

Investigation of sulfur speciation in particles from small coal-burning boiler by XANES spectroscopy*

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Abstract Sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy was employed to study the speciation of sulfur in raw coal, ash by-product and fine particulate matter from a small coal-burning boiler. By means of least square analysis of the XANES spectra, the major organic and inorganic sulfur forms were quantitatively determined. The results show that about 70% of the sulfur in raw coal is present as organic and a minor fraction of the sulfur occurs as other forms: 17% of pyrite and 13% of sulfate. While in bottom ash, fly ash, and PM_{2.5}, the dominant form of sulfur is sulfate, with the percentage of 80, 79 and 94, respectively. Moreover, a number of other reduced sulfur including thiophenic sulfur, element sulfur and pyrrhotite are also present. During coal combustion, most of organic sulfur and pyrite were oxidized and released into the atmosphere as SO₂ gas, part of them was converted to sulfate existing in coal combustion by-products, and a small part of pyrite was probably reduced to elemental sulfur and pyrrhotite. The results may provide information for assessing the pollution caused by small boiler and developing new methods for the control of SO₂ pollution.

Key words XANES, sulfur, coal, PM_{2.5}, speciation

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1 Introduction

In China coal is the dominant energy source and accounts for about 70% of the total primary energy consumption in recent years. As a result, coal combustion has become a major source of SO₂ and airborne particulate matter (PM). SO₂ can exert harmful effects on the air, water and living organism and human beings. Numerous epidemiological studies show that PM has a great influence on human health and the elevated fine PM concentrations in the air are associated with morbidity and mortality from cardiovascular and respiratory illnesses^[1]. Since then many studies have focused on the source of PM, particularly those emitted from the combustion of coal.

It is estimated that about 20% of coal is consumed

in small coal-burning boilers in China^[2]. Coal used by small boilers in urban areas of China has decreased due to policies on substitute gas and other cleaner burning fuels, but in the suburbs and rural areas, it seems to be on the rise. Emission of SO₂ and PM from small boilers is more serious than large scale combustion devices in coal-burning power plants. For small boilers, pollution control measures are usually absent and the combustion temperature is lower. Although the need to understand the particulate matter and gas emission from small boilers has been increased, there are not many data on sulfur speciation in PM^[3, 4]. Removing sulfur from coal is an effective method for reducing the environmental pollution caused by SO₂. A full understanding of the characterization and species of sulfur in coal and combus-

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tion by-products is essential for the development of a coal cleaning process and resolution of problems on SO₂ pollution. Synchrotron radiation X-ray absorption near-edge structure (XANES) spectroscopy is a powerful method for the direct, nondestructive, and quantitative determination of elemental speciation^[5]. In the past ten years, sulfur K-edge XANES spectroscopy has been successfully used to characterize sulfur species in coal and PM^[6–8]. This work focuses on the determination of sulfur speciation in coal and PM from a small coal-burning boiler by using XANES.

2 Experimental section

2.1 Sampling

The experiment was performed in a 600 kg/h coal-burning boiler. The feed coal was anthracite from Shanxi Province. The bottom ash was collected at the bottom of the furnace and the fly ash from the entrance to the chimney. PM_{2.5} was collected on the millipore cellulose filters by medium-volume air sampler at the chimney exit. Samples of the feed coal, bottom ash, and fly ash were crushed, sieved and ground to very fine size, and then pressed into 3 mm thick pellets. Samples of standard compounds such as pyrite, elemental sulfur, dibenzothiophen (DBT), sulfoxide, sulfone, Fe₂(SO₄)₃, which represent the principal sulfur functional forms believed to occur in coal, were prepared by mixing them thoroughly with boron nitride (1 wt% sulfur) and then pressing the mixtures into pellets. The purpose of mixing the standard compounds with boron nitride was to reduce the self-absorption effect that commonly happens for solid samples with higher concentration. The self-absorption effect was corrected using the self-absorption routine of IFEFFIT package^[9]. It was reported that self-absorption is not a problem for a thin sample (30 μm) if the sulfur weight concentration is less than 5%^[10, 11]. In this work, the impacts of self-absorption in thick samples on sulfur quantitative analysis can be neglected after self-absorption correction.

