-fired furnace at Plant D. Some plants in the dataset had SCR and SNCR units for NOx control. Since the Se chemistry across these units is unclear, we did not include any additional chemistry in the simulations. For Plants B and D that contain an SCR, we included an isothermal stage in the thermal history at approximately 350°C for a nominal residence time of 1 s. Plants F and G firing subbituminous coals had FFs. No flyash compositions or PSDs were reported for any of these tests and, consequently, the default ash specifications were implemented.

The predicted Se capture on flyash is compared with the measured values for the ICR plants in Fig. 2. The only glaring discrepancy appears in the comparisons for Plant B. The predictions for Plants A and D that fire bituminous coal are in good agreement with the measured values. The inclusion of an isothermal stage for the SCR and the higher bottom ash partitioning in Plant D due to the cyclone furnace appear to be crucial for accurate predictions for this plant. The operating conditions at Plants A and B are similar except that Plant B includes an SCR. Unless the SCR at Plant B introduces unusual chemistry into the Se partitioning, the very high Se capture in solids in excess of 90 % seems inconsistent with the measurements on Plants A and D. For Plants F and G firing subbituminous coals and having a FF, close to 90 % Se is predicted in the solid phase suggesting that the equilibrium sorption limit for Se is reached in these devices. The predicted Se retention in FF filtercakes is in good agreement with the measured values considering that the overall mass balance closures for Plants F and G are 110 and 90 %, respectively.

Given the satisfactory interpretation of our field test database, we clarified the determining factors on Se emissions with parametric case studies. The predicted Se capture among plants with ESP is highest at the Spanish plant tested by Cordoba et al. that has the highest ash loading. To parametrically examine the effect of ash loading, we choose Plant Yates, which fires a bituminous coal with about 11 % ash and 3 daf wt. % coal-S. For these baseline conditions, both the measured and predicted Se capture was about 41 %. When the ash content was halved to 5 wt. %, the predicted Se capture decreased to 34 % and when the ash loading was tripled to 30 wt. %, 57 % Se capture is predicted. Therefore, for a change in ash content from 5 to 30 wt. %, the Se capture in flyash increased by 27 %, as shown in Fig. 3-6.

Reducing the ESP temperature at Yates from 178 to 140 to 100ºC did not increase the Se on flyash by more than 5 % for the same overall residence time and flyash loading. Increasing the coal ash levels from 5 to 20 wt % increased adsorbed Se by approximately 10 %. This relatively minor increase in adsorbed Se can be explained by an abundance of flyash surface area relative to trace concentrations of Se in flue gas. For the same operating temperatures and flyash loadings, an increase in the flue gas residence time in the ESP from 1 to 5s increases the adsorbed Se on flyash from 34 to 56 %. The parametric studies indicated that the flue gas residence time affects the Se adsorption more than variations in the ESP temperature and flyash loading. The stronger effect of residence time on Se partitioning also explains the high levels of Se capture on systems with FF.

The competition between SeO_2 and SO_2 for adsorption sites was examined by varying the coal-S levels between 0.5 and 5.5 daf wt. % for the conditions at Plant Yates which has a baseline coal-S of 3 daf wt.%. Increasing the coal-S from 0.5 to 3 daf wt. % decreased the Se capture by about 23 %. Further increase in coal-S to 5.5 daf wt. % decreased the Se capture by only 4 %. This suggests that a coal-S level of 3 daf wt. % is sufficient to show the maximum extent of inhibition towards Se capture.

Finally, we present the parametric simulations evaluating the effect of SeO_2 concentration on its adsorption characteristics. Since Se is present in only trace concentrations in the flue gas stream, it cannot affect the transformations of any other species. The initial concentration of Se may nevertheless affect the rate of adsorption/desorption of SeO_2. The coal–Se was increased from 0.54 to 5.2 ppmw daf corresponding to gas phase SeO_2 concentrations of approximately 10 and 100 ppb, respectively. The final fraction of adsorbed Se was predicted to decrease from 41 to 38 %. Note that the net rate of adsorption of SeO_2 is faster at the higher concentrations but the final partitioning of Se expressed as a percentage is lower.

