

Environmental impacts of steel slag reused in road construction: A crystallographic and molecular (XANES) approach

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Abstract

Basic oxygen furnace (BOF) steel slag is a residue from the basic oxygen converter in steel-making operations, and is partially reused as an aggregate for road constructions. Although BOF slag is an attractive building material, its long-term behaviour and the associated environmental impacts must be taken into account. Indeed BOF slag is mainly composed of calcium, silicon and iron but also contains trace amounts of potential toxic elements, specifically chromium and vanadium, which can be released. The present research focuses (i) on the release of Cr and V during leaching and (ii) on their speciation within the bearing phase. Indeed the mobility and toxicity of heavy metals strongly depend on their speciation. Leaching tests show that only low amounts of Cr, present at relatively high concentration in steel slag, are released while the release of V is significantly high. X-ray absorption near-edge structure (XANES) spectroscopy indicates that Cr is present in the less mobile and less toxic trivalent form and that its speciation does not evolve during leaching. On the contrary, V which is predominantly present in the 4+ oxidation state seems to become oxidized to the pentavalent form (the most toxic form) during leaching.

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1. Introduction

Reuse of waste material has become very important during the past decade because of the reinforcement of environmental regulations that require minimizing waste disposal. Steel making operations are specifically concerned by this problem because of generation of a huge quantity of by-products. Basic oxygen furnace (BOF) steel slag is a by-product in steel-making operations, with an estimated 12 million tons generated annually in Europe [1,2]. Precisely, BOF slag is a residue from the basic oxygen converter, where the pig iron is converted into steel by injecting pure oxygen. Some of this slag is recycled to the blast furnace (the first step of steel making) while a significant portion

is used in road construction (e.g. asphaltic or unbound layer) due to its very high stability and superior skid and wear resistance [3]. But even if BOF slag is attractive as a building material in civil engineering, its environmental impacts must be taken into account. Indeed BOF slag contains trace amounts of potential toxic elements which can be released. This specially applies to Cr and V, which are among the most abundant heavy metals within the slag (Cr, 2400 mg/kg and V, 690 mg/kg) [1,4–6]. For the management of wastes from large scale industrial plants and the decision to either landfill or reuse these materials, information on their environmental properties is needed [7].

To our knowledge, the leaching potential of hazardous elements from BOF slag has received little attention. Geiseler [1], Motz and Geiseler [8] and Proctor et al. [4] have concluded that the release of element from BOF slag was insignificant in terms of environmental impact. But these investigations were performed using only one standardized leaching test and leaching is

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a complex phenomenon where many factors may influence the release of specific components from a waste. Single tests without a proper context are therefore of limited relevance for interpretation and decision-making purposes. van der Sloot et al. [9] explains that without a detailed knowledge of release/retention mechanisms and long-term leaching behaviour, the decision based on current tests (standardized leaching tests) suffer from lack of relation to reality.

The aim of our project is to predict the long-term release rates and mechanisms of V and Cr present in BOF slag as traces by coupling a kinetic and a multiple scale structural study. The methodology applied was developed by Benard [10,11] to assess long-term behaviour of Pb and Cr present in trace amounts in a cement matrix. In the present study, the interest was focused on the oxidation states (and their evolution during leaching) of Cr and V within the slag. Indeed, the potential toxicity (and mobility) of these elements in ecosystems depends not only on their total concentration but also and more significantly on their chemical form or speciation (oxidation state, molecular geometry and coordination environment) [12].

