Zn distribution and speciation in zinc-containing steelmaking wastes by synchrotron radiation induced μ-XRF and μ-XANES spectroscopy

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Abstract. Zinc is an important element in steelmaking industry not only for its impact on environment but also for its hazardous influence to steel production. Collecting information about the chemical association of zinc in zinc-containing steelmaking wastes is fundamental for monitoring its behavior during further treatment. In the work presented here, the spatial distribution, and chemical forms of zinc in accumulated particles of zinc-containing steelmaking wastes, including electric arc furnace dust (EAFD) and basic oxygen furnace OG sludge (BOF OG), have been investigated using synchrotron radiation induced μ-XRF and μ-XANES spectroscopy. Results of μ-XRF analysis showed that zinc distributed in two ways. One was shared with iron and its distribution showed a positive correlation with that of iron. The other was accumulated in some well-defined hot spots with high amount and its distribution showed negative correlation with that of iron. For EAFD, results of μ-XANES spectroscopy indicated that zinc was mainly present in the form of ZnFe₂O₄ within the whole particles no matter the spots with high or low zinc content. Whereas for BOF OG, ZnFe₂O₄ was the main constituent in well-defined hot spots while in other regions zinc was mainly in the form of zinc carbonate. These results indicated that chemical reaction between zinc and other components occurred during the formation of accumulated OG sludge particles. If the above findings could be confirmed by more systematic investigations, it will provide valuable information for treating and utilizing these metallurgical residues.

1. Introduction

In steelmaking industry, zinc is one of those elements which should be paid attention to in particular. This element is usually easy to volatilize during the metallurgical process due to its boiling point below the melting temperature in furnace and subsequently condenses and accumulates to form particles in the form of dust or sludge when passing through the gas-cleaning system. Therefore, a large amount of such kind of residues is generated. Generally these dust and sludge must be disposed of on a hazardous waste disposed
For this kind of metallurgical residues is often composed of fine particles, it is easy to be discharged into atmosphere and accumulated in soils during the transportation and landfill, which will cause risks on environments. On the other hand, landfill will bring high transportation and disposal cost. These costs could be reduced if metals, such as iron, zinc, and so on, can be recovered or sold. The most common way to utilize these dust and sludge is reusing them as a secondary source of raw material due to the high iron content. However, when they are reused inside enterprises, undesirable consequences will occur. In particular, the presence of zinc will damage the production equipment. Take blast furnace for example. When these dust and sludge are back recycled in blast furnace, zinc will accumulate on the walls, penetrate the lining, take part in the lining’s deformation and disintegration and subsequently damage the blast furnace.[1,2] To find an effective and safe method to handle and recycle such kind of steelmaking wastes, a thorough characterization of these particles is a very important step.

Theoretically, knowledge of spatial elemental distribution and speciation in the accumulated particles is necessary for developing new recycling strategies and providing information on potential problems that could be encountered during the processing of such steelmaking wastes. To get these information, synchrotron radiation induced μ-X-ray fluorescence and μ-X-ray absorption fine structure spectroscopy are employed here. The reason why these two techniques are used is that, in previous studies, the power of the combination of synchrotron radiation induced μ-XRF and μ-XANES spectroscopy as micro-analytical tools to investigate the spatial distribution and speciation of heavy metals in small regions of typically a few micrometers in size was demonstrated.[3,4,5] Thus in the present research, elemental maps are created by scanning the particle in a regular grid pattern by the X-ray micro-beam and detecting the induced fluorescence intensities at each position. Depending on these patterns of distribution, μ-XANES spectroscopy were used to determine directly the chemical forms of zinc in micro-sized areas where zinc in high or low content. It is a preliminary research with the purpose to find useful information which might lead to new innovations helpful to create better recycling strategy.

2. Samples and methodologies

2.1 Samples and sample preparing

Zinc-containing steelmaking wastes, including electric arc furnace dust (labeled EAFD) and basic oxygen furnace OG sludge (labeled BOF OG), analyzed in this study were collected from the gas-cleaning system of carbon steelmaking operation in China. In previous studies, chemical analysis showed that the main compositions contained in EAFD were: total Fe 38.0%; ZnO 20.4%; SiO2 4.1%; MgO 2.5%; CaO 8.3%; Al2O3 1.0%; MnO 3.0%; P2O5 0.4%. And the main compositions contained in BOF OG were: total Fe 54.1%; ZnO 3.4%; SiO2 1.2%; MgO 5.7%; CaO 12.7%; Al2O3 0.2%; MnO 0.7%; P2O5 0.2%. For μ-XRF and μ-XANES analysis, the samples were pressed in an organic resin by cold cure, grounded and polished with silicon carbide paper. During the experiments, the polished cross section was first detected by μ-XRF spectroscopy. And then the areas with different zinc content were analyzed to obtain the chemical information of zinc by means of μ-XANES spectroscopy.

