



Characterization of industrial secondary desulphurization slag by chemical fractionation with supportive X-ray diffraction and scanning electron microscopy



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ABSTRACT

Secondary desulphurization slag from integrated carbon steelmaking was investigated to attain information on respective utilization possibilities or effects upon final disposal. Pseudo-total element concentrations were determined during a six-week sampling period with EN 12457-2/12457-3 compliance test recoveries, scanning electron microscopy + X-ray microanalysis (SEM-EDS) and trace element fractionation with supportive X-ray diffraction (XRD) of parallel extraction residues. Only trace elements Cr and V showed significant pseudo-total recoveries with 210 and 1270 mg kg⁻¹ (d.w.), respectively. 88% of the respective Cr was attained in the residual fraction of the extraction procedure, as a labile H₂O-extractable Cr(VI) concentration of 1.6 mg kg⁻¹ (d.w.) was attained during the EN 12457-2 test. The RSD value of Cr (32%) in the determined pseudo-total contents of weekly subsamples indicated that fluctuation in slag composition can have a significant effect on the trace element contents of the material. In the case of V, 28% (353 mg kg⁻¹, d.w.) of the respective pseudo-total concentration was recovered in the NH₂OH-HCl-extractable fraction, in which XRD suggested only the potential dissolution of larnite. A majority of V (i.e., 65%) was recovered in the residual fraction coupled with the potential dissolution of magnetite and merwinite, as recovery in the HOAc-extractable fraction remained below the limit of quantitation. Additional SEM-EDS investigations proved unsuccessful in exclusively identifying potential V association in the slag samples due to overlapping with additional peaks.

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1. Introduction

Integrated carbon steelmaking from virgin ore, conventionally managed through the blast furnace (BF)/basic oxygen furnace (BOF)-process route (Cottrell, 1975), generates a variety of non-metallic residues due to the removal of raw material gangue and the molten impurities of iron or steel (Dippenaar, 2005). To remove material impurities from liquid metal, lime is generally used as a fluxing agent to generate a separate residual slag phase which can be effectively decoupled from the desired product. Alkalies, such as Na or K, S, P, or trace elements, such as As, Cu, Cr, Ni, Pb, V or Zn, can have undesired effects on the operation of the BF or the quality of carbon steel. In addition to primary BF or BOF slags, secondary slag residues are generated during the intermediate desulphurization of crude iron prior to converting into steel in the BOF

and during secondary metallurgy when the quality of liquid steel is finalized in a ladle before casting (Posch et al., 2002).

Compared to primary BF and BOF slags which are generated ca. 230 and 70 kg per metric ton of steel produced, respectively, the production volumes of secondary desulphurization and steel ladle slags are significantly lower, in the range of 20–30 kg per metric ton of steel produced (Eloneva et al., 2008; Manso et al., 2005). In general, the main oxidic components of steel industry slags are CaO, SiO₂, Al₂O₃, MgO and FeO, as the respective properties and mineral compositions of solidified slags are largely dependent of the exact chemical composition of the molten phase and subsequent cooling conditions (Adolfsson et al., 2011; Lampris et al., 2008; Shi, 2004). Prior to further utilization or disposal, the slags are generally processed for metal-removal and crushed to a size of ≤25–250 mm (Proctor et al., 2000). The final utilization rates of primary BF slags in, e.g., cement, construction or fertilization applications are generally higher than those of BOF slags (Dippenaar, 2005; Proctor et al., 2000). Secondary desulphurization and steel ladle slags however lack commercial applications and, in Finland, are respectively disposed of in private industrial landfills.

As industrial residue utilization or disposal involves materials which have been willingly removed from a unit process to minimize the effect

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of so-called non-process elements to the properties of the main product or stability of production, the respective potential environmental impacts should be investigated in detail. Single extractions can be used for estimating available element fractions through desorption and possible dissolution of easily soluble solid phases (Cappuyns and Swennen, 2008; Rigo et al., 2009) or in support of risk assessment concerning residue utilization or disposal (Fällman, 2000; Krüger et al., 2012; van der Sloot and Kosson, 2012). Sequential extractions can provide information for a more comprehensive evaluation of the effect of varying environmental conditions and lack the difficulties of, e.g., finding a single reagent effective in dissolving the non-residual trace element forms without attacking the residual matrix (Tessier et al., 1979).

However, as trace element speciation can primarily be regarded as a function of the mineralogy and solid fraction chemistry of a material (Ryan et al., 2008), X-ray based analytical techniques have been deemed necessary for a more specific interpretation of operationally defined sequential extraction data (Bacon and Davidson, 2008). The precision of these methods can however prove inadequate for the identification of specific compounds and further microstructural methods may be required. Hence this work describes the application of the BCR (The European Community Bureau of Reference, now the Standards, Measurement and Testing Programme) sequential extraction procedure (Rauret et al., 1999) with supportive X-ray diffraction and scanning electron microscopy (SEM) for trace element fractionation in desulphurization slag. As published information regarding potential trace element mobility from secondary steel slags is not available, the objective of this work was to provide information on the environmental characteristics of secondary desulphurization slag and to assess the BCR method in the respective context.