Chromium is a redox active metal that persists as either Cr(III) or Cr(VI) in the environment [13,14]. These two oxidation states have opposed toxicity and mobility properties: trivalent chromium is an essential nutriment at low amounts and a little-toxic element at higher content and is mostly insoluble in water, while hexavalent chromium is very toxic and readily transported. Vanadium is a metal which exists in oxidation states ranging from 0+ to 5+ and the most common valence states are 3+, 4+ and 5+ [15,16]. The multiplicity of oxidation states and the ease, with which changes its coordination environment and oxidation states, confer a level of complexity to the chemistry of vanadium well above that of many metals. Its characteristics have just begun to emerge. Vanadium at trace amounts represents an essential element for normal cell growth, but can be toxic when present at higher concentration [17–20]. The vanadium compounds have different nutritional and toxic properties: their toxicity usually increases as the valence increases [21,22]. Hence pentavalent compounds are the most toxic. Thus quantitative speciation of Cr and V and its variation with time are a prerequisite for long-term risk assessment.

Synchrotron-based X-ray absorption spectroscopy (XAS) is the best-known analytical method permitting direct and in situ determination of speciation of trace elements present in complex solid samples at very low concentration [12]. XAS is an element-specific, bulk spectroscopic method that yields information about the average local structural and chemical environment of an absorbing atom (e.g. its oxidation state).

2. Materials and methods

2.1. Leaching tests

The leaching behaviour of the BOF slag from the VOEST-VAI steel plant (Linz, Austria) has been studied. BOF slag grains (grains >2 mm) were leached in a mechanically stirred tank for a period of 47 days. The aim of this test (inspired from the standardized pH-static test [23]) is to accelerate the leaching

phenomenon in order to obtain rapidly an sufficiently altered solid matrix. To accelerate the leaching phenomenon, the temperature of the tank was maintained at 40 °C and the acidity at pH 5, using HNO₃. The liquid to solid (L/S) ratio of 30 was kept constant, because solutions were regularly sampled in the tank. Eluates were filtered through a 0.2 μm filter and released metal contents were analyzed by plasma emission spectrometry ICP-AES.

To get information on long-term behaviour in the field situation, lysimeter tests were performed by the Laboratoire Central des Ponts et Chaussées (Nantes, France) within the framework of an European project called SESAR. A sample of this BOF slag, subjected to natural ageing in a lysimeter of 1 m³ placed outdoors for a period of 2 years (“called aged BOF slag”) was provided by the LCPC and analyzed by multi-scale structural techniques.

2.2. Multiple-scales structural study

Our methodology is based on a precise experimental characterization of the leached slag matrix, especially on Cr and V speciation assessment. Three structural techniques have been used: X-ray diffraction (XRD), scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) micro-analyses and X-ray absorption spectroscopy (XAS).

2.2.1. Characterization at the macroscopic scale

XRD and EDS micro-analyses allows us to identify the main constitutive minerals of BOF slag, and thus the potential Cr and V bearing phases.

2.2.1.1. X-ray diffraction (XRD). Solids were ground to fine powder and analyzed by X-ray diffraction with a Philips PW 3710 X-ray diffractometer using a Co K α radiation at 40 kV and 40 mA. The diffractograms were acquired in the 2θ [8–90°] interval with a counting time of 13 s/step.

2.2.1.2. Microscopic technique. Microstructure and elemental compositions of the samples were obtained using a Phillips XL30 SFEG scanning electron microscope (SEM) coupled to an Oxford Instruments energy dispersive spectrometer (EDS). The SEM was operated at 15 keV. BOF slag grains (from 200 to 500 μm) were impregnated with resin, and then polished. Semi-quantitative analyses of selected micro-areas were obtained. The counting time was in the 60–200 s/point range.

2.2.2. XANES X-ray absorption spectroscopy (XAS)

An XAS experiment records a spectrum of the modulation of the absorption coefficient as a function of photon energy. The experiment consists of exposing a sample to an incident monochromatic beam of X-rays, which is scanned over a range of energies below and above the absorption edge (K, L, M) of the element of interest. The energy region extending from just below to about 50 eV above the edge is the X-ray absorption near-edge structure (XANES) portion of the absorption spectrum and is used to examine the oxidation state of the absorbing element.

