

**Experiment title:**

Environmental impact of Steel slag used as aggregate in road construction: evolution of the crystallographic sites of vanadium and barium during leaching.

**Experiment  
number:  
ME 1095**

|                          |   |                                    |
|--------------------------|---|------------------------------------|
| <b>Beamline:</b><br>ID21 | <b>Date of experiment:</b><br>from: 9 June 2005 to: 14 June 2005    | <b>Date of report:</b><br>26/08/05 |
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**Report:***Aim of the project*

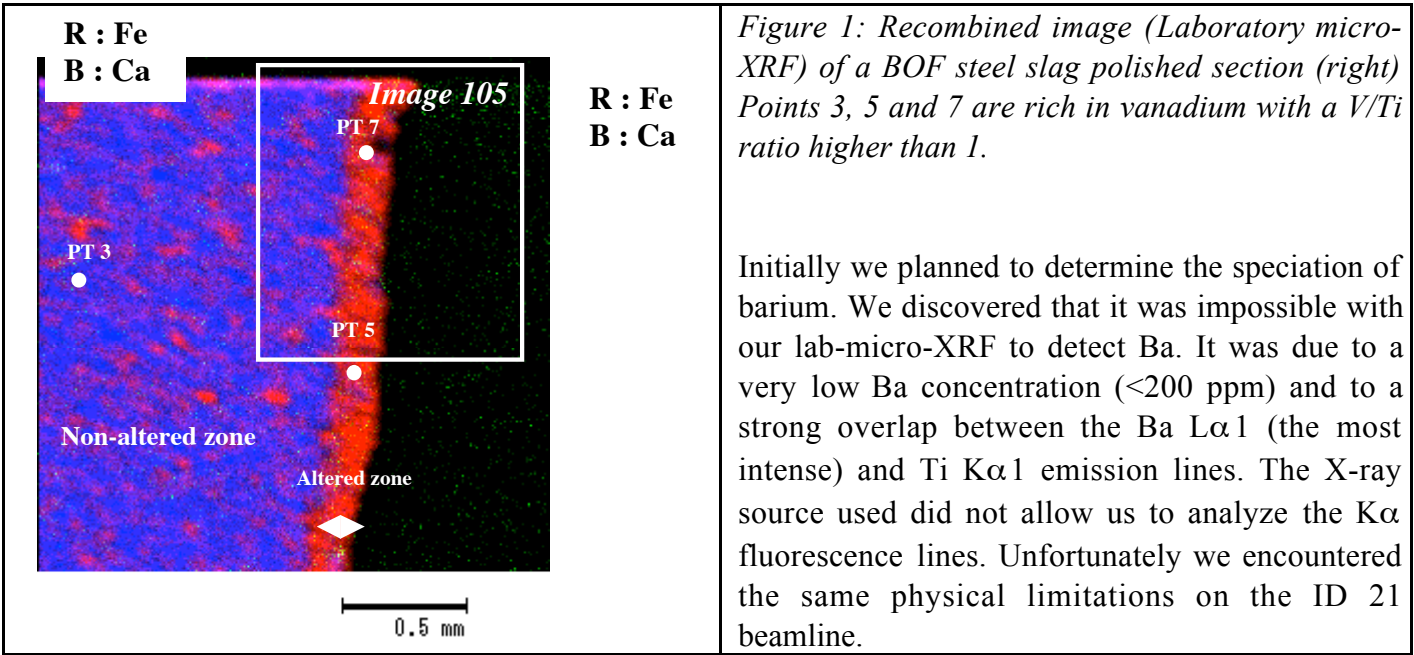
Reuse of waste materials has become very important within the past decade because of the reinforcement of environmental legislations that require minimizing waste disposal. Steel making operations are specifically concerned by this problem because of generation of a huge quantity of by-products.

Basic Oxygen Furnace (BOF) steel slag is a by-product in steel-making operations. Precisely, it is a residue from the basic oxygen converter, where the pig iron is converted into steel by injecting pure oxygen which is partially reused as an aggregate for road constructions. It is mainly composed of calcium, silicon and iron but also contains potential toxic elements present as traces, like vanadium (690 mg/kg), which can be released. Dynamic leaching tests, at a laboratory scale, using the CTG-leachcrete apparatus developed by Moudilou (Moudilou, 2000), were performed to assess leaching behaviour of BOF slag. These tests showed that vanadium is significantly released (6.19 µg of V per cm<sup>2</sup> of slag). Thus the objective of our project is to describe the long-term release mechanisms of vanadium present in steel slag as traces by coupling multiple scales structural study, from semi-local to molecular scale.

The aim of this experiment was to determine the speciation (especially the oxidation state) of vanadium within BOF steel slag and its change during leaching. It is an essential step in our study because the mobility and the toxicity of vanadium strongly depend on its atomic environment and oxidation state. Vanadium exists in oxidation states ranging from 0 to +5 and the most common valence states are +3, +4 and +5. The multiple oxidation states and the facility, with which vanadium changes its coordination environments as well as its oxidation states, confer a level of complexity to the chemistry of V and the characteristics of which have just begun to emerge. The vanadium compounds have different nutritional and toxic properties: their toxicity usually increases as the valence increases (Barceloux, 1999). Hence pentavalent compounds are the most toxic.

