

TRACE METALLIC ELEMENTS IN COAL, COAL ASH AND GYPSUM MEASURED BY FLUORESCENCE X-RAY ABSORPTION NEAR-EDGE STRUCTURE

Coal combustion plants are widely utilized as a source of thermal and electric energy. Coal, which consists of organic compounds and inorganic minerals, contains trace elements. As shown in Fig. 1, these trace elements are emitted into the flue gas as gaseous compounds or particle-bound forms in coal combustion processes. In a flue gas stream, trace elements are fixed in ash particles and in by-products such as gypsum and sludge if wet flue gas desulfurization (wet-FGD) unit is equipped. To understand their chemical forms in coal ash and by-products is very useful for utilization and disposal of these products. Conventional X-ray analysis, however, is not effective because the concentrations of these elements are generally very low. In this research, ultra-brilliant X-ray source of SPring-8 was applied to X-ray absorption fine structure (XAFS) spectra analysis to characterize trace elements in these complex systems.

We have attempted to measure the XAFS spectra from trace elements such as arsenic (As), selenium (Se) and chromium (Cr) in the NIST standard samples (NBS1632c: bituminous coal, NBS1633b: fly ash) at beamline BL16XU. Figure 2 shows X-ray absorption near-Edge structure (XANES) spectra at an As *K*-edge and a Se *K*-edge [2,3] from the NIST standard samples, several As and Se compounds. The XANES spectra of the NIST standard samples were detected using a wavelength-dispersive fluorescence X-ray spectrometer installed in the experimental station as shown in Fig. 3, which avoids the influence of coexisting elements and background. The XANES spectra of As and Se compounds were measured by the ordinary transmission method. XANES spectra are element specific and sensitive to the local structure and physical state of the element. It is easy to understand the oxidation and chemical states of the element by

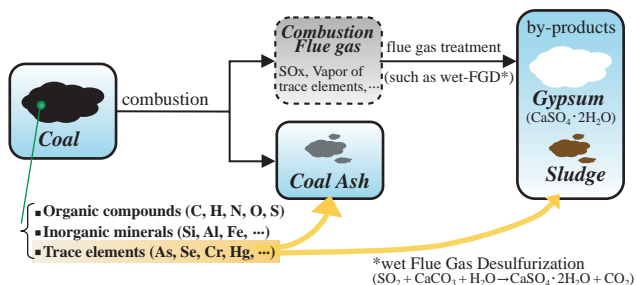


Fig. 1. Behavior of trace elements in coal combustion and flue gas stream.

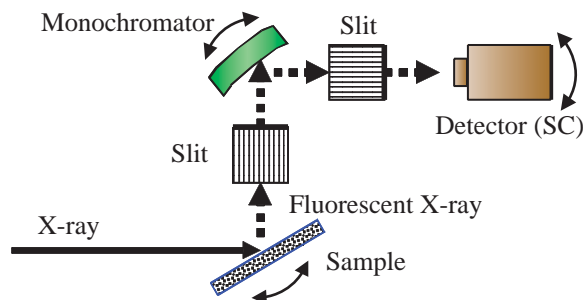


Fig. 2. As-*K* edge and Se-*K* edge XANES spectra of NIST standard samples, arsenic and selenium compounds. (NBS1632c: As 6ppm, Se 1 ppm NBS1633b: As 136 ppm, Se 10 ppm)

comparison with the spectrum of a standard compound. As and Se exist in the environment in several oxidation states. The most common oxidation states of As are three and five, whereas those of Se are primarily four and six. In this study, the position of the maximum X-ray absorption energy is clearly related to the oxidation states of As and Se. We conclude that the oxidation states and ratios of As and Se in coal ash are higher than those in coal. We are able to predict that these elements exist in coal ash as the chemical forms of arsenate (AsO₄³⁻), arsenite(AsO₃³⁻), selenate (SeO₄²⁻), and selenite (SeO₃²⁻). In addition, we are able to understand that As and Se in coal are a mixture of at least three different oxidation states. We think that As and Se coexist in a more reduced form as a substituted pyrite(FeAs(Se)S)-like substance in coal.

We attempted the transmitted type and two kinds of fluorescence XAFS measurements. It became clear that fluorescence XAFS measurement using solid state detector (SSD) was applicable to the characterization of trace elements in a range above 10 mg/kg. In addition, XAFS measurements become capable of detecting a few mg/kg of trace elements using the WD-XRF spectrometer, as shown in Fig. 4 [3]. It was difficult to detect XAFS signal of mercury in the NIST standard samples because the concentrations of mercury are very low.