Table 1
Chemical composition of the BOF slag studied

| | Major component (%) | | | | | | | | Traces (g/kg) | |
|----------|---------------------|--------------------------------|------------------|-----|-----|--------------------------------|------------------|-------------------------------|--------------------------------|-------------------------------|
| | CaO | Fe ₂ O ₃ | SiO ₂ | MnO | MgO | Al ₂ O ₃ | TiO ₂ | P ₂ O ₅ | Cr ₂ O ₃ | V ₂ O ₃ |
| BOF-slag | 41.3 | 31.2 | 12.5 | 6.1 | 4.3 | 2.4 | 0.8 | 1.1 | 0.35 | 0.10 |

This technique is non-destructive and is not susceptible to matrix effects.

Cr and V K-edge XANES measurements were performed on (i) beamline FAME at the European Synchrotron Radiation Facility (ESRF) (Grenoble, France), storage ring operated at 6 GeV with a current of 200 mA and (ii) beamline BL-11.1 at Elettra (Trieste, Italy), storage ring operated at 2 GeV with a current of 300 mA, respectively. To record Cr and V K-edge XANES spectra, the Si(111) double crystal monochromator was stepped from about 100 eV below the edge to about 200 eV above the edge (Cr-edge near 5989 eV and near V-edge near 5465 eV). All spectra were calibrated in energy against the edge position of a thin metal foil (Cr and V, respectively). Due to the very low Cr and V contents, the fluorescence detection mode was selected and measurements were made using a multi-element detector that collected X-rays only in an electronically gated energy interval appropriate for fluorescence X-rays of the absorbing element.

Crystalline standards containing V or Cr at different valences (from V(III) to V(V), Cr(III) and Cr(VI)) were also analyzed. The spectra of standard compounds were collected in the transmission mode.

Spectra are averages of several data sets (number of spectra depending on the element content) from the same sample that were processed using standard edge step normalization procedure.

3. Results and discussion

3.1. Chemical and mineral composition of BOF slag

Table 1 shows the chemical composition of BOF slag obtained by ICP-AES and ICP-MS measurements. BOF slag is mainly composed of calcium, silicon, iron and manganese and contains also Cr and V “potential toxic elements” present as traces. The combined results of chemical analyses, XRD and EDS micro-analyses enabled the identification and characterization of four principal phases within BOF slag (Fig. 1):

- (1) β -Dicalciumsilicate (Ca_2SiO_4) as large grains, containing a solid solution of $\text{Ca}_3\text{P}_2\text{O}_8$.
- (2) Calcium ferrite: $\text{Ca}_2\text{Fe}_2\text{O}_5$, containing Ti et Al and CaFeO_2 .
- (3) Solid solution rich in iron ((Fe, Mn, Mg, Ca)O). XRD spectrum of this phase is close to wustite (FeO) spectrum lines [5].
- (4) Calcium hydroxide ($\text{Ca}(\text{OH})_2$) formed from quick lime hydration and calcite (CaCO_3) from hydrated lime during ageing (atmospheric carbonation).

Then SEM-EDS micro-analyses indicate that vanadium and chromium are associated within the same phase: the dicalcium-ferrite containing Ti and Al. This technique identifies well the chromium and vanadium-bearing phase.

3.2. Cr and V release

The Cumulative Leaching Efficiencies (CLE) of V and Cr from sample of BOF slag were obtained from the total content of V and Cr in the sample (in $\mu\text{g g}^{-1}$ sample), the total eluate content of V and Cr at the end of the leaching procedure (in $\mu\text{g l}^{-1}$ eluate) and the L/S ratio (in l g^{-1}). Leaching results show little Cr release, while vanadium is significantly released (Fig. 2). Thus, in terms of environmental impact, V is the most critical element. In spite of its relatively high concentration, Cr does not involve negative impacts. It shows that the total concentration is not sufficient for environmental impact assessment.

