

Synchrotron-radiation-induced oxidation of selenite to selenate in coal-derived fly ash

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Systematic changes observed in consecutive XANES spectra of selenium in samples of fly ash from a power plant in Alberta, Canada, burning subbituminous coal have been interpreted as arising from synchrotron-radiation-induced oxidation of a selenite species to selenate. It was estimated that about 15–20% of the selenite was oxidized to selenate during the 2 h exposure of the fly ash to the synchrotron beam. In contrast, the XANES spectra of arsenic (and other trace elements not documented herein) showed no variation. It is believed that this is the first time that radiation-induced changes have been observed for an element in coal-derived fly ash.

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Printed in Singapore – all rights reserved**Keywords:** XAFS spectroscopy; selenium; arsenic; coal combustion; fly ash; X-ray-induced oxidation.

1. Introduction

Selenium is one of a number of potentially hazardous volatile elements that can be released into the environment during commercial coal combustion. Such releases are typically of two types: (i) as a component in fugitive emissions (gas and very fine particulate matter) that avoid capture by environmental control devices in a power plant and are released into the atmosphere *via* the combustion stack, and (ii) in fly ash captured by environmental control devices and disposed of by storage under water in ash waste impoundments, which can lead to the leaching and release of Se and other elements into groundwater. The division of selenium between these two types of environmental contamination is controlled by the coal combustion process, in particular the environmental control devices in place at the plant, and to a lesser extent by what forms selenium is found in the coal and the volatility of such forms. Normally, selenium follows sulfur in its occurrence in coal and may be found substituting for sulfur in pyrite (FeS₂) or in organic sulfur species, such as organic sulfides and thiophenes, associated with the carbonaceous components of coal (Senior *et al.*, 2000), although other selenium forms have also been reported in coal (Swaine, 1990; Dreher & Finkelman, 1992, 1994). During pulverized coal combustion, selenium is released from these occurrences as volatile elemental Se and immediately reacts with oxygen in the combustion zone to form SeO₂ or a closely related species (*e.g.* selenous acid, H₂SeO₃). As these species journey through the power plant, they enter the heat-exchanger region where the temperature rapidly drops. Here, the acidic Se(IV) species can react with metal ions and condense on fly ash particulate matter in the form of selenites. Selenium occurrences in coal and in fly ash samples derived from pulverized coal combustion have been investigated by X-ray absorption fine-structure (XAFS) spectroscopy (Senior *et al.*, 2000; Huggins *et al.*, 2007; Al-Abed *et al.*, 2008), as well as by less direct methods that generally involve sequential extraction followed by selenium determinations using ion chromatography (Jackson & Miller, 1998), inductively coupled plasma mass spectrometry (Jackson

& Miller, 1998; Narukawa *et al.*, 2005), high-performance liquid chromatography (Wadge & Hutton, 1987; Narukawa *et al.*, 2005), hydride generation atomic absorption spectrometry (Martens & Suarez, 1997) or other methods.

In a recent XAFS investigation of sulfur and seven potentially hazardous trace elements (As, Cr, Ni, Pb, Se, V, Zn) in a suite of seven fly ash samples obtained from combustion of a subbituminous coal at a full-scale power plant in Alberta, Canada, the Se XAFS spectra of the fly ash were observed to change in a consistent manner between consecutive scans on the same sample. In contrast, the spectra of arsenic and the other trace elements were unchanged between consecutive scans. It is the purpose of this short communication to document the changes in the spectra for selenium by contrasting its behavior with that of arsenic in this respect. Although radiation-induced changes have been previously observed in organoselenium compounds (*e.g.* Holton, 2007), this is believed to be the first time such changes have been observed for coal-derived fly ash, a predominantly inorganic material. The changes observed in the Se XAFS spectra with time of exposure to the synchrotron beam are attributed to radiation-induced oxidation of a selenite species in the fly ash. Detailed accounts of the investigation of selenium and other elements in the Canadian coal and derived fly ash samples and their environmental consequences will be presented elsewhere (Sanei & Huggins, 2011).

