

On the distribution and bonding environment of Zn and Fe in glasses containing electric arc furnace dust: A μ -XAFS and μ -XRF study

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Abstract

We apply synchrotron radiation assisted X-ray fluorescence (SR-XRF), SR-XRF mapping as well as micro- and conventional X-ray absorption fine structure (μ -XAFS and XAFS) spectroscopies in order to study the bonding environment of Fe and Zn in vitrified samples that contain electric arc furnace dust from metal processing industries. The samples are studied in the as-cast state as well as after annealing at 900 °C. The SR-XRF results demonstrate that annealing does not induce any significant changes in the distribution of either Fe or Zn, in both the as-cast and annealed glasses. The μ -XAFS spectra recorded at the Fe-K and Zn-K edges reveal that the structural role of both Fe and Zn remains unaffected by the annealing procedure. More specifically, Fe forms both FeO₆ and FeO₄ polyhedra, i.e. acts as an intermediate oxide while Zn occupies tetrahedral sites.

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1. Introduction

Electric arc furnace dust (EAFD) is one of the largest solid waste streams produced by steel mills, and is classified as a waste under the Resource Conservation and Recovery Act (RCRA) of the U.S. Environmental Protection Agency (EPA). Steel production by electric-arc furnace (EAF) technology has been of increasing importance over the past 20 years, and it is expected that, in the coming years, it will dominate the steel production. During the EAF production of steel, about 15–20 kg of dust is formed per tonne of steel. This dust contains heavy metals and thus is considered as a toxic waste. These metals are found both as free oxides (e.g. PbO, ZnO) as well as in the form of composite structures with iron oxides (e.g. ZnFe₂O₄). More specifically, EAF dusts contain iron, zinc, calcium and silicon in the form of simple or mixed oxides, as well as copper, manganese, chromium, cadmium and lead which either originate from the scrap iron raw material or are introduced as additives

[1,2]. Successful recycling of the valuable metals (iron, zinc and lead) reduces the disposal problems and results in resource conservation. Hydrometallurgical or pyrometallurgical processes can recover only a part of heavy metals (such as Zn) from the EAFD [2,3] and hence it is of major importance to develop an additional process that stabilizes metallic Zn and the other heavy metals found in the residues of Zn recovery processes. One of the promising methods for safe disposal of the EAF dust is vitrification [4,5] that leads to the production of chemically stable materials, vitreous or glass-ceramic, that can be safely disposed or used for construction and decorative applications [6,7].

The aim of this work is to determine the distribution, the bonding environment and the oxidation state of Fe and Zn ions in the glass matrix of vitrified EAFD-rich industrial wastes. It is known that the structural role of Fe depends on its valence state [8,9]: Fe²⁺ acts as a glass modifier and participates in the formation of FeO₆ polyhedra while Fe³⁺ is an intermediate oxide, i.e. can also act as a glass network former by constituting FeO₄. On the contrary, in such oxide materials Zn is known to be stable only in its 2+ oxidation state and can occupy tetrahedral sites [10]. Therefore it is quite important to study the structural role of both Fe and Zn oxides, since the structural integrity of the glass

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matrix depends strongly on the type of polyhedra that the Fe and Zn ions form. It should be pointed out that the glass forming role of Fe depends also on the waste content [11]. Furthermore, heating at temperatures above the glass transition temperature can induce devitrification [12–14]. More specifically, annealing induced modifications in the bonding environment of Fe were previously reported in a series of Pb- and Fe-rich waste contaminated glasses [12].

In this paper we present the characterization of Fe- and Zn-rich solidified-stabilized EAFD glasses in the as-cast state as well after annealing by means of synchrotron assisted X-ray fluorescence (SR-XRF) mapping and X-ray absorption fine structure (XAFS) measurements at the Fe-K and Zn-K edges. SR-XRF mapping is a non-destructive characterization technique that permits the two-dimensional imaging of the distribution of different elements in an inhomogeneous sample with ppm detectability. The use of capillary optics reduces the beam size (in our set-up to 5 μm) and thus improves the spatial resolution. The XAFS spectrum, which shows the dependence of the X-ray absorption coefficient on the impinging photon's energy above the absorption edge of a specific element, consists of two regions: the extended X-ray absorption fine structure (EXAFS) region and near-edge extended X-ray absorption fine structure (NEXAFS) region. The former reflects the bonding environment (as that is determined by the nearest neighbour distances and coordination numbers) of the absorbing atom. The latter reflects the density of empty states of the absorbing atom and it is affected by the symmetry, the local coordination geometry and the valence of the absorbing atom, which can be derived by proper analysis of the NEXAFS spectra. Local changes in the bonding environment around Fe and Zn can be identified and mapped over selected areas of the sample using micro-XAFS (μ -XAFS).