3.3. Cr and V speciation within initial and leached BOF slag

3.3.1. Chromium K-edge XANES spectra

The Cr(III) and Cr(VI) oxidation states in solids can be readily distinguished in chromium XANES spectra by the intensity of the pre-edge peak [24]. As shown in Fig. 3, the pre-edge peak is generally very weak (typically less than 0.05 times the edge step in normalized spectra) for trivalent chromium, whereas the pre-edge peak is usually almost as intense as the edge-step for hexavalent chromium. This prominent pre-edge peak is due to a 1s to 3d electronic transition, that is a forbidden transition for octahedral Cr(III) which has a center of symmetry. However,

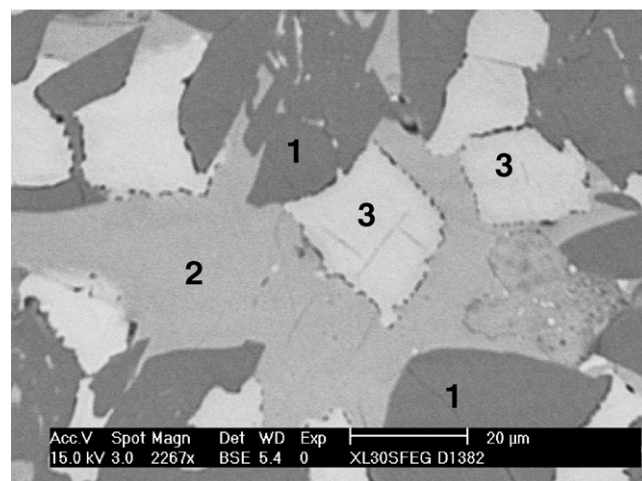


Fig. 1. SEM photography of a BOF slag polished section (grains >2 mm).

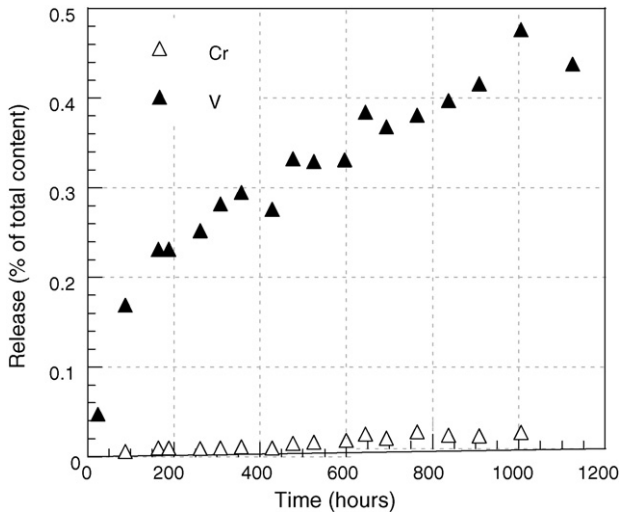


Fig. 2. Release (% CLE) of Cr and V from BOF steel slag during pH_{stat} test (pH 5, L/S=30).

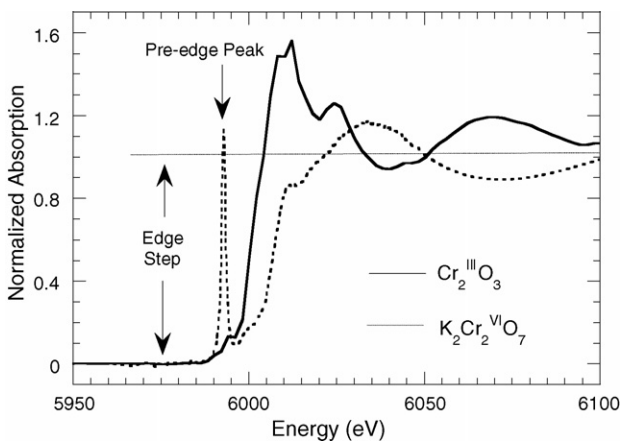


Fig. 3. Normalized K–Cr XANES spectra for Cr standards: K₂Cr₂^{VI}O₇ and Cr₂^{III}O₃.