2. Experimental

Fly ash samples were collected daily over the course of a week at a combustion plant in Alberta, Canada, while the same coal was being burned so that the source material for all seven fly ash samples was essentially unchanged. The fly ash samples were collected using standard bulk material collection methods; the collected samples were typically <200 mesh (75 µm) and were subdivided system-

atically to provide representative small aliquots (5–10 g) for XAFS analysis.

XAFS spectra of selenium and arsenic were collected at wiggler beamline 4-1 of the Stanford Synchrotron Radiation Lightsource (SSRL), Palo Alto, CA, USA, from approximately half-gram samples of the fly ash suspended in the synchrotron X-ray beam in ultrathin (5 μm) polypropylene baggies. For selenium, the samples were exposed to radiation of energy varying between 12.5 and 13.2 keV by the rotation of a Si(220) monochromator. Owing to the low concentrations of Se in the original coal (0.6 $\mu\text{g g}^{-1}$) and resulting fly ash samples (6–15 $\mu\text{g g}^{-1}$), a multi-element germanium fluorescence detector (Cramer *et al.*, 1988) was used to collect the XAFS spectra. Both Soller slits and a 6 μ arsenic filter (Stern & Heald, 1979) were used to augment the signal/noise ratio and four scans were collected for each of the seven fly ash samples. XAFS spectra of arsenic in the fly ash were collected in identical fashion over the range 11.75–12.65 keV, but with a 6 μ germanium filter. Analysis of the Se and As XAFS spectra was performed using the software package *SixPack* (Webb, 2005).

3. Results and discussion

A major result of the investigation that will be documented and discussed in detail elsewhere (Sanei & Huggins, 2011) was the lack of any significant variation of the XAFS spectra for most elements for the suite of seven fly ash samples collected at different times. All seven spectra for a given element were essentially identical regardless of when they were sampled. Furthermore, for all elements except selenium, the individual scans of the spectrum of an individual fly ash sample showed no significant variation.

For selenium, however, systematic variation was noted between successive XAFS spectral scans of the same sample for all seven fly ash samples, especially in the X-ray absorption near-edge structure (XANES) region. Furthermore, it was observed that the first scans for all seven fly ash samples were essentially similar, much more so than the first and second scans of the same sample. The second and subsequent scans also exhibited similar trends. Consequently, it was decided to average the first scans and subsequent scans for all seven samples to obtain four time-averaged Se XANES spectra. As each selenium XAFS scan took approximately 30 min to collect, the four time-averaged spectra represent exposure of the samples to the synchrotron beam on average for 15 min, 45 min, 75 min and 105 min. Unfortunately, no fly ash sample was exposed to the synchrotron beam for more than four Se XAFS scans, so it was not established whether further changes might be observed with longer exposure to the synchrotron beam. The four time-averaged spectra are shown in Fig. 1. In comparison with similarly averaged arsenic spectra shown in Fig. 2, it can be seen that the four Se scans show a significant variation in both the XANES and derivative XANES spectra, whereas the variation among the corresponding As scans is negligible. Hence, whereas the selenium spectra show systematic changes as a function of time, those of arsenic (and other elements) in the same samples do not.

The XANES spectra establish that selenium in the fly ash undergoes a chemical change in response to exposure to the synchrotron beam. The major peak in the averaged first-scan spectrum occurs at an energy of 12664.5 eV, which is consistent with the Se(IV) oxidation state found in selenite (SeO_3^{2-}) containing compounds (Huggins *et al.*, 2007). As shown in Fig. 1, not only does this peak broaden and shift slightly to higher energy, but there is a significant shift in the overall selenium absorption to higher energy with increasing time of

Table 1

Results of least-squares fitting of the Se EXAFS/RSF region data for the Se–O nearest-neighbor coordination shell using *IFEFFIT* methods.

Spectra were fit over the range in k -space from 3 to 10 \AA^{-1} and from 0.7 to 1.8 \AA in R -space.