2.2 XANES spectroscopy

The sulfur K-edge XANES spectra were collected as fluorescence excitation spectra using a Si(Li) detector at Beamline 4B7A of the Beijing Synchronization Radiation Facility (BSRF). The electron energy was about 2.5 GeV and the beam current was 80–180 mA. A Si(111) double-crystal monochromator was

used to vary the X-ray energy from 50 eV below to 200 eV above the sulfur K-edge (2472 eV). The X-ray beam was maintained in vacuum all the way from the synchrotron ring to the experimental hutch in order to minimize the absorption of soft X-rays by air. The X-ray energy was calibrated by elemental sulfur and the white-line maximum of the elemental sulfur XANES spectrum was assigned as 2472 eV.

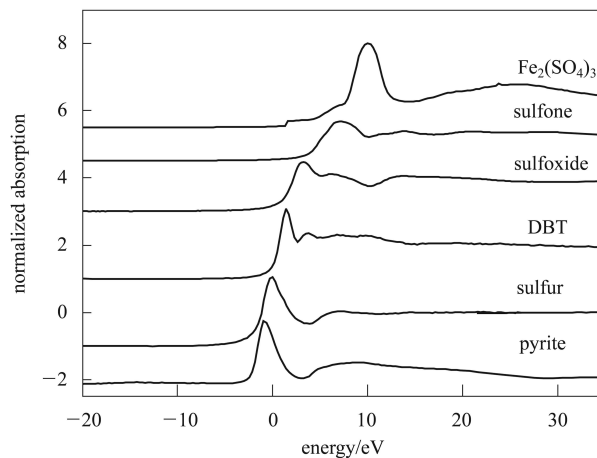


Fig. 1. Normalized sulfur K-edge XANES spectra for sulfur standard compounds.

XANES is the region of X-ray absorption spectrum within about 50 eV of the absorption edge. It is strongly sensitive to electronic oxidation state and geometry so often serves as the fingerprint to identify different compounds and types of binding, and moreover, it is usually stronger than EXAFS oscillation, and this makes XANES particularly useful in the dilute systems. Fig. 1 illustrates the sulfur K-edge XANES spectra of sulfur compounds. The first strong peak, also named white line, comes from the transition of electron from 1s level to 3p level. The remaining broadening peaks above the edge mainly come from the low energy resonance scattering and multiple-scattering. It is found that the energy shift of edge which increases with the oxidation state of sulfur is positive in the case of cations and negative in the case of anions, and both the energies and intensities of these whitelines depend sensitively on the valence and electronic binding of the absorbing sulfur atoms^[7, 8]. The energy shift of XANES shows a nearly linear dependence on oxidation state and is about 13.0 eV from S⁻² to S⁺⁶ as shown in Fig. 1. It is because the loss of valence electrons from sulfur decreases shielding of the 1s electrons from the nucleus when sulfur is in higher oxidation states and results in a net increase of 1s to 3p transition energy, and the absorption edge shift is mainly affected by the dipole allowed transition from 1s to 3p despite

the impact of covalent bond and electric structure. In a compound the K-orbits of the absorption atoms are less influenced by external factors in comparison with the outer orbits which participate directly in the formation of the chemical bonds, since the inner levels are comparatively closer to the nucleus and the overlap of wave functions of the ligand atoms is only significant for the outer levels. Chemical shift is due to the modification of the outer level distribution and depends largely on the magnitude and nature of the charge on the absorption ion^[12].

The correlation between the oxidation state, intensity and peak position of white-line makes possible the quantitative analysis of sulfur speciation. In XANES analysis, there are two common methods for quantitatively determining the composition of a mixture of species. One is least square linear combination fitting using various reference samples and the other one is the principal component analysis. The species in coal are certainly too complex to know how many standards are needed. The selection of standards is very crucial and needs to be consistent with answers. In this paper we used least square fitting method developed by Huffman and Xia^[7, 8, 10]. Background removal, normalization and deconvolution of XANES spectra were carried out using IFEFFIT package^[9].