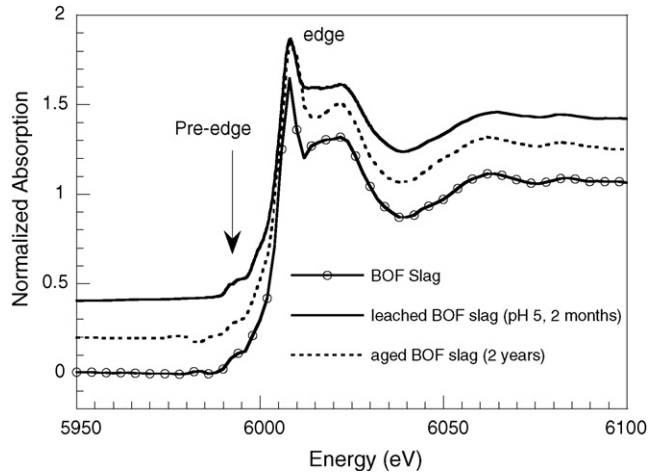


Fig. 4. Normalized K–Cr XANES spectra for BOF slag samples (>2 mm).

it is allowed for the non-centro symmetric tetrahedral Cr(VI) molecule due to mixing of Cr(3d) and Cr(4p) orbitals. This difference in the height of the pre-edge peak has been used as the basis for a direct and non-destructive method for the determination of chromium oxidation states [24–27].

Fig. 4 shows normalized XANES spectra recorded at Cr K-edge for samples of BOF slag. The absence of pre-edge peak indicates that chromium is present in octahedral coordination and in the trivalent form (the less mobile and less toxic form), and that its speciation does not change during leaching or natural ageing.

3.3.2. Vanadium K-edge XANES spectra

Fig. 5 shows normalized V K-edge XANES spectra for vanadium standards and BOF slag samples. The edge energy (E_i) of each sample was measured at half way normalized-edge step, i.e. where the absorption is equal to 0.5. The X-ray edge energy (at half way) of V standards displays a positive shift with increasing oxidation state of V (Figs. 5 and 6). The observed V K-edge energy shifts are consistent with those reported in the literature [28]. Thus the vanadium edge is a clear signature of its oxidation state. This method was followed because the energy values mea-

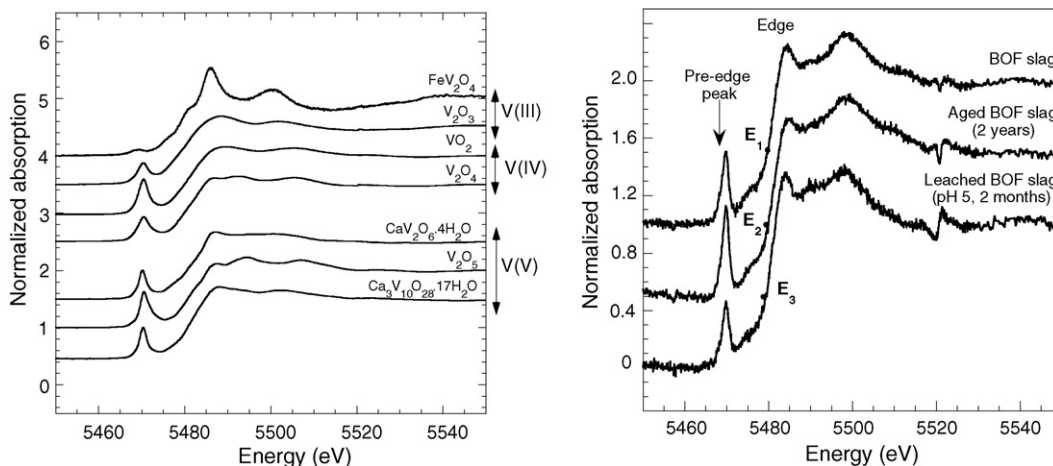


Fig. 5. V K-edge normalized XANES spectra for V standards and BOF slag samples.