CONCLUSIONS

Our simulation results have been validated with a database from twelve full-scale cleaning systems in the U.S., Europe, and China. The predicted Se capture levels on flyash are within 10 % of the measured values in nine of those cases. Across the database, the measured captures vary from 30 to 110 %, while the predicted captures vary from 35 to 85 %, so the analysis clearly delivers Se captures on flyash within useful quantitative tolerances. Moreover, the predicted captures closely track important variations in the measured Se captures due to different firing configurations, coal ash contents, ash CaO levels, coal-S, and the thermal histories across the PCDs. At this stage in the model development, it is encouraging that the results appear to properly account for all the most important factors affecting Se partitioning onto flyash. In two of the three outliers, the discrepancies in the predicted Se capture levels are entirely due to contributions for Se in bottom ash that exceed 15 % of the Se inventory, which are much greater than the negligible-to-a-few-percent levels reported for all other tests. We suspect that furnace-specific factors are responsible for these elevated bottom ash recoveries, and will watch for clues to explain the unusual behavior as the Se field test database develops further. The only outright discrepancy is the 45 % predicted capture vs. 85 % measured for Plant B in the ICR dataset. This measured value is inconsistent with the measurements from two other ICR plants with similar fuels and cleaning conditions. Perhaps distinctive characteristics of the fuel or cleaning conditions came into play, since the under-prediction was necessarily based on numerous default values because the ICR dataset omitted most of the required input data for our Se transformation simulations.

Whereas the accurate Se capture predictions for cases covering such a broad domain of fuel properties, firing configuration, and cleaning conditions validate the analysis for practical applications, parametric case studies clarified the relative impact of the numerous factors affecting Se partitioning. Ash loadings are most important. They are determined by the coal ash content in conjunction with the firing configuration, because cyclone firing gives roughly half to one-third the flyash loading as T- and wall-firing. Se capture also increases for progressively longer residence times in the PCD, so that FFs give the greatest Se captures on flyash because the contact conditions are favorable enough to achieve adsorption equilibrium. Coal-S is the most important inhibitor of Se capture, especially for coal-S levels from 0.5 to 3 daf wt. %. Variations in the PCD temperature and coal-Se level were inconsequential.

ACKNOWLEDGEMENT

Financial support for this work from Japan's New Energy Development Organization, with administration through the Coal and Environment Research Laboratory of Idemitsu Kosan Co., Ltd., is gratefully acknowledged.

REFERENCES

[1] Senior, C.L., Van Otten, B., Wendt, J.O.L., and Sarofim, A.F., "Modeling the behavior of selenium in Pulverized-Coal Combustion Systems," Combust. Flame 157, 2095-2105, (2010).
[2] Noda, N. and Ito, S., "The release behavior of mercury, selenium, and boron in coal combustion," Powder Technol., 180, 227-231 (2008).
[3] Helble, J.J. et al. Fundamental study of ash formation and deposition: Effect of reducing stoichiometry. Quarterly Report under U.S. DoE contract # DE-AC22-93PC92190, 1993.
[4] BATTELLE, "A study on toxic emissions from a coal-fired power plant utilizing an ESP/Wet FGD system," Final Report to U.S. DoE under contract # DE-AC22-93PC93251, July 1994.
[5] Radziwon, A. and Winter, E., "Summary of air toxics emissions testing at sixteen utility power plants," Final Report to U.S. DoE under Contract # DE-AC22-94PC92100, July 1996.
[6] Chu, P., Epstein, M., Gould, L., and Botros, P., "Evaluation of air toxics emissions from advanced and conventional coal-fired power plants," proc. Conf. New Power generation Technology, San Francisco, CA, Oct 1995.
[7] Huang, Y., Jin, B., Zhong, Z., Xiao, R., Tang, Z., and Ren, H., "Trace elements (Mn, Cr, Pb, Se, Zn, Cd, and Hg) in emissions from a pulverized coal boiler," Fuel Process. Technol., 86, 23-32 (2004).
[8] Alvarez-Ayuso, E., Querol, X., and Tomas, A., "Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterization of combustion by-products," Chemosphere, 65, 2009-2017 (2006).
[9] Cordoba et al., "Partitioning of trace inorganic elements in a coal-fired power plant equipped with a wet Flue Gas Desulphurization system," Fuel 92, 145-157, (2012).
[10] Otero-Rey, J. R. et al., "As, Hg, and Se flue gas sampling in a coal-fired power plant and their fate during combustion," Environ. Sci. Technol., 37, 5262-5267 (2003).
[11] Senior, C.L., Blythe, G., and Chu, P., "Multi-media emissions of selenium from coal-fired electric utility boilers." Proc. Air Quality VIII Symposium, Virginia, 2011.