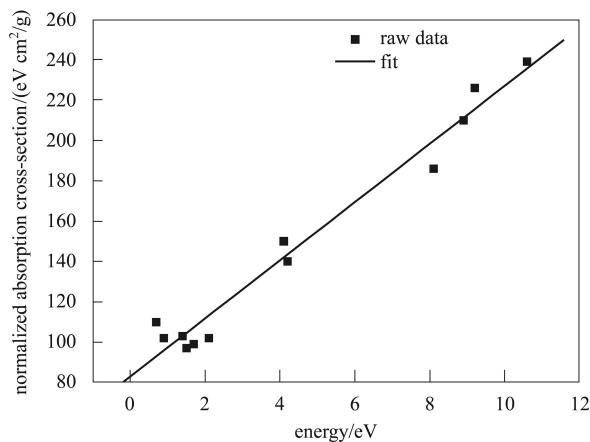


Fig. 2. Correlation between the energies of peaks in the XANES and the atomic X-ray absorption cross-section of sulfur^[11].

The least square method for analysis of the sulfur K-edge XANES spectra is based on the assumption that the experimental spectrum can be modeled as the sum of one or two arctangent functions representing the transitions of photoelectron to the continuum, and a number of Gaussian functions representing the absorption peaks arising from the $1s$ to $3p$ electronic transition of the various sulfur forms. Each of the absorption peaks is fundamentally Lorentzian shaped, but broadened as a Gaussian function. The energy of

the white line is used to identify the oxidation states of sulfur and the peak area is transformed to relative abundance of each sulfur species. The following methods were used in the fitting process: (1) Arctangent step functions represent the transition of ejected photoelectrons to the continuum; (2) Gaussian functions represent $1s$ to $3p$ transitions; (3) The full width at half-maximum (FWHM) of each Gaussian function is constrained depending on their intensity and resolution. For low-valent sulfur (less than or equal to 4) FWHM is less than 1.0 eV, for high-valent (+5,+6) is between 1.6—2.0 eV; and (4) The speciation of sulfur was identified by the energy position of the Gaussian peak and the relative abundance of each sulfur was determined from the peak area. The peak position depends on sulfur functionality thereby allowing the assignment of different sulfur forms: -0.5 eV for pyritic, 0.7 eV for sulfidic, 1.3 eV for thiophenic, 3.4 eV for sulfoxide, 7.5 eV for sulfone, 9.9—10.1 eV for sulfate. The areas were corrected for the change in absorption cross section with increasing oxidation state. It is tested that the peak area is proportional to the absorption cross-section and the number of $3p$ vacancies and thus should increase as the oxidation state increases^[11], as illustrated in Fig. 2. The error for the estimation of the percentage of each sulfur group is 5%^[7].

3 Results and discussion

Figure 3 is the comparison of the normalized sulfur K-edge XANES spectra of these samples. The zero energy is placed on the white line peak in the spectrum of elemental sulfur (2472 eV). Two major absorption peaks are observed in the spectrum for raw coal: one in the 2471—2473 eV region, and the other in the 2480—2484 eV region. While in the XANES spectra for bottom ash, fly ash, and $PM_{2.5}$ samples, only a single white line peak at about 10 eV is observed. The sulfur XANES spectra were deconvoluted and fitted as discussed above to derive quantitative information. The typical fitted XANES spectrum of the coal is shown in Fig. 4. By comparing the relative energy shift with the standard samples and published experimental results^[7, 8, 13, 14], the species of sulfur were decided.

The spectrum of coal in Fig. 4 shows the presence of 5 Gaussian peaks. The first small peak starting on the left-hand side of Fig. 4 at -0.5 eV is from pyrite, the second peak at 0.7 eV is from sulfidic sulfur, and the third peak at 1.3 eV corresponds to thiophenic sulfur, while the peaks from oxidized sulfur species

come at approximately 8 eV (sulfone) and 10 eV (sulfate). The relative percentage of each sulfur species in coal was calculated as shown by the bar diagram in Fig. 5. About 70% of the sulfur in raw coal occurs as the organic (sum of sulfide, thiophene, and sulfone). A minor fraction of the sulfur occurs as inorganic forms: 17% of pyrite and 13% of sulfate.