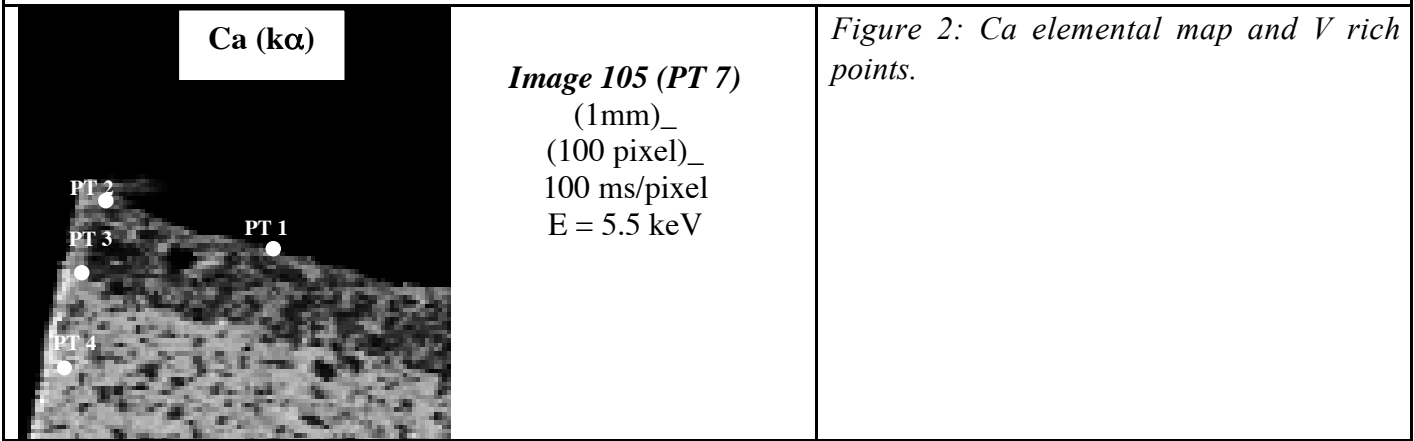
*Preliminary experiments:*

The leached grain of BOF steel slag (leached during 600 hours in CTG-leachcrete, at natural pH ≈ 8.5 and liquid to solid ratio of 20), was previously studied by SEM-EDX, XRD and laboratory micro-XRF (with a Horiba XGT-5000 that was installed at the CEREGE in May 2005). The studied grain was embedded in vanadium free resin and polished to obtain a polished section. The combination of spatially resolved laboratory techniques allowed us to define regions of interest that are V rich zones in the altered and non-altered region (figure 1).



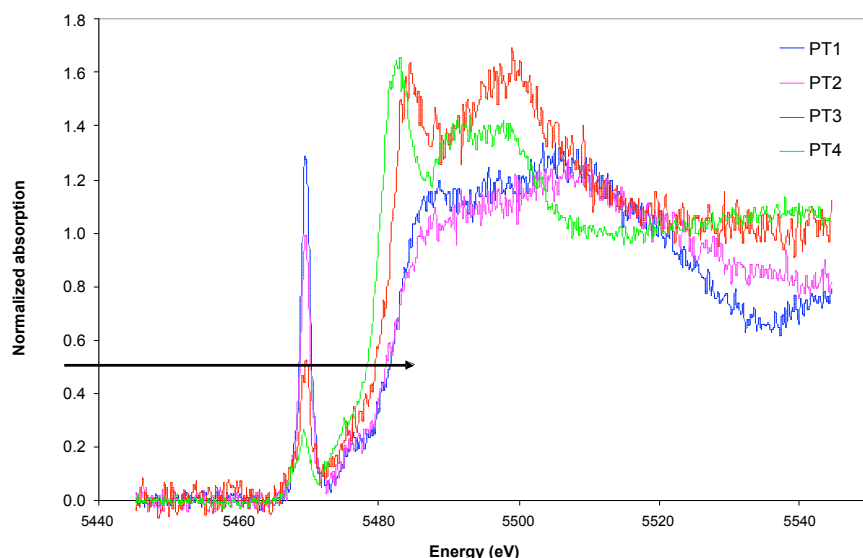
*Experimental strategy to get round physical limitations:*