Spectrum	CN [†]	Se–O (\AA)	σ^2 (\AA^2)	R_{factor}
15 min average	3	1.69	0.0009	0.0289
45 min average	3.6	1.70	0.0039	0.0675
75 min average	3.3	1.70	0.0027	0.0465
105 min average	3.3	1.70	0.0028	0.0877
Estimated errors [‡]	± 1.3	± 0.02	± 0.0040	

[†] A value of 3 was assumed for the Se–O coordination number (CN) for the 15 min average. [‡] Estimated errors are similar for all samples.

exposure to the synchrotron beam. In particular, there is growth in the absorption over the region 12666–12672 eV, which is where a peak for Se(VI) as selenate (SeO_4^{2-}) at about 12667.5 eV would be expected to emerge. Attempts to use linear combinations of standard spectra to simulate the Se XANES spectra of the fly ash were only partially successful. As documented in the supplementary information¹, the trends for the Se XANES and derivative XANES spectra shown in Fig. 1 could be approximately simulated by combining the corresponding spectra for K_2SeO_3 and K_2SeO_4 . Based on the simulations, it is estimated that 15–20% of the selenite in the fly ash had undergone oxidation during the entire 2 h time of exposure to the synchrotron beam. However, actual least-squares fitting of the fly ash XANES spectra using data for the two potassium compounds was clearly inadequate.

The variation in the XANES spectra with time is indicative of selenium becoming more oxidized as a result of the exposure to the synchrotron beam. The changes involving oxidation of the Se(IV) in the fly ash must result in the rearrangement of the Se–O environment and formation of selenate anions *via* reaction with oxygen. It should be noted that such variations in Se XANES spectra were not reported in previous XAFS investigations of Se in fly ash and related samples from other, mostly US, coals (Huggins *et al.*, 2007; Al-Abed *et al.*, 2008).

Arsenic and selenium radial structure function (RSF) spectra were also prepared from the extended X-ray absorption fine-structure (EXAFS) regions for the time-averaged X-ray exposure scans (Fig. 3). Compared with the XANES spectra, however, the selenium EXAFS/RSF spectra showed less variability, but somewhat more so than the comparable arsenic EXAFS/RSF spectra. The radiation-induced changes in the EXAFS/RSF spectra are less apparent since it is not possible to resolve separate peaks for the Se(VI) and Se(IV) oxidation states in selenium RSF spectra because the average Se–O distances in selenates and selenites differ by only 0.06 \AA (Huggins *et al.*, 2007). This was effectively confirmed by using *IFEFFIT* least-squares fitting methods (Ravel, 2001; Ravel & Newville, 2005; Webb, 2005) to model the Se EXAFS/RSF region data for the Se–O nearest-neighbor coordination shell. The results of this fitting, summarized in Table 1, showed that any differences in coordination number (CN), Se–O distance and Debye–Waller factor (σ^2) among the four time-averaged spectra were not significant relative to estimated experimental errors. Such results therefore confirm that it is only a relatively minor fraction of the Se(IV) in the fly ash samples that has undergone oxidation since a major change in oxidation state

¹ Supplementary data for this paper, containing details of the simulation of the Se XANES and derivative XANES spectra shown in Fig. 1, are available from the IUCr electronic archives (Reference: OT5633). Services for accessing these data are described at the back of the journal.