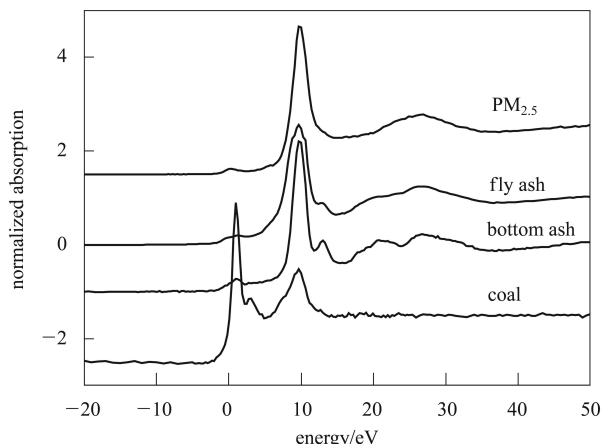


Fig. 3. Normalized K-edge XANES spectra for coal, bottom ash, fly ash, and $PM_{2.5}$.

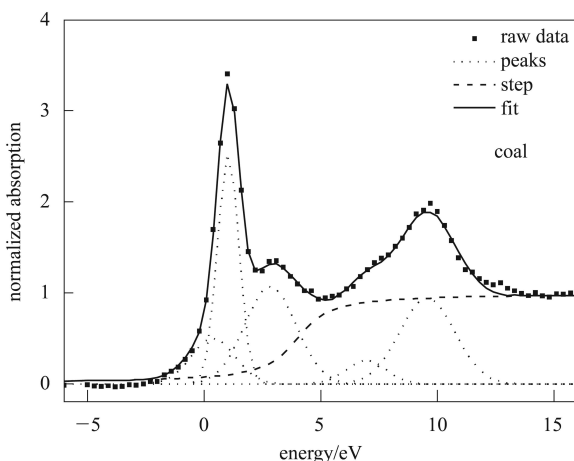


Fig. 4. Least square fits sulfur K-edge XANES spectra for coal.

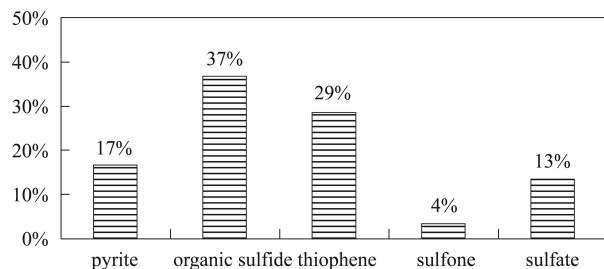


Fig. 5. Sulfur percentages derived from the XANES for coal. (total organic sulfur 70% = organic sulfide+thiophene+sulfone)

The contents of major sulfur oxidation groups in fly ash, bottom ash and $PM_{2.5}$ are summarized and

grouped into reduced sulfur (sum of pyritic, sulfide and thiophene), intermediate sulfur (sum of sulfoxide sulfur, sulfonic sulfur), and oxidized sulfur (sulfate). As shown in Fig. 6, sulfate is dominant in bottom ash, fly ash, and $PM_{2.5}$ with relative percentage of 80%, 79% and 94%, respectively. A minor reduced sulfur is also observed in these samples. This is associated with incomplete combustion or nonequilibrium conditions within the combustion system. In fly ash, 4% of sulfur exists as intermediate sulfur. Like the occurrence of reduced sulfur, the occurrence of intermediate sulfur may also reflect the unburned carbon.

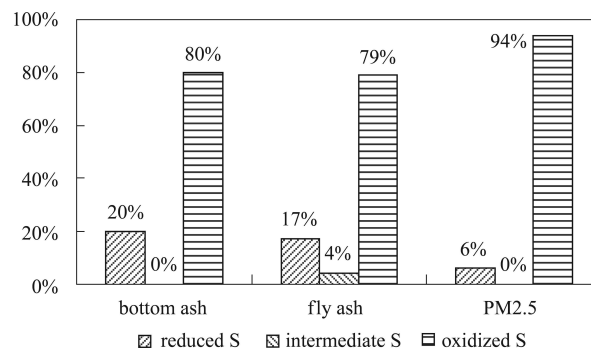
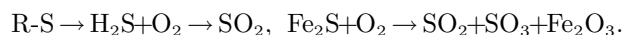


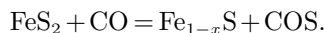
Fig. 6. Sulfur percentages derived from the XANES for bottom ash, fly ash, and $PM_{2.5}$.

