

Microscopic Analysis of Iron and Steel Slag Used as a Source of Cationic Precipitation Agents in Water Treatment

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Abstract: Iron and steel slag represent a high-volume solid waste material from heavy industry. Despite several applications in the construction industry, most slag is still deposited in landfills, where it represents an increasing environmental nuisance. Over the last decade, it has been shown that many slags can be used for environmental remediation, particularly in the treatment of contaminated water resources, where the waste product can substitute for expensive high-speciality reagents. This is important in reducing the cost of water treatment. Most authors describe the action of the slag as adsorption; recently, strong evidence has been presented that they act as a source of ions, which promote precipitation. Considering the complex composition and mineralogy of slags and large variety of slags produced in the iron and steel industry, precise identification of candidate materials for specific applications is a challenge. This brief paper will summarise some applications and show how optical and electron microscopy serve as a tool to identify active components in the product and help elucidating the contaminant removal mechanisms.

1 INTRODUCTION

Slags are a by-product of extractive metallurgy and originate from the molten mixture of gang materials, fluxes and additives used to control the composition of the melt and purity of the metal. Depending on cooling velocity, slags will form aggregates or powders, with amorphous to fine-crystalline structures. Each metallurgical process will produce its own specific type of slag. In iron and steel industry, the most important sources of slag are the blast furnace (BF) process, the basic oxygen furnace (BOF), electric arc furnace (EAF) and electric induction furnace (EIF).

The high CaO content of BOF slag makes it a valuable resource as a substitute for Portland cement and increases the resistance of concrete in aggressive environments. Precise control of cooling speed and granulometry is required to achieve these results (Kourounis et al., 2007; Piatak et al., 2015). Other slags present less useful properties but can be used as an aggregate in cement and concrete (Maslehuddin et al., 2003; Qasrawi et al., 2009; Abu-Eishah et al.,

2012). As these uses are economically less attractive, such products are often disposed of in landfills.

More recently, the use of slag as a resource for environmental applications has attracted attention. The use of BOF-slag for the elimination of phosphorus from agro-industrial wastewater and wetland remediation was reviewed by (Vohla et al., 2011; Chazarenc et al., 2008; Barca et al., 2012). A review on the use of slag in water treatment was provided by (Mercado-Borrayo et al., 2018 a).

In earlier work, the authors have analysed the removal of As (III) and (V) with BOF slag (Schouwenaars et al., 2017), the removal of As and B by EAF slag (Mercado-Borrayo et al., 2018b) and the removal of heavy metals by EIF slag (Mercado-Borrayo et al., 2018c). These papers show that very high removal efficiencies can be achieved through process optimisation. It is often assumed that removal occurs by adsorption. However, the literature provides clear indications that selective leaching of cations from the slag and re-precipitation with the contaminant ions or formation of silicates (Dimitrova and Mehanjiev, 2000) is responsible for contaminant removal, as exemplified in Figure 1.

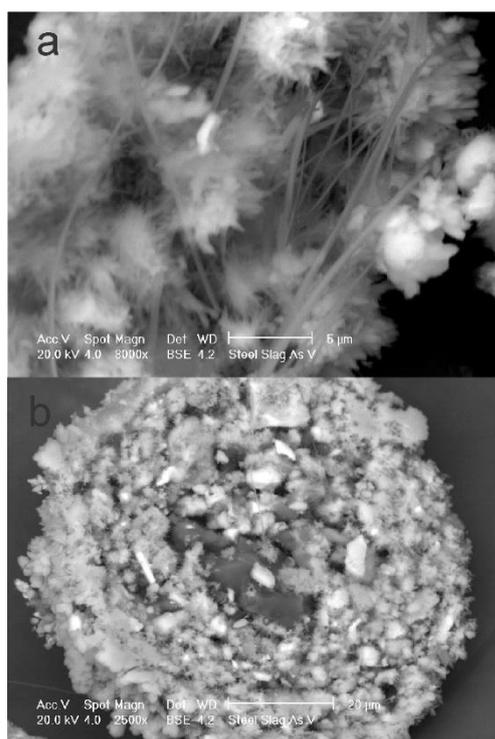


Figure 1: Precipitates formed during treatment of water contaminated with As (V). a) supernatant formed during the process. b) precipitation on a slag particle. The experimental conditions are described by (Schouwenaars et al., 2017).