2.2 Methods

Both μ-XRF and μ-XANES measurements were performed at beamline BL15U at Shanghai Synchrotron Radiation Facility (SSRF). SSRF is a third-generation synchrotron operating at a current of between 130
and 210 mA and energy of 3.5 GeV. Beamline BL15U at SSRF is an undulator beamline equipped with liquid-He-cooled Si(111) monochromator that has an energy resolution of 1.5 eV at 10 keV and Si(311) monochromator that has an energy resolution of 0.5 eV at 10 keV. The monochromatorized light was focused by K-B optics system. The sample stage consisted of multiple motor-stages: two for scanning the sample in horizontal and vertical directions and a third one in order to align the sample into the image plane of the focusing device. The minimal step size of the motor-stages was 20 nm.

During the measurements, the intensity of the incoming X-ray was monitored by an ionization chamber, which was used for normalizing the measured X-ray intensity of the sample. For both EAFD and BOF OG, the characteristic X-ray fluorescence of elements contained in particle 1 and 2 were detected by 7-element Si(Li) detector. And the spot size at the sample location were 2×2 μm² (H×V). Both the detectors were placed at 90° to the incoming X-ray in order to decrease the intensity of the Compton scattering. All the μ-XRF experiments were performed by using monochromatic radiation at an exciting energy of 10 keV.

Zn K-edge μ-XANES experiments were performed on pure Zn compounds and zinc-containing steelmaking wastes particles as well. The reference compounds used here (Zn, ZnO, ZnFe₂O₄, ZnS, Zn₅(OH)₆(CO₃)₂, ZnSiO₃) were chosen due to their possibility to be present in EAFD and BOF OG sludge. Each reference material was bought from chemical agents in China. And before measurements, each pure compound were mixed with LiF and pressed to form pellets. The reference XANES spectra were recoded in transmission mode. Due to the small dimensions of zinc-containing steelmaking wastes particles, their XANES spectra were recorded in fluorescence mode with the detector of 7-element Si(Li) detector. All the μ-XANES spectra were obtained at room temperature by scanning the energy in the 9610-9740 eV range in 0.5 eV steps with dwelling time of 1s. XANES spectra were analyzed with the aid of WinXAS software. Background was subtracted with Victoreen mode and then normalized in the range of 9680-9730 eV. After that, the normalized XANES spectra could be compared with the XANES spectra of reference materials.

3. Results and discussion

3.1 Zn reference compounds

Zn K-edge μ-XANES spectra of pure Zn compounds, including Zn foil, ZnO, ZnFe₂O₄, ZnS, ZnSiO₃, Zn₅(OH)₆(CO₃)₂ were measured prior to the particle analysis. And normalized XANES spectra were reported in Figure 1. As shown in Fig. 1, each reference material has its characteristics in the absorption area. In brief, for the zinc metal, the white line peak was at around 9669 eV. The XANES spectrum of ZnFe₂O₄ showed three resolved peaks at around 9665, 9669, 9673 eV respectively and an additional structure at around 9686.7 eV. For ZnS, the white line peak was at around 9665 eV with the shoulder at around 9662 eV and the additional structure at around 9669 eV. The XANES features of ZnO were the white line peak at around 9669 eV, a shoulder at around 9663 eV, and the additional structure at around 9679 eV. As for Zn₅(CO₃)₂(OH)₆, the white line peak was at around 9667 eV with shoulders at around 9665 eV and 9672 eV and the additional structure at around 9684 eV. While Zn K-edge XANES spectrum of ZnSiO₃ had two resolved peaks at around 9665 and 9668 eV. Depending on these characteristics, chemical form of Zn distributed in different regions can be investigated.
3.2 Electric arc furnace dust (EAFD)

Two particles of EAFD were detected by means of μ-XRF and μ-XANES spectroscopy. Figure 2 showed the distribution of elements (Ca, Fe, Mn and Zn) and Zn K-edge XANES spectra taken at interested spots for particle 1 of EAFD (EAFD 1). Here zinc was accumulated in some well-defined hot spots where with high amount and its distribution showed negative correlation with that of iron. And spot A, B, C, D, and E

![Fig. 1. Zn K-edge XANES spectra of the measured Zn reference compounds](image1.png)

![Fig. 2. (Colour online) The distribution of elements (Ca, Fe, Mn and Zn) and Zn K-edge XANES spectra taken at interested spots for particle 1 of EAFD (EAFD 1).](image2.png)
corresponded to the interested spots where zinc content decreasing from high to low. As it can be seen in Figure 2, all the XANES spectra were similar. Comparison with the XANES spectra of Zn pure compounds, it could found that zinc ferrite (ZnFe$_2$O$_4$) was present as the main constitutes in these analyzed spots within the cross section of EAFD 1.