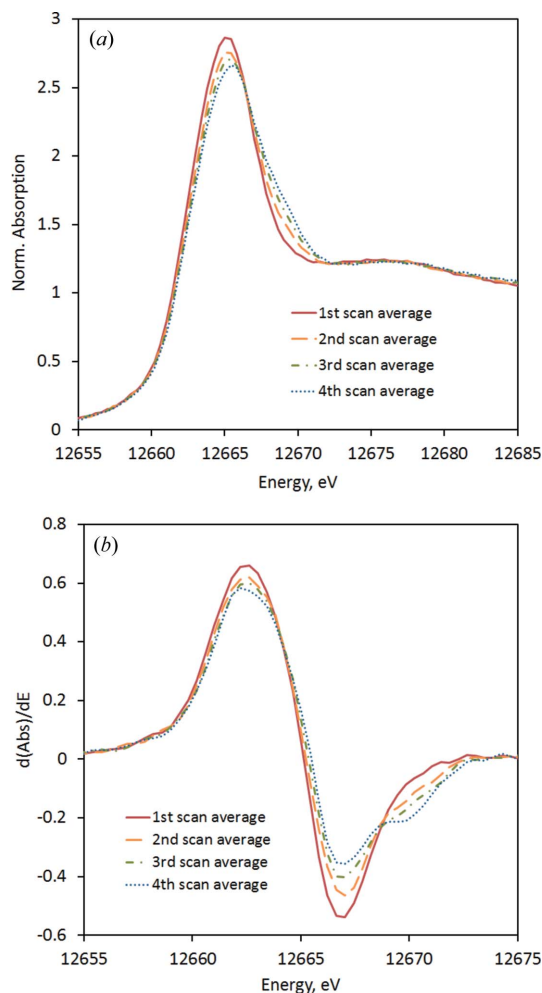


Figure 1
 (a) Selenium XANES and (b) derivative XANES spectra for four averaged scans representing exposure of the fly ash samples to the synchrotron beam for 15, 45, 75 and 105 min.

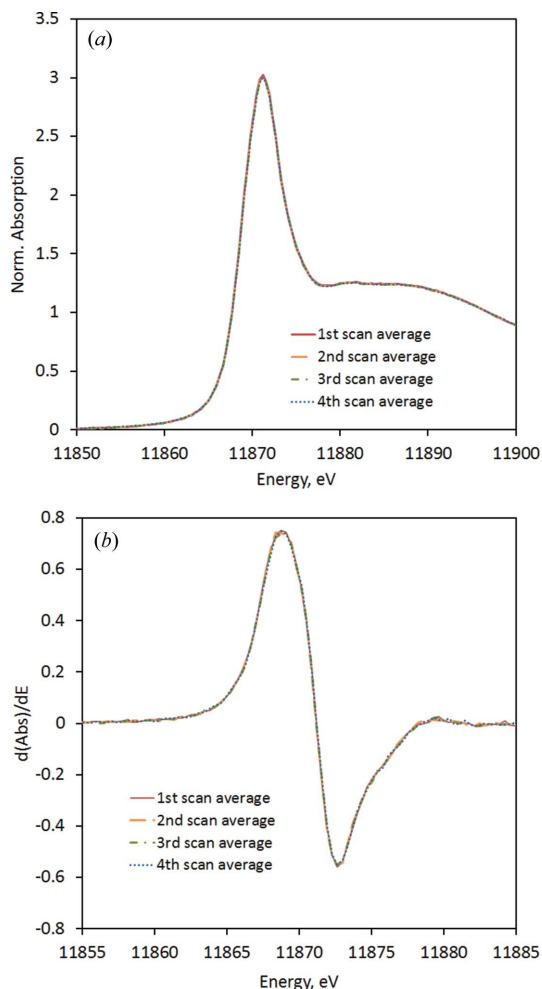


Figure 2
 (a) Arsenic XANES and (b) derivative XANES spectra for four averaged scans representing exposure of the fly ash samples to the synchrotron beam for 15, 45, 75 and 105 min. All four scans for arsenic superimpose upon each other.

from Se(IV) to Se(VI) would be expected to give rise to a demonstrable shortening of the Se–O distance, as well as a prominent selenate peak in the XANES region.

20% of the total selenite in the fly ash has undergone oxidation to selenate during the 2 h exposure of the fly ash to the synchrotron beam.

4. Conclusions

The XANES spectra of Se in a suite of seven fly ash samples collected at a power plant in Alberta, Canada, show consistent and systematic variations with length of time of exposure to the synchrotron radiation. In contrast, the spectra of As (and other elements not documented herein) in the same samples effectively show no variation. These variations for Se suggest that there is at least one selenite form in the fly ash from this particular power plant that is capable of undergoing oxidation to selenate when exposed to synchrotron radiation. Based on simulation of the observed Se XANES trends, as well as the lack of significant changes observed in the Se EXAFS/RSF spectra, it is estimated that only about 15–