Generally, the study of a removal process consists of the determination of reaction isotherms and/or kinetics, combined with the characterisation of the slag by XRD, XRF and SEM. XRF only provides an approximate quantification of the main elements in the product. XRD allows for the determination of crystalline species but cannot detect minority components or amorphous phases and is semi-quantitative at best. The benefits and limitations of SEM, are summarised in the standard work by (Goldstein et al., 2017). High spatial resolution can be achieved in combination with localised chemical analysis by EDX. However, the latter is only semi-quantitative and spatial resolution is limited by the electron beam-sample interaction volume, which is often larger than the size of the individual phases in a slag material. Specific surface area is determined by means of physical adsorption of N_2 . A broad spectrum of characterisation methods was used by (Mercado-Borrayo et al., 2013). The present work will not explore new applications for slag in water treatment but will explore petrographic microscopy (Nesse, 2009) as an additional tool for slag characterisation.

2 EXPERIMENTS

Thin slices (300 μm) of slag were observed using polarised light optical microscopy (OM) in reflection and transmission with a Zeiss Axiolmager POL. Results are presented for an EAF and a BOF slag, which were described in earlier publications (Schouwenaars et al., 2017, Mercado Borrayo et al., 2013, Mercado-Borrayo et al., 2018b).

XRD measurements were performed on an Empyrean X-ray diffractometer with a Ni filter and fine focus tube using $\text{Cu K}\alpha$ radiation at a step of $0.05^\circ/\text{min}$ in a 2θ -range of 20 to 90° . Crystalline phases were identified using the Powder Diffraction File and the Rietveld method with Fullprof 2000.

3 RESULTS AND DISCUSSION

Table 1 presents the mineral composition, as determined by XRD, is given in Table 1 for the BOF and in Table 2 for the EAF.

Table 1: Mineral composition of BOF slag (XRD).

Mineral name	composition	Wt. %
Brucite	$\text{Mg}(\text{OH})_2$	38.1
Portlandite	$\text{Ca}(\text{OH})_2$	29.9
Ca-Fe oxide	CaFe_2O_4	12.9
	$\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$	12.5
Hydrated Larnite	$\text{Ca}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$	6.6

Table 2: Mineral composition of EAF slag (XRD).

Mineral name	composition	Wt. %
Wüstite	FeO	54.9
Brucite	$\text{Mg}(\text{OH})_2$	31.3
Merwinite	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$	9.2
Ghelenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	4.7

Figure 2 is a low-magnification image of the BOF slag. Using reflected light, two types of globular inclusions are seen. Silicate phases are transparent and appear dark; reflecting particles are probably CaFe_2O_4 , which has a cubic (optically isotropic) spinel structure. In transmitted light, needle-like structures predominate. The elongated twinned needles are brucite (Figure 2a). The darker zones in Figure 2b correspond to portlandite, shown in detail in Figure 3b.

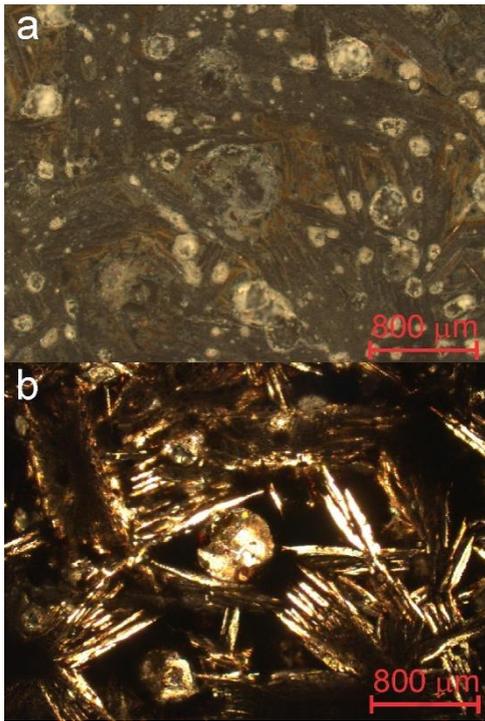


Figure 2: Low-magnification images of BOF-slag. a) is the reflected light image, b) corresponds to transmitted light, both under crossed polarisers.

