

**Experiment title:**

Environmental impact of Steel slag used as agregate in road construction: evolution of the crystallographic sites of vanadium during leaching

Experiment number:
EC-57

Beamline:

BM30b

Date of experiment:

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18

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Report:***Aim of the project***

Steel making operations are specifically concerned by the reinforcement of environmental legislations that require minimizing waste disposal due to the generation of a huge quantity of by-products (12 million tons generated annually in Europe). Basic Oxygen Furnace (BOF) steel slag is a residue from the basic oxygen converter, where the pig iron is converted into steel by injecting pure oxygen. A significant portion of the slag is used in road construction (e.g. asphaltic or unbound layer) due to its very good physical proprieties. But the environmental impacts of BOF slag must be taken into account. Indeed, potential toxic elements are present as traces like Cr (2600 ppm), V (690 ppm) and Ba (225 ppm), and can be released. Our recent results, based on leaching test, indicate that vanadium represent the most potential toxic elements: the total release fraction (TRF) of vanadium exceeds 3% (after leaching test conducted at pH=5 during 7 days).

The aim of the experiment was to determine the mechanisms of vanadium release and vanadium speciation evolution in the matrix (evolution of the redox state and speciation).

Previous results:

Prior to Fame experiment, we had coupled successfully various laboratory and synchrotron spatially resolved techniques (cryogenic SEM coupled to EDX mapping, lab-micro-XRF (Horiba XGT-5000) and synchrotron micro-XRF/XANES on the ID21 beam-line). Micro-XRF indicated that vanadium is associated to calcium ferrite in the non-altered zone. But most interestingly, micro-XANES results (report ME1095) (Chaurand et al, 2006a, 2006b) indicated that the vanadium initially present under 3+ and 4 + oxidation states was oxidized to the 5+ form i.e. the most toxic oxidation state in the most altered zone.ADDINADDIN

Unfortunately, the strong differences between the micro-XANES spectra of the unaltered and the altered zones are difficult to attribute accurately to the oxidation state. We were only able to identify the trend (i.e. oxidation of V during leaching) but it was difficult from our micro-XANES results to determine the mechanisms of V oxidation. Unlike chromium for which the 3+ oxidation state is associated to the octahedral symmetry and the 6+ to a tetrahedral environment, the relation between the symmetry and the oxidation state of vanadium is not so trivial. Therefore modifications of the pre-edge intensity and position as well as the edge structures do not lead to a calibration curve related to the oxidation state and symmetry of vanadium and as it is possible in the case of Cr or Fe.

To overcome the difficulty to accurately interpret the XANES spectra evolution as well as to identify the V fixation sites EXAFS at the V K-edge on the FAME beam-line (BM-30b) were necessary. The review of Shindler et al. [9] and results of Shobu et al. [12] indicate that the V-O interatomic distances are more efficient to distinguish the various vanadium oxidation states and coordination environment.

Experiment

The experiment was conducted on BM-30b beamline 'FAME' in march 2006. The samples were analyzed in the fluorescence mode due to the very low concentration of V (~700 ppm). Unfortunately the sample was also rich in titanium (8400 ppm). Therefore the Kbeta fluorescent line of Ti was superimposed with the Kalpha fluorescent line of V. The energy resolution of the very sensitive Ge 30 elements EDX fluorescent detector was not enough to separate both lines. To decrease at maximum the titanium fluorescence and increase the V/Ti fluorescence intensity ratio, aluminum foils were used as filters. The consequence was to decrease the influence of the titanium but also to decrease the number of counts on the detector. Therefore the acquisition time was between 6 to 10 hours for each sample !!! Even with such main physical limitation we were able to obtain XANES spectra with good signal/noise ratio. For the EXAFS part an other problem occurred: the presence of the Ba LII edge (figure 1). The concentration of Ba is in a 200-300 ppm range.