2. Materials and methods

2.1. Slag sampling and sample preparation

A six-week sampling program was performed to attain representative desulphurization slag samples for chemical analyses. A weekly sample of approx. 9 kg (ca. 20 dm³) was collected on two three-week intervals during seven weeks from the slag pit of the respective steel mill. The sampled slag was sealed in 10 dm³ polyethylene containers and represented metal-separated slag generated during each week. The individual weekly samples were processed twice with a spinning riffler to attain weekly subsamples of approx. 150 g. Subsequently, after preserving ca. 15 g for respective pseudo-total element concentration determinations, the subsamples were combined, homogenized and processed again to attain a six-week representative combined sample for sequential extraction with respective mineralogical analysis. Additional representative samples were also gathered during both three-week intervals for single extraction by the one- and two-stage batch tests described in Section 2.4.

2.2. Reagents and instrumentation

All reagents used for pseudo-total and sequential chemical extractions were of analytical reagent grade and all standards, reagent solutions and samples were stored in high-density polyethylene (HDPE) containers. All glass and plastic ware were acid washed prior to use and reverse osmosis and ion-exchange purified water (resistivity 18 M Ω cm⁻¹) was used in the preparation of reagent solutions. Acetic acid (HOAc), hydroxylamine hydrochloride (NH₂OH·HCl), hydrogen peroxide (H₂O₂), ammonium acetate (NH₄OAc), and hydrochloric (HCl) and nitric acid (HNO₃) were of ultrapure or pro-analysis quality. Element concentrations in the attained extracts were quantified with a Thermo Fisher Scientific iCAP6500 Duo inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Fisher Scientific Inc., Cambridge, UK) or, in the case of Hg, with a PerkinElmer AAnalyst 7000 cold vapor atomic absorption spectrometer (CVAAS, PerkinElmer,

Norwalk, USA). Calibration standards for the ICP-OES were generated by serial dilution of relevant Accustandard (AccuStandard Corp., Accutrace®, New Haven, USA) multi-element stock solutions. After separation the eluates were acidified by adding 200 μ L 54% Suprapure® HNO₃ to minimize precipitation.

2.3. Trace element fractionation

The revised four-stage BCR sequential extraction procedure outlined in Table 1 was used for trace element fractionation in the six-week combined slag sample. After each sequence the extractant was separated by centrifugation and decantation, and then the supernatant was acidified and stored in a HDPE container at 4 °C until chemical analysis. The respective solid residues were washed with 20 mL distilled water by shaking for 15 min followed by centrifugation and decantation. Subsequently, the decanted supernatants were discarded. In addition to the combined slag sample, a certified reference material (CRM) BCR-701 (Pueyo et al., 2001) was also subjected to the same procedure for providing information on quality control (Sutherland, 2010).

2.4. Single extractions

Circa 0.5 g of the weekly subsamples and the six-week combined slag sample were subjected to microwave-assisted *aqua regia* (9 mL HCl + 3 mL HNO₃) digestion at 175 °C for 10 min. Subsequent to extraction, the cooled solutions were diluted to volume with ultrapure water in 100 mL volumetric flasks. Water-soluble recoveries were determined from both representative three-week slag samples with a two-stage batch test according to European standard EN 12457-3. The EN 12457-3 two-stage batch test is a compliance test for granular wastes with high solids contents using water (5 < pH < 7.5, electrical conductivity < 0.5 mS m⁻¹) at liquid to solid (L/S) ratios 2 (shaking time 6 h) and 8 (shaking time 18 h), making a final cumulative L/S 10. In addition, a one-stage batch test EN 12457-2 (L/S 10, shaking time 24 h) was used specifically for Cr(VI) extraction. The element and anion concentrations in the EN 12457-3 extracts were quantified with a Thermo X-Series inductively coupled plasma-mass spectrometer (ICP-MS, Thermo Electron Corp., Winsford, UK) and a Dionex DX-120 (Thermo Fisher Scientific Inc., UK) ion chromatograph, as Cr(VI) was spectrophotometrically (PerkinElmer Lambda 25, Norwalk, USA) quantified on the 540 nm wavelength after (1,5)-diphenylcarbazide addition.

2.5. Mineralogical and SEM analyses

The mineralogy of the combined slag sample during sequential extraction was monitored by performing a total of 10 parallel and identical extractions and identifying the mineralogy of the base sample and respective extraction residues by XRD analysis with a A Philips PW 3040 X'Pert MPD diffractometer (45 kV, 40 mA). An iron filter was installed as the diffractometer is frequently used in attaining information on the mineralogy of a wide variety of slag samples from steelmaking. The International Centre for Diffraction Data (ICDD) PDF2003 database (ICDD, Pennsylvania, USA) was used for the identification of spectral peaks. Prior to the analyses, the residues from the parallel extractions were air-dried at 40 °C (Sulkowski and Hirner, 2006). Additional SEM analyses were also performed on the combined slag sample with a LEO 1450 W-cathode instrument (Leo Electron Microscopy Ltd., Oxford, UK) equipped with an energy dispersive (EDS) analyzer (Oxford Instruments Inca, UK). The acquisition time for a total image area analysis was ca. 20 min and for point analysis 30 s with an acceleration voltage of 15 kV and a beam current of approx. 1 nA.

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