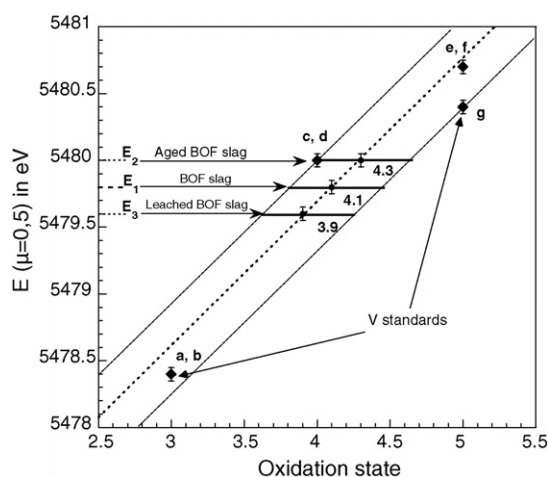


Fig. 6. Position of the absorption edge of vanadium vs. its oxidation state: (a) FeV_2O_4 ; (b) V_2O_3 ; (c) VO_2 ; (d) V_2O_4 ; (e) V_2O_5 ; (f) $\text{Ca}_3\text{V}_{10}\text{O}_{18}\cdot 17\text{H}_2\text{O}$; (g) $\text{CaV}_2\text{O}_6\cdot 4\text{H}_2\text{O}$.

sured at half way up the edge step appear to be more dependent on the overall edge energy and a more accurate determination of the vanadium valence [29–34]. The experimental error on the energy measurement is ± 0.05 eV.

Fig. 5 shows the correlation between the edge energy and the oxidation state obtained from seven V standards. The error on the valence determination (± 0.3) is due to the method and the edge energy differences of V standards at the same valence (due to their geometry). An analysis of the energy position of the edge reveals that V is predominantly present in the 4+ oxidation state in steel slag (bulk oxidation state of 4.1). It also indicates that the average oxidation state of vanadium in BOF slag seems to decrease during leaching at pH 5 (3.9) and to increase during natural ageing (4.3). Thus V seems to become oxidized to the pentavalent form (the most toxic form) during natural ageing.

Standard bulk XAS technique probes an area of several mm^2 and provides information on the average local chemical environment. Thus, where an element is present at more than one oxidation state, bulk XANES will detect only the average valence in the bulk sample. And the altered layer of leached slag is only of a few 100 μm . Consequently, minor changes in V oxidation state may not be easily detected with bulk analyses. Since we detect a V oxidation state variation, it shows that changes at the local scale are significant. μ -XANES spectroscopy using a microfocused beam will be the appropriate mean for precisely detecting local valence variation.

4. Conclusion

The results of the multiple scale structural study allowed to describe the main mineral phases composing BOF slag and to identify the bearing phase of chromium and vanadium: a dicalciumferrite. Then leaching tests showed that little Cr is released, and therefore not mobile. XANES investigations at Cr K-edge agreed with this result because they showed that Cr is present in BOF slag in the trivalent form, the less mobile and less toxic one, and remains in this form during leaching. Unlike Cr, V is significantly released and predominantly present in BOF slag in the

4+ oxidation state (one of the toxic forms). Moreover vanadium seems to become reduced during leaching at pH 5 and to become oxidized to the pentavalent form (the most toxic) during natural ageing. However, analyses were performed on the bulk and the results obtained are averaged. These observations need to be confirmed by local structural analyses in the altered zone (μ -fluorescence X and μ -XANES cartographies). This work shows the relatively high release of V within BOF steel slag during acid leaching and gives some first keys to understand its comportment (especially on its oxidation state evolution).

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