The current XANES results are also in qualitative agreement with those reported earlier.^[15, 16] The forms of sulfur in China's coal are pyritic, organic, sulfate and elemental sulfur. Organic sulfur and pyritic mainly account for most of the sulfur in coal, followed by sulfate, elemental sulfur is only in trace^[17]. In the process of coal combustion, organic and pyrite sulfur in coal are combustible and participate in reactions, while sulfate is not combustible even at high temperature. Organic sulfur (R-S), pyrite sulfur can participate in the following reaction during combustion:



Most of them will become volatiles and form various sulfur oxide compounds releasing into the atmosphere as gaseous products and particulate mater, some will remain in particulates such as ash by reaction with alkali and alkaline earth compounds. Coal ashes are the residues of organic and inorganic substances left after coal combustion and its composition is dependent on the quality of coal and the condition of combustion. Under reductive atmosphere, pyritic sulfur could transform to elemental sulfur at elevated temperatures, which is thermodynamically favorable and has been reported in several studies^[18]. Reduction

of pyrite to pyrrhotite produces sulfur, which in turn reacts with H_2 and CO by the following reactions:



Thiophenic sulfur possesses good thermal stability with high decomposition temperature, Taghiei^[18] found that thiophenic sulfur remained nearly constant at temperature up to 450°C during pyrolysis. It is reported that oxidation of sulfide can result in synthesis of sulfone^[19]. Based on these facts, it can be concluded that the reduced sulfur in bottom ash, fly ash, and $PM_{2.5}$ may be elemental sulfur, pyrite, pyrrhotite and thiophenic sulfur, while intermediate sulfur in fly ash may be sulfone. They are byproducts of incomplete combustion due to poor condition with insufficient oxygen and low temperature in the boiler direct burning of raw coal.

The presence of pyrite, pyrrhotite and organic sulfur suggested that there is a fraction of iron and carbonaceous materials in bottom ash, fly ash, and $PM_{2.5}$. Recent toxicological studies have shown that iron is of significant concern to human health from inhalation of particles and it can catalyze the formation of free radicals that might lead to oxidative stress within the cardiovascular system. Pulmonary instillation studies showed that the severity of lung injury could be correlated with the carbon content of ash and the presence of transition metal (i.e. Fe) complexes would increase the toxicity by promoting reactive oxygen species, oxidation-reduction cycling, and oxidative stress^[20]. So ash and particles generated by incomplete combustion of coal which consist of metal

and unburned carbon have a significant health risk.

Because small boiler is difficult to operate continuously and has very poor air pollution control devices, it poses more serious pollution to the environment. It is reported that coal-burning boilers are the second great pollution source of air pollution by sulfur dioxide in China. It is necessary to take effective measures to control the pollution of coal-burning boiler including forbidding direct burning of raw coal, adopting clear fuels, eliminating small boilers, and applying clear combustion technologies.

4 Conclusions

To study the speciation of sulfur in feed coal, fly ash, bottom ash and airborne particles from a small coal-burning boiler, a direct spectroscopic method XANES was used. The principal results are summarized below. Most of the sulfur in raw coal occurs as the organic and a minor fraction of the sulfur exist as other forms. While in bottom ash, fly ash, and $PM_{2.5}$, the dominant form of sulfur is sulfate. A number of other reduced sulfur including thiophenic sulfur, element sulfur and pyrrhotite is present in bottom ash, fly ash, and $PM_{2.5}$. The reduced sulfur in combustion by-products is associated with incomplete combustion in the small boiler for poor condition with insufficient oxygen and low temperature. This shows that small boilers pose more serious pollution to the environment. Eliminating small-capacity boiler and prohibiting direct burning of raw coal and using clean processed products are needed to control SO_2 pollution.

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