We have also attempted to measure the XAFS spectra of mercury captured in gypsum to investigate the chemical forms of mercury [3,4]. A mixed gas consisted of N₂, CO₂, O₂ and Hg²⁺ was fed into 9.3wt% gypsum slurry at 313 K to make a mercury/gypsum mixture. The XAFS spectra of seven pellet samples: five standard materials (HgCl₂, HgO, silver amalgam, HgS, and HgSO₄), a mixture of

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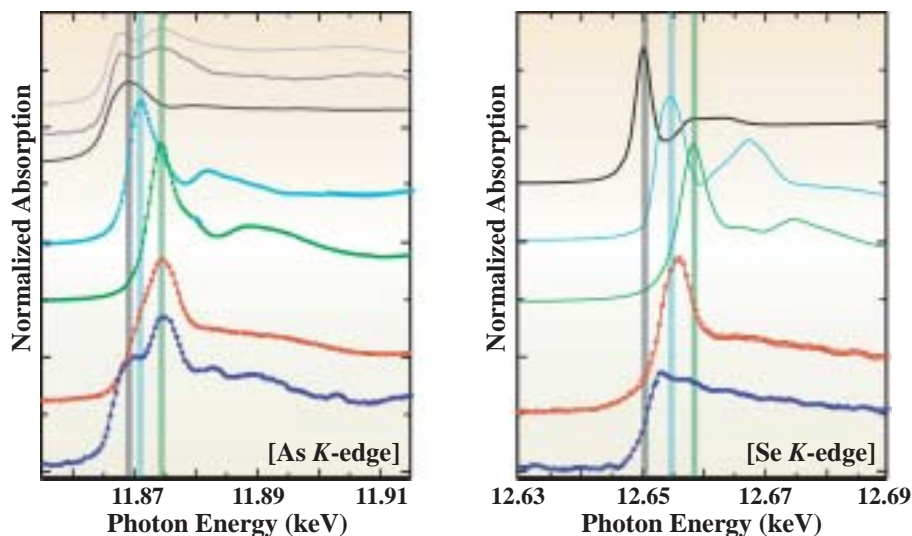


Fig. 3. Schematic diagram and photograph of wavelength-dispersive fluorescence X-ray (WD-XRF) system.

standard HgSO_4 and gypsum, and the above-mentioned mercury/gypsum mixture were measured. Figure 5 shows the Hg-L_{III} XANES spectra of those samples. The XANES spectra of the mercury/gypsum mixture and standard HgSO_4 /gypsum mixture were detected using the wavelength-dispersive fluorescence X-ray spectrometer. The XANES spectra of the other five standard materials were measured by the ordinary transmission method. These XANES spectra reflect the chemical forms of the samples. The spectrum of the mercury/gypsum mixture is overwritten on the spectrum of the standard HgSO_4 /gypsum mixture as shown in Fig. 5. Since the spectrum of the mercury/gypsum mixture is similar to

the spectrum of the standard HgSO_4 /gypsum mixture, mercury in the gypsum exists as HgSO_4 [4].

The XAFS measurement technique will be applied to characterize the chemical forms of trace elements in liquid samples at beamlines BL16XU and BL16B2.

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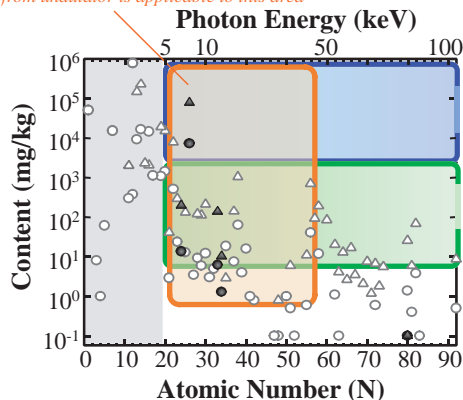


Fig. 4. Capability of XAFS analysis of various elements in NIST standard samples.

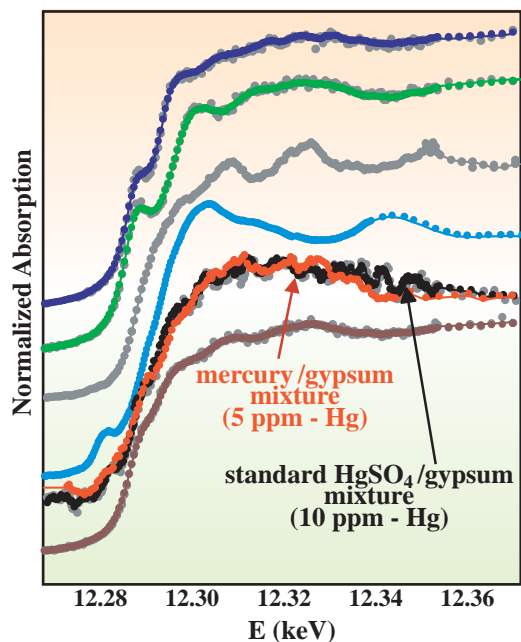


Fig. 5. Hg-L_{III} XANES spectra of mercury/gypsum mixture and standard materials.

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