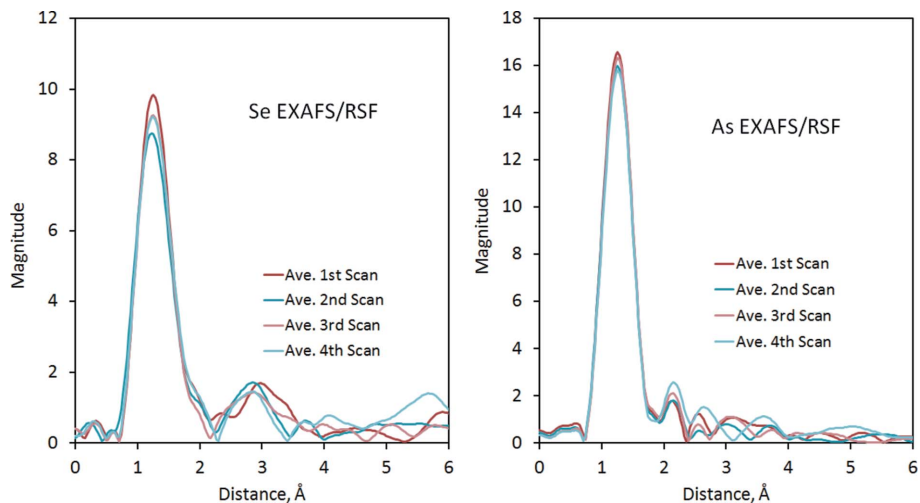


Figure 3
 Comparison of EXAFS/RSF spectra for selenium (left) and arsenic (right) for the four averaged scans representing exposure of the fly ash samples to the synchrotron beam for 15, 45, 75 and 105 min.

Selenium and arsenic XAFS spectroscopy was carried out at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the US Department of Energy, Office of Basic Energy Sciences.

References

- Al-Abed, S. R., Jegadeesan, G., Scheckel, K. G. & Tolaymat, T. (2008). *Environ. Sci. Technol.* **42**, 1693–1698.
- Cramer, S. P., Tench, O., Yocum, N. & George, G. N. (1988). *Nucl. Instrum. Methods Phys. Res. A*, **266**, 586–591.
- Dreher, G. B. & Finkelman, R. B. (1992). *Environ. Geol. Water Sci.* **19**, 155–167.
- Finkelman, R. B. (1994). *Fuel Proc. Technol.* **39**, 21–34.
- Holton, J. M. (2007). *J. Synchrotron Rad.* **14**, 51–72.
- Huggins, F. E., Senior, C. L., Chu, P., Ladwig, K. & Huffman, G. P. (2007). *Environ. Sci. Technol.* **41**, 3284–3289.
- Jackson, B. P. & Miller, W. P. (1998). *J. Anal. At. Spectrom.* **13**, 1107–1112.
- Martens, D. A. & Suarez, D. L. (1997). *Environ. Sci. Technol.* **31**, 133–139.
- Narukawa, T., Takatsu, A., Chiba, K., Riley, K. W. & French, D. H. (2005). *J. Environ. Monit.* **7**, 1342–1348.
- Ravel, B. (2001). *J. Synchrotron Rad.* **8**, 314–316.
- Ravel, B. & Newville, M. (2005). *J. Synchrotron Rad.* **12**, 537–541.
- Sanei, H. & Huggins, F. E. (2011). In preparation.
- Senior, C. L., Zeng, T., Che, J., Ames, M. R., Sarofim, A. F., Olmez, I., Huggins, F. E., Shah, N., Huffman, G. P., Kolker, A., Mroczkowski, S., Palmer, C. & Finkelman, R. B. (2000). *Fuel Proc. Technol.* **63**, 215–241.
- Stern, E. A. & Heald, S. M. (1979). *Rev. Sci. Instrum.* **50**, 1579.
- Swaine, D. J. (1990). *Trace Elements in Coal*, pp. 148–153. London: Butterworths.
- Wadge, A. & Hutton, M. (1987). *Environ. Pollut.* **48**, 85–99.
- Webb, S. M. (2005). *Phys. Scr.* **T115**, 1011–1014.