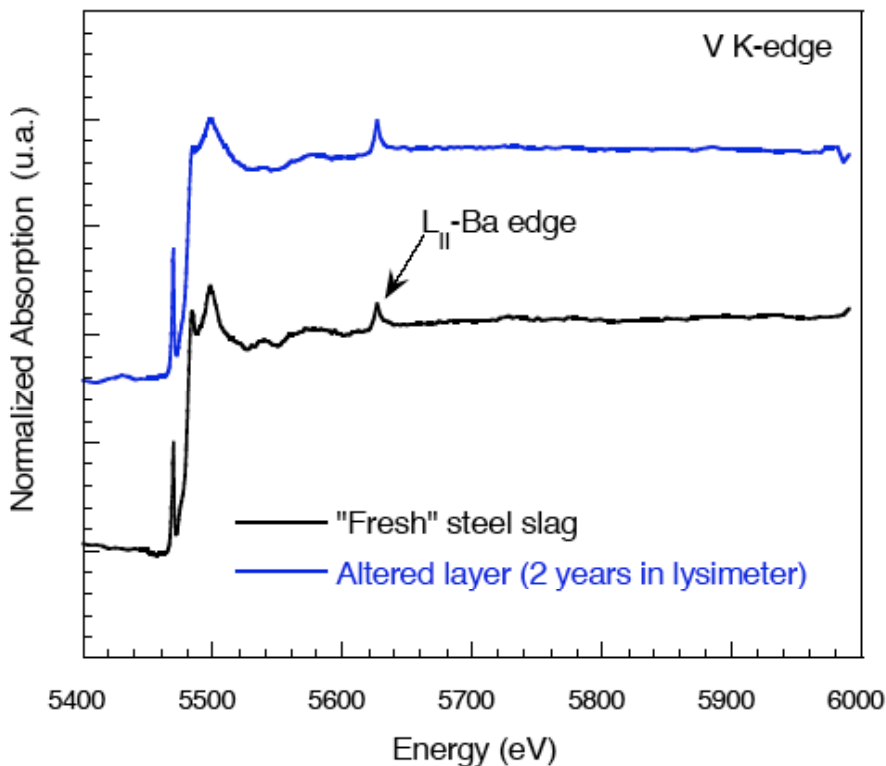


Figure 1 : absorption spectra of non-altered and altered steel slag

Therefore L fluorescent lines of Ba were also detected. We tried to modify the energy range of the filter of the detector to decrease at maximum the Ba LII edge but it was impossible to remove it.

This point reveal, if necessary the very high sensitivity of the FAME beamline to diluted elements: even by trying to decrease the influence of Ba (200 ppm) it was impossible to remove totally the presence of the edge!!!

The presence of Ba lead to a major difficulty in the EXAFS data treatment. We tried to 'mathematically' removed the LII edge using lorentzian peak to decompose the spectra, but the peak was too high to be perfectly removed during the fit.

The Ba LII edge appeared on the EXAFS spectra as a high frequency signal. From the Fourier transform it seemed that it did not really affect the low frequency corresponding to the V-O atomic shell (figure 2). Therefore we tried to fit the first atomic shell of V.

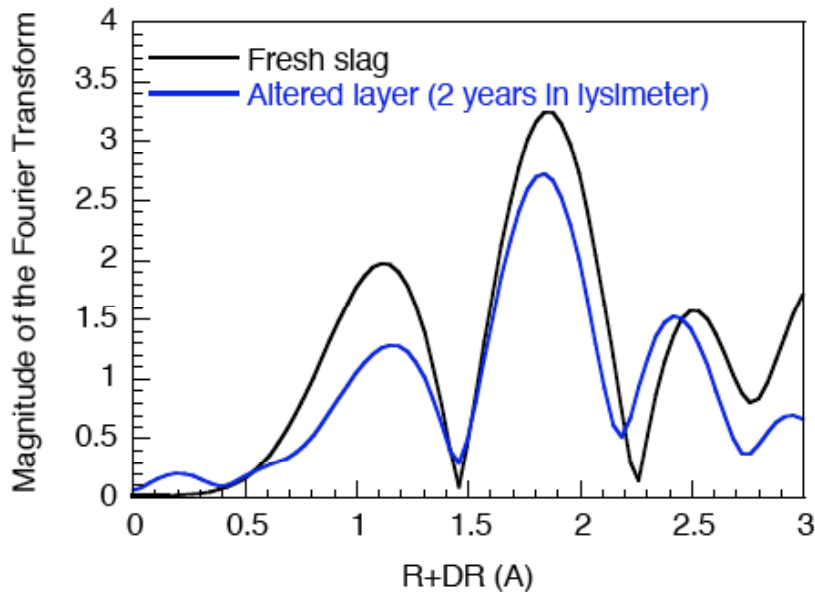


Figure 2: Fourier transform of EXAFS spectra of non-altered and altered steel slag

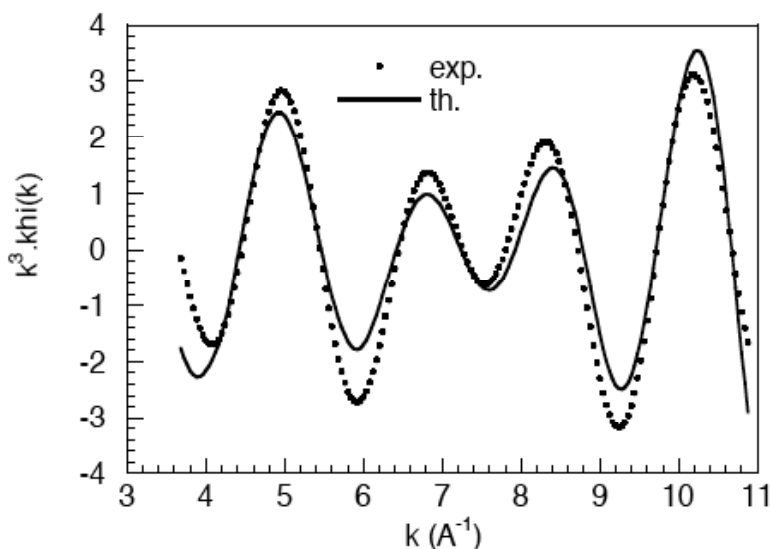


Figure 3 : experimental and calculated partial EXAFS curve corresponding to the first coordination sphere of V in the slag.

For all spectra two V-O interatomic distances were necessary to fit the experimental spectra. The V-O distances $1.78 \text{ \AA} \pm 0.05$ and $1.98 \text{ \AA} \pm 0.05$ revealed the presence of V³⁺ and V⁵⁺ oxidation state. The main difference between altered and non-altered slag was the increase of the V⁵⁺ contribution (i.e. increase of the 1.98 \AA V-O contribution) in the spectra.

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