1. The first step was to define V rich regions where we could record micro-XANES spectra at the V K-edge. Laboratory micro-XRF mapping allowed us to define V rich region with a spatial resolution of 20  $\mu\text{m}$  (the beam spot size). The concentration of vanadium in steel slag is quite low, 690 mg/kg, and vanadium is not concentrated in localized place. So its detection is not easy. Moreover the main component of BOF steel slag is calcium (296 g/kg). Therefore, because of the saturation of the fluorescence detector due to calcium, we had to move back the detector and to add a 240  $\mu\text{m}$  kapton filter. In this configuration, the number of counts due to calcium decreases but also the vanadium counts rate (cuts 90% of Ca emission and 60% of V emission). And unfortunately, our sample is also rich in titanium (8400 mg/kg), therefore the  $K_\beta$  fluorescence line of Ti superimposes with the  $K_\alpha$  fluorescence line of V. To find a V rich zone, we calculated the Ti  $K_\beta$  line (or V  $K_\alpha$  line) to Ti  $K_\alpha$  line ratio. This ratio lead to highly contrasted images and we were able to define regions with higher V content and lower Ti content (ratio  $(\text{Ti}K_\beta + \text{V}K_\alpha)/\text{Ti}K_\alpha \geq 1$ ) (figure 2 (image 105)). Even with such main physical limitations we were able to obtain XANES spectra with reasonable signal/noise ratio.



The second step was to scan micro-XANES spectra at V K-edge with a focused beam spot (2  $\mu\text{m}$ ). The spectra were scanned from 5450 to 5550 eV. A vanadium metal foil was used to energy calibrate the vanadium K-absorption edge. The energy step was 0.2 eV. Due to the low V concentration, 4000 seconds scans were necessary to obtain a good signal/noise ratio.

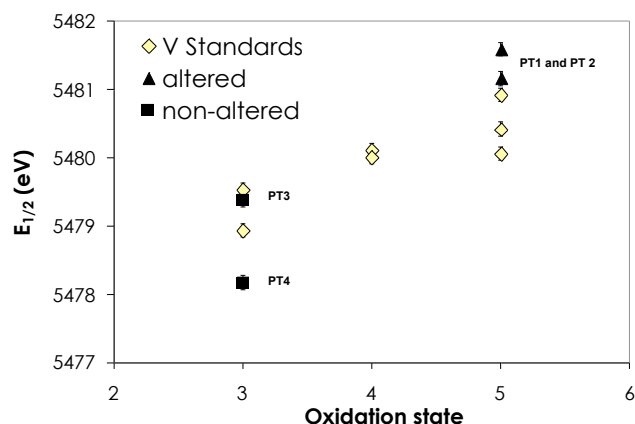
Four  $\mu$ -XANES spectra were recorded at different regions of image 105: points 1 and 2 in the altered zone and points 3 and 4 in the non-altered zone (figure 3). Moreover seven crystalline standards containing V at different valence were also analysed: 2 compounds with V(III), 2 with V(IV) and 3 with V(V). In transmission, each spectrum required a data acquisition time of 1000 seconds. The signal/noise ratio of the XANES spectra was extremely good in transmission as well as in the fluorescence mode.



*Figure 3 : XANES spectra at the v K-edge for various points of interest.*

### Results :

The position of the edge for each sample was measured half way up the normalized-edge step, or where  $\mu$  (the absorption) is 0.5. This method was followed because this energy values appear to be more dependent on the overall edge energy and to provide a more accurate depiction of the vanadium valence (Mansour et al., 2002, Mckeown et al., 2002, Rodella et al., 2003, Rossignol et al., 2001). The X-ray edge energy (at half way) of the V standards displays a positive shift with the increase in the oxidation state of V. The observed V K-edge energy shifts are consistent with those reported in the literature (Haskel et al., 2004, Rossignol et al., 2001) and with those recorded at Elettra in Italy. That way the vanadium edge is a clear signature of its oxidation state.



*Figure 4:energy position of the half edge jump as a function of the V oxidation state.*

The analysis of the energy position of the main edge indicates that vanadium is present in the +3 oxidation state in the non-altered region.

The edge energy displays a positive shift from the non-altered to the altered zones. Thus the oxidation state of vanadium changes during leaching and vanadium becomes oxidized in V(V).

The intensity of the pre-edge peak is related with the symmetry of V in the oxides (Rodella et al., 2003). Indeed, the area under the pre-edge peak shows a strong dependence on the local structure of V. The pre-edge peak amplitude increases as the vanadium site symmetry is lowered (McKeown et al., 2002).

The pre-edge peak observed in the V K-edge XANES spectrum is high in the altered zone and decreases in the non-altered zone. This result indicates that the vanadium site symmetry decreases with leaching. This result also validates observation concerning V oxidation state. Since a strong pre-edge exists in the case of V(V) and its intensity decreases for V(IV). In the case of V(III) the intensity of the pre-edge is really low.

We can notice that the pre-edge peak of steel slag samples displays a negative shift compared to those of V standards, but we still did not understand this shift.

#### *Conclusion:*

The determination of oxidation state of vanadium in a spatially resolved region by micro-XANES was successful, even with physical limitations : low vanadium content, high Ti and Ca contents. We determined the oxidation state of vanadium in altered and non-altered regions. Results show that vanadium, present in steel slag at the trivalent form (and maybe also at the  $V^{4+}$  form), is oxidized in  $V^{5+}$  during leaching, the most toxic form and moreover its site symmetry decreases during leaching

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