2. Sample preparation and experimental details

The samples under study are vitrified products of EAF dust which mainly consists of zinc (34.9 wt.% ZnO) and ferric oxides (in the form of ZnFe_2O_4 at 33.9 wt.%). The elemental composition and the structural analysis of the EAF dust were performed using energy-dispersive X-ray spectrometry (EDS) and X-ray diffraction (XRD), respectively [15]. The loss on ignition (LOI) mass, as determined with EDS after the EAFD powder was heated to 1000 $^\circ\text{C}$, amounts to 7.2 wt.% [15]. The two main constitutive oxides of EAFD are zinc ferrite (ZnFe_2O_4) and zinc oxide (ZnO), while traces of MgO, Al_2O_3 , SiO_2 , K_2O , CaO, MnO and PbO were also identified. The composition of the as-cast glass was determined by EDS analysis which revealed that the weight percentage of Fe, Zn, Ca, Na and Si is approximately 8.2, 6.7, 31.1, 12.6 and 50.0 wt.%, respectively. Details on the composition of the EAFD powder and the as-cast product are listed in Table 1.

The vitrification process involves mixing of the EAF dust with SiO_2 , Na_2CO_3 and CaCO_3 powders and co-melting at 1400 $^\circ\text{C}$ for 2 h in a Pt-crucible, followed by quenching in air [11–15]. The sample under study consists of 20 wt.% EAFD, 55 wt.% SiO_2 , 15 wt.% CaO and 10 wt.% Na_2O . After quenching the sample was heated at a temperature 20 $^\circ\text{C}$ above the glass

Table 1
Composition of EAFD powder and as-cast product as determined by EDS

EAFD powder		As-cast product	
Compound	wt.% ($\pm 1\%$)	Element	wt.% ($\pm 1\%$)
MgO	0.7	Si	50.0
Al_2O_3	0.9	Ca	21.1
SiO_2	4.1	Mn	1.4
K_2O	1.4	Fe	8.2
CaO	4.6	Zn	6.7
MnO	3.3	Na	12.6
Fe_2O_3	33.9		
ZnO	34.9		
PbO	6.2		
LOI	7.2		
Humidity	2.0		

transition temperature ($T_g = 583.8^\circ\text{C}$) for residual stress relaxation. Next, the sample was subjected to a two-stage isothermal treatment process (annealing). In the first stage (20 min at 680 $^\circ\text{C}$), nucleation of wollastonite CaSiO_3 takes place and in the second (30 min at 900 $^\circ\text{C}$) crystal growth occurs [15]. The temperatures for the annealing process were determined from the differential thermal analysis results reported previously [15]. Recently reported transmission electron microscopy (TEM) observations and XRD analysis showed that the initial product was amorphous while EDS analysis revealed that all elements were homogeneously dispersed into the vitreous matrix [15]. Furthermore, upon annealing surface crystallization of wollastonite (CaSiO_3) initiates from the edges towards the center [15].

The XRF, XAFS and μ -XAFS measurements were conducted at the KMC2 beamline at the synchrotron radiation (SR) facility BESSY in Berlin. The beamline is equipped with a double-crystal monochromator and capillary optics that reduce the beam diameter to 5 μm . The XRF spectra were recorded with acquisition time 400 s. The XRF maps were recorded using excitation photons of 9600 eV, i.e. higher than the Fe-K and Zn-K absorption edges and acquisition time 1 s/point. The angle of incidence of the SR beam was 45 $^\circ$ and the energy dispersive (Röntec) fluorescence detector was positioned normal to the beam. The Fe-K and Zn-K edge fluorescence photons emitted from the sample were discriminated by setting electronically the energy range of interest from 6097 to 7181 eV and 8037–9092 eV, respectively. The μ -XAFS spectra (beam diameter 5 μm) were recorded at the Fe-K and Zn-K edges, in the fluorescence yield mode, at two spots: one at the edge (position E) and the other at the centre (position C) of the annealed sample. Measurement at two spots was decided because, according to previous reports [15], the crystallization of wollastonite starts at the edges and progresses towards the centre of the sample. Therefore local inhomogeneities might occur across the sample surface. The spectrum of the Fe_2O_3 reference sample was recorded in the transmission mode using ionization chambers. The conventional EXAFS spectra (capillary removed, beam size 200 $\mu\text{m} \times 800 \mu\text{m}$) for the as-cast and annealed samples were recorded at the Fe-K and Zn-K edges in the fluorescence yield mode using a Si-PIN pho-

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