Environmental Impact of Steel Slag reused as Aggregates in Road Manufacturing: Molecular Mechanisms of Chromium and Vanadium Release

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Abstract. The speciation of chromium (Cr) and vanadium (V), two potential pollutants, present as traces in a residue from steel-making operations (BOF slag) and their leaching behavior were studied to assess the environmental compatibility of this waste as a recycled material for road making. A multi techniques approach (XAS, XANES, micro-XANES, micro-XRF and micro-XRD) was required to assess the molecular mechanisms of Cr and V release. Leaching tests have shown that Cr is little released and moreover remains at its initial trivalent form, less toxic, even during leaching. One part of octahedral Cr(III) ions replaces structurally the octahedral Fe(III) in a dicalcium aluminoferrite phase and the other part is associated to a solid solution (Fe, Mn, Mg)O. Spatially resolved techniques allowed showing that Cr is tightly bound to a secondary phase formed during leaching which controls its solubility. V present in BOF slag is environmentally more critical because its release is relatively high and it is oxidized to its most toxic form (V(V)) during leaching. Micro-XRF coupled with chemometric analysis (SIMPLISMA) indicates that V is also associated to a dicalcium aluminoferrite.

Keywords: micro-XANES, EXAFS, micro-XRF, micro-XRD, speciation, leaching behavior.

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INTRODUCTION

Basic Oxygen Furnace (BOF) slag is a residue from the basic oxygen converter in steel-making operations, which is partially reused as an aggregate for road constructions. This waste is mainly composed of iron, calcium, silicon and manganese but also contains trace elements potentially mobile and harmful to the environment. Therefore fundamental scientific solid knowledge on the environmental impact (particularly from the durability aspect) associated to the reuse of BOF slag is required. The speciation (e.g. oxidation state and local structural environment) of chromium (2400 mg/kg BOF slag) and vanadium (690 mg/kg BOF slag) and their evolution during leaching were studied by coupling XAS (XANES, micro-XANES, EXAFS) at Cr and V K-edges, laboratory micro-XRF and laboratory micro-XRD. The objective of this work was to assess the potential of Cr and V for release to the aqueous environment by giving the keys to understand the molecular release/retention mechanisms associated. The originality of this work was to use X-ray micro beams (from synchrotron or from laboratory X-ray sources) to identify variations at the altered layer scale (tens of microns).

RESULTS & DISCUSSION

Chromium and Vanadium Release

Dynamic leaching tests at a laboratory-scale (using a modified soxhlet extractor) and natural weathering (in lysimeter, 606 days) showed that Cr and V have opposite behavior. The release of Cr is very low. In the laboratory its cumulative leaching efficiency (CLE) remains <0.05 % after 130 days, while V is relatively mobile (CLE of 7.1 %).
Chromium Speciation

The low mobility of Cr suggests that this element is tightly bound in little soluble phase(s) or that a secondary phase controls its solubility.

Cr Oxidation State

Cr oxidation state has been evaluated with XANES (FAME, ESRF-France) and micro-XANES (ID21, ESRF) at Cr K-edge (the micro-beam was pointed on Cr-rich ROI (region of interest) in non-altered core and altered layer). The presence of Cr(VI) was suspected because of basic conditions (pH ≈ 12) and high Mn content. But recorded spectra do not show any pre-edge peak, and this reveals an absence of Cr(VI) (Figure 1). Only octahedral trivalent Cr is present, a less toxic and mobile form. No oxidation of the initial Cr(III) to the toxic Cr(VI) occurs during leaching.

Cr Bearing Phases

Cr(III)-bearing phases were successfully identified with laboratory micro-XRF and EXAFS at Cr K-edge (FAME, ESRF). The Simple-to-use Interactive Self-modeling Mixture Analysis (SIMPLISMA) approach\(^2\) (chemometric analysis) allowed to extract three spectra that statistically explain a data set of 145 micro-XRF spectra (10 µm spot size, 15 kV, 1000 s, Rh X-ray target source) and correspond to the 3 main phases that compose non-altered BOF slag\(^3\). The Ti, Mn and Si fluorescence Kα lines were interactively selected as “pure variables” showing highest variations in intensity. The resolved spectra well identify the dicalcium aluminoferrite (Ca\(_2\)Fe\(_2-x\)Al\(_x\)O\(_5\)) as a Cr-bearing phase and also show the presence of a second Cr-bearing phase: a solid solution (Fe, Mn, Mg)O.