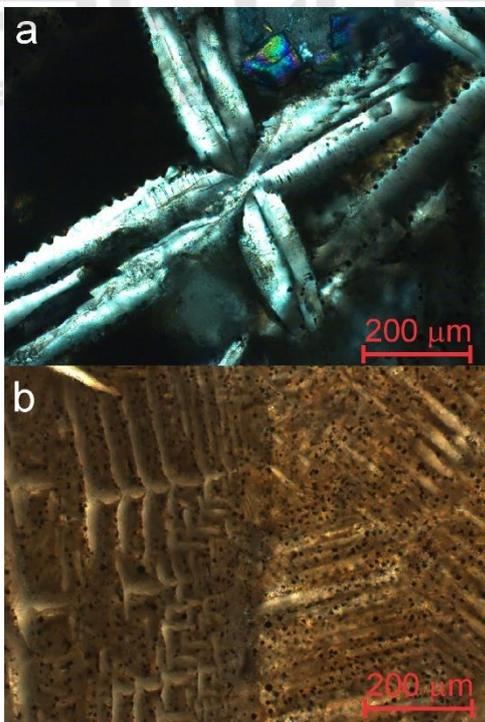


Figure 3: Detailed images of the main minerals in the BOF-slag. a) represents brucite, b) is portlandite (transmitted light, crossed polarisers).

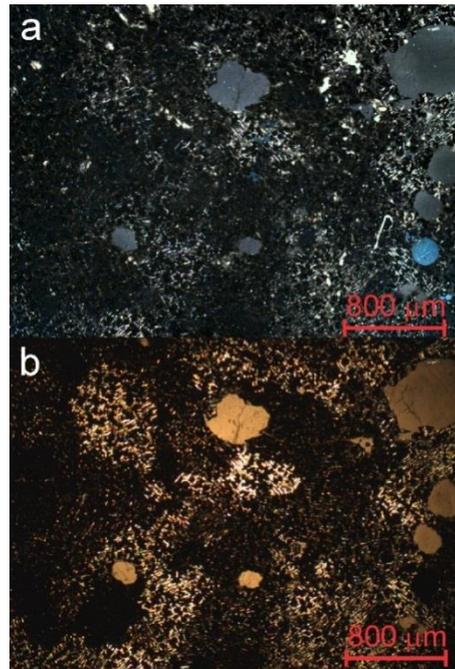


Figure 4: Low-magnification images of EAF-slag. a) is the reflected light image, b) corresponds to transmitted light, both under crossed polarisers.

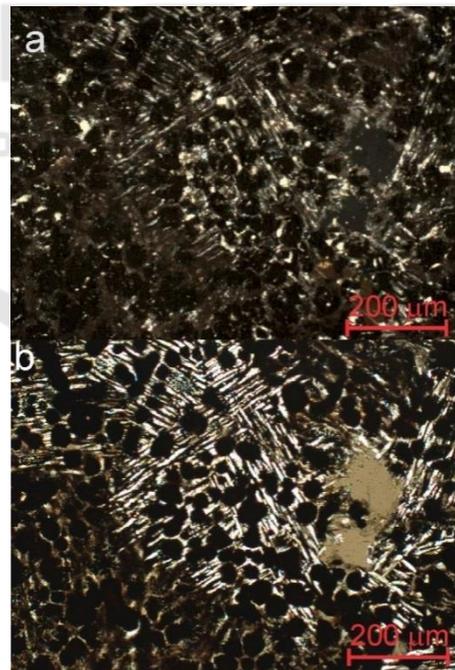


Figure 5: Details of the EAF-slag. a) is the reflected light image. b) transmitted light, brucite shows up bright. Both under crossed polarisers.

Figure 4 shows the microstructure of the EAF-slag. Some strongly reflecting, highly

anisotropic grains which were not detected by XRF are probably sulphides. Spherical particles which appear dark in both transmitted and reflected light correspond to wüstite. Brucite forms the fine eutectic structure, probably with wüstite needles.

Structures like the ones in Figure 3b and 5 are too fine to be analysed correctly by EDX in SEM. Also, different phases will only show grey tone contrast in SEM. XRD cannot detect phases which are present in small amounts, nor amorphous components, which are readily identified in OM. As EDX cannot quantify oxygen, discrimination between different metal oxides and hydroxides is often not possible, while it is fairly straightforward in a petrographic microscope.

For the present materials, the limited resolution of OM poses no problem. One drawback is that most reference works on OM refer to geological materials. Reference to man-made waste materials is not available. Additional SEM/EDX analysis of the thin slices may help to solve this limitation in future work.

4 CONCLUSIONS

Selection of slag materials for specific applications of environmental engineering requires the identification of potentially active components. Petrographic microscopy is a classical tool used by geologists to elucidate the mineralogical composition of rocks but is rarely used outside this speciality and has been partially substituted by SEM. Here it was shown that it provides valuable details on the microstructure and phase distribution in slags, especially when combined with SEM, EDX and XRD. The technique has proven particularly useful in the analysis of the oxides and hydroxides of Fe, Mg and Ca, which play a fundamental role in contaminant removal.

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