Figure 3 showed the result of particle 2 of EAFD (EAFD 2). In this case, zinc was shared with iron and its distribution showed a positive correlation with that of iron. Spot A and B corresponded to the interested spots where zinc content were high and low respectively. The XANES spectra of these spots showed the similar results with that of EAFD 1. And zinc ferrite (ZnFe$_2$O$_4$) was also considered as the main constitute in the analyzed spots within the cross section of EAFD 2.

Fig.3. (Colour online) The distribution of elements (Ca, Fe, Mn and Zn) and Zn K-edge XANES spectra taken at interested spots for particle 2 of EAFD (EAFD 2).

3.3 Basic oxygen furnace OG sludge (BOF OG)

There were also two particles of BOF OG which were detected by means of μ-XRF and μ-XANES spectroscopy. Figure 4 showed the distribution of elements (Ca, Fe, Mn and Zn) and Zn K-edge XANES spectra taken at interested spots for particle 1 of BOF OG (BOF OG 1). Here zinc was accumulated in some well-defined hot spots where with high amount. And spot A, B, C, D corresponded to interested spots where with high zinc content, low iron content, low zinc content and high calcium content showed in the distribution maps of Zn, respectively. As it can be seen in Fig. 4, these XANES spectra showed similar features, that were the white line peak at around 9668 eV, shoulders at around 9665 eV and 9671 eV, and an additional structure at around 9685 eV. Comparison with the XANES spectra of zinc pure compounds, the similarity with that of Zn$_5$(CO$_3$)$_6$(OH)$_2$ could be observed, especially for spot D. This finding indicated that zinc carbonate was present as the main constitutes in these analyzed spots within the cross section of BOF OG 1.
On the contrary, for particle 2 of BOF OG (BOF OG 2), Zn K-edge XANES spectra showed obvious variations from high Zn content to low Zn content as in Fig. 5. In this case, zinc was also accumulated in some well-defined hot spots with high amount. Spot A were selected for its highest zinc content. And Zn content decreased from high to low as from spot B to spot D. Among these spots, the XANES spectra of spot A showed the triplet structure between 9665 and 9675 eV (see peak a, b, c in Fig. 5). Results obtained by the comparison with these Zn K-edge XANES spectra of Zn pure compounds indicated the significant component of ZnFe$_2$O$_4$. While in case of spot D, the XANES spectra showed the similar characteristics with that of Zn$_6$(CO$_3$)$_6$(OH)$_2$ which also suggested the significant presence of zinc carbonate as in case of BOF OG 1. And the XANES features of spot B showed the combination of zinc carbonate and ZnFe$_2$O$_4$ to some extent. For further understand this variation, spot E, which was next to spot A, was chose. And its XANES spectra also showed the combination of ZnFe$_2$O$_4$ and zinc carbonate.
The variation of zinc species contained in regions with different zinc content indicated that chemical reactions between zinc species and other components occurred during the formation of BOF OG 2. For ZnFe$_2$O$_4$, it is one of the most common phases that can be found in zinc-containing steelmaking wastes,[6,7] such as electric arc furnace dust, basic oxygen furnace dust, and so on. In general, ZnFe$_2$O$_4$ has a normal spinel structure which forms at high temperature and in oxidizing conditions. Such spinel structure is very stable and difficult to be destroyed.[8,9] On the contrary, Zn carbonate was a type of very soluble phase. It was seldom mentioned in previous studies.[10] These information pointed out the possibility to separate the fine particles with different zinc species by controlling the relative manufacturing parameters at high temperature. However, how these two phases formed and present together during the formation of BOF OG sludge is difficult to give a clear explanation only by results obtained here. A thorough study is needed in the future.

4. Conclusions
To summarize, μ-XRF analysis showed that zinc distributed in two ways. One was shared with iron and its distribution showed a positive correlation with that of iron. The other was accumulated in some well-defined hot spots with high amount and its distribution showed negative correlation with that of iron. For EAFD, results of μ-XANES spectroscopy indicated that zinc was mainly present in the form of ZnFe$_2$O$_4$ within the whole particles no matter the spots with high or low zinc content. Whereas for BOF OG, ZnFe$_2$O$_4$ was the main constituent in well-defined hot spots while in other regions zinc was mainly in the form of zinc carbonate.

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