EXAFS fitting results suggest that the mean Cr local structural environment is consistent with that of the octahedral Fe(III) in the dicalcium aluminoferrite (Figure 2a). This phase contains planes of octahedrally-coordinated trivalent ions (Fe or Al) and chains of tetrahedrally-coordinated trivalent ions (Fe or Al)\(^4\) and is known to be able to accommodate significant amount of Cr in its structure, the Cr(III) ions structurally substituting for Fe(III) on the octahedral sites only. The similarities between the experimental EXAFS spectra of non-altered and altered samples suggest that the mean atomic environment of Cr does not change dramatically with leaching. Only slight variations modify the oscillation centered near 7 Å\(^-1\) and can be explained by visual comparison with linear combination between BOF slag (non-altered) and chromite (spinel-type phase) EXAFS spectra (Figure 2b). Micro-XANES validate this observation since spectra recorded in the altered region show modifications in the edge features with high similarities with the chromite spectrum (Figure 1). Moreover, the micro-XRD pattern obtained with the micro-beam pointed on the same ROI confirms the presence of a spinel-type phase. We can conclude that Cr is associated to a spinel-type phase in the altered layer and that its solubility is controlled by the presence of this secondary phase stable in the environment\(^5\).

Vanadium Speciation

The same experimental approach was used to identify the speciation of V in leached BOF slag and try to understand why this element is released.
After comparisons between methods dedicated to the interpretation of V K-edge XANES features, correlations between normalized pre-edge peak area and its centroid position have been identified as the most reliable method to assess both V oxidation state and coordination environment\(^6\). Bulk XANES (BL 11.1, Elettra-Italy) indicated that the mean V oxidation state in non-altered BOF slag is +4. This value corresponds to an average between +3 and +5 since V K-edge EXAFS (FAME, ESRF) clearly distinguishes two kind of V-O interatomic distances (1.73 and 1.97 Å) typical of tetrahedral and octahedral coordination, respectively. Then micro-XANES (ID21, ESRF) allowed elucidating the micro-distribution of V speciation in leached BOF slag. V exhibits an important evolution from the unaltered to the altered phases. Its oxidation state increases from +3 to +5 (the most toxic and mobile form) together with the decrease of its symmetry (from octahedral to tetrahedral) (Figure 3). In altered layer, V is principally present as V(V).

![FIGURE 3. Normalized pre-edge peak and the model calculated with 1 to 2 contributions (ROI1, 2 in the non-altered core and ROI3 in the altered layer).](image)

**V Bearing Phase**

V K-edge EXAFS does not enable to determine the local environment (e.g. bearing phase) of V in BOF slag because of the Ba L\(_{II}\)-edge (5624 eV) that interferes the EXAFS oscillations (220 mg Ba/kg BOF slag). Only the first coordination shell (V-O bonds) can be extracted. However, the V-bearing phase was successfully identified thanks to the combination of micro-XRF and SIMPLISMA approach. Because Ti K\(_{\beta}\) and V K\(_{\alpha}\) fluorescence lines overlap (5 g Ti/kg BOF slag), a fourth spectrum was extracted with the V K\(_{\alpha}\) line selected as a “pure variable”. This method allows separating XRF spectra with Ti and V contributions. V is associated with the dicalcium aluminoferrite. As V exhibits two distinct symmetry it can be assumes that V is present in the two sites (tetrahedral and octahedral). Its release can be linked to the alteration of its bearing-phase that presents incongruent dissolution. Moreover, secondary V-bearing phase was not detected contrary for Cr.

**CONCLUSION**

Results showed that Cr(III) ions, little released, replace structurally the octahedral Fe(III) in a dicalcium aluminoferrite phase or are associated to a solid solution (Fe, Mn, Mg)O. Moreover, Cr is tightly bound to a secondary phase formed during leaching which controls its solubility. On the other hand the relatively high release of pentavalent V, the most toxic form, has to be considered. The oxidation of the initial V(III) to V(V) during leaching can partially explain the V mobilities. Moreover, secondary V-bearing phase was not detected.

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