## On the role of Zn/Fe ratio on the mineralogy of Electric Arc Furnace Dust for optimization of Zn recovery

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Electric Arc Furnace Dust (EAFD) is the solid residue abated by the fume capture systems produced during melting and bath refining at the electric arc furnace, yielding 10-20 kg per ton of steel produced (De Buzin, Heck and Vilela, 2017). Although EAFD treatment through carbothermic reduction in a rotary kiln for Zn extraction began more than fifty years ago (Hoffmann, 1928; Rütten, 2006), the continuous variations of scrap quality and mix (scrap/DRI ratio) in the electric furnace have resulted in a gradual decay in the efficiency of the Zn extraction process (Alizadeh and Momeni, 2016). Moreover, an increase in the concentrations of other essential metals such as Cr, Cu, and Pb present in these residues has been observed. Consequently, in the last 5 years, interest has been rekindled in the development of more efficient treatments of such powders in order to maximize the extraction of all valuable elements. Currently, the plants reprocessing EAFD for Zn recovery adopt as unique characterization method the measurement of chemical composition through X-Ray Fluorescence (XRF) due to its fast implementation, sample preparation and response time. The operative parameters of rotary kilns are hence based on the concentration of Zn in the dust. However, due to the variation in dust quality, although high available Zn concentration, the recovery yield highly oscillates, apparently without any correlation with the initial Zn content. Such a behaviour can be explained by the mineralogy of the dust, since Zn can be either be present as pure zincite (ZnO) or in a spinel-like phase (ZnFe<sub>2</sub>O<sub>4</sub>). Among the two compounds, zincite is the favourable one due to high reducibility at medium temperature (900-1000°C) while the spinel is not well accepted due to poorer reducibility and intrinsic lower yield. In particular, reduction of spinel, especially if it is in form of franklinite, requires a two step reduction, with the iron oxide that consumes more carbon and reacts first than zincite (He et al., 2022; Qiu et al., 2023; Hou et al., 2024). Thus, it is necessary to improve the knowledge of input dust through a detailed characterization that include other analytical methods, like X-Ray Diffraction (XRD).

In this work more than fifty different EAFD collected all around Europe were investigated through XRF and XRD in order to determine an empirical relationship between the ratio of elemental Zn/Fe and zincite/spinel. Zn, Fe and other major elements concentration were determined by means of a S8 Tiger Bruker Wavelength Dispersive XRF (WD-XRF) spectrometer. Samples were calcined at 850 °C prior to analysis, in compliance to EN ISO 12677:2011. Mineralogy was determined by means of XRD by means of Rigaku SmartLab SE diffractometer in  $\theta$ - $\theta$  configuration (Cu-K $\alpha$  radiation:  $\lambda$  = 1.54 Å at 40 kV. 40 mA) to evaluate the mineralogy of the samples. The analysis was accomplished with a scan range of 5-90° 2 $\theta$  through a 1D D/teX Ultra 250 detector featured by XRF suppression filter; the powdered materials were scanned at 0.5°/min with a step size of 0.01° and rotated at 60 rpm. Due to the specific lack of standards for mineralogical analyses by XRD, mineralogical analysis is based on the Crystallographic Open Database (COD). Rietveld method was followed to quantify the mass fraction of each crystalline compound within the dust.

The results show that Zn and Fe are the main elements of the dust, as expected by literature, accounting for more than 60 wt.% with an average ratio of 1:1, followed by calcium and other alkaline oxides (**Figure 1**).

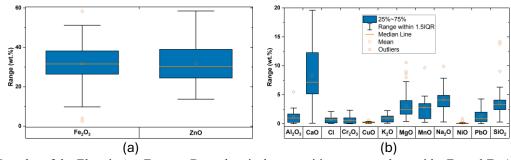
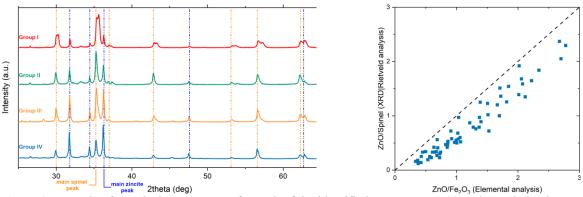


Figure 1 Boxplot of the Electric Arc Furnace Dust chemical composition expressed as oxide: Fe and Zn (a) and other major elements (b)

Then, the dust can be classified in four different groups according to their mineralogy based on the relative intensity of the main diffraction peak of zincite and spinel with a progressive increase of zincite/spinel ratio from Group I to Group IV (Figure 2a).



**Figure 2** Example of a typical XRD pattern for each of the identified EAFD group (a) and correlation between Zn/Fe and zincite/spinel ratios (b)

Finally. a linear correlation between Zn/Fe and zincite/spinel ratios is identified and by increasing the Zn/Fe ratio the proportion of zincite on spinel increases, too (**Figure 2**b). Such a correlation is of a practical relevance regarding the correct setup of the reduction process in the rotary kiln since it allows to predict the easily recoverable Zn from ZnO without increasing the amount of carbon and temperature to reduce also the Zn-bearing spinel. Indeed, when high spinel-containing dust are charged, the kiln would require a higher energy to fulfil the reduction but this led to the simultaneous reduction, carburization and melting of iron and the formation of ring crusts that self-catalyses this detrimental phenomenon (Min *et al.*, 2024).

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