



ESRF

Experiment title:**Effect of leaching on the crystallographic sites of trace metals associated with natural cements (site of Maqarin, Jordan): case of Cr****Experiment****number:
ME 399**

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Cements and similar materials are used to stabilize/solidify a variety of hazardous wastes and then reduce their toxicity. The characterization of water effect on the cement-waste mixture is a crucial step to assess the reliability of the stabilization processes and their potential environmental risk. Leaching tests are generally used to predict the long-term behavior of the materials formed. But these experiments are time limited. A neat alternative is the study of natural analogue systems and in this context the Maqarin site (Jordan) represents an interesting analogue for leached cements over geological timescales. The cements were formed after spontaneous metamorphic combustion of marls and limestones 10^5 - 10^6 years ago and the concentration of different heavy metals can reach relatively high levels. In the case of chromium the concentration evolves from 300 to 400 ppm depending on the alteration level of the natural cement. The aim of this study is to determine the leaching mechanisms of Cr after the interaction of the cement with water by determining the speciation of Cr in the fresh and leached cements from Maqarin site. The interest of using micro X-ray beam is to assess the spatial variability as a function of the alteration level.

Experimental setup

The experiments were conducted using the Scanning Microscope operated in fluorescence mode. The fluorescent line of Cr and Ca were simultaneously acquired with an energy dispersive spectrometer associated to a multichannel analyzer. The intensity of the beam was checked with the Ca $K\alpha$ fluorescent line intensity. The beam spot was focused down to $1 \times 1 \mu\text{m}$ using a Fresnel Zone Plate lens.

The evolution of Cr in the material was assessed by scanning X-ray microprobe across the sample. Transverse scans and fluorescence 2D maps were performed at three energies: $E_1=5.980$, $E_2=5.999$ and $E_3=6.022\text{eV}$ characteristic of the background, the presence of Cr(VI)(pre-edge) and total Cr respectively. The ratio $[(E_2-E_1)/(E_3-E_1)]$ of the spectra lines and the 2D Cr speciation images depicts the Cr(VI) distribution. This procedure allowed us to obtain 2D chemical maps at the micro scale. XANES spectra were collected at different points of interests (POIs).

Results

Three samples were investigated: marl, altered and unaltered cements.

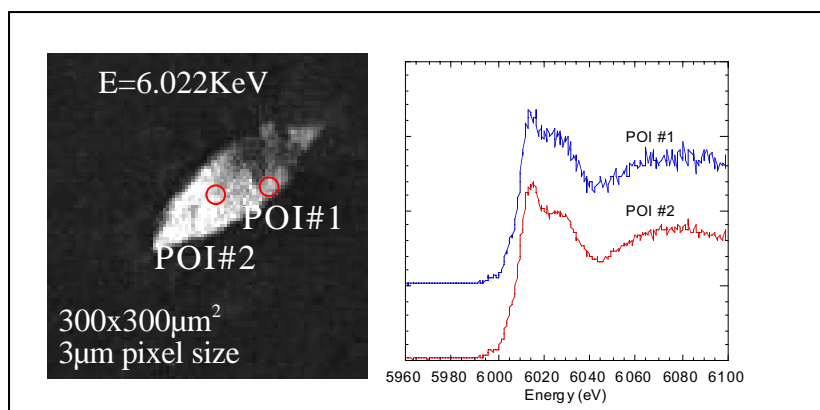
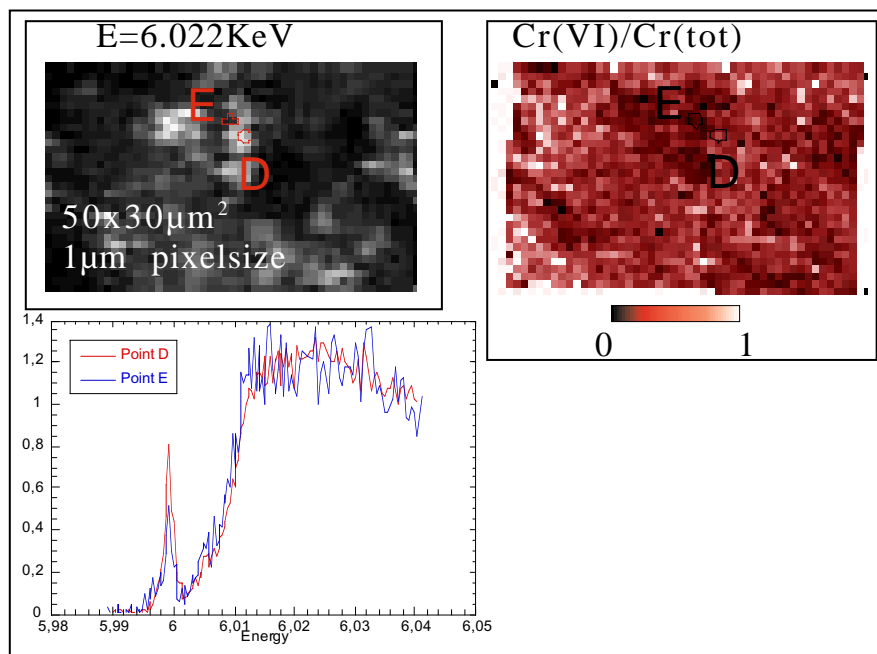


Figure 1: Cr Fluorescence image and XANES spectra of Cr rich zones from the marl.

The analysis of all Cr rich areas from the **marl** indicates that Cr is always under the Cr(III) form. This result shows that the Cr was not oxidized before the formation of the cement through combustion.

Figure 2 : Cr fluorescence image and Cr(VI)/Cr(tot) chemical map of the altered cement. The Cr(VI)/Cr(tot) ratio determined from the chemical map was confirmed on two points (E, D) with XANES.

This Cr(VI)/Cr(tot) chemical map at the micro scale and for dilute natural cement (300 ppm) reveals the extremely high spatial heterogeneity of the oxidation state of Cr for the **altered cement**. The interesting point from these Cr maps, is the contrast



inversion observed between the Cr(tot) and Cr(VI)/Cr(tot) images suggesting that the rich Cr areas exhibit a low Cr(VI)/Cr(tot) ratio. The 500 µm line scans indicate that the higher Cr(VI)/Cr(tot) ratio are observed at the interface between the cements and percolating zones (presence of fractures and highly porous zones).

The line scans and XANES spectra performed for the **unaltered cement** indicate that the Cr is mainly at the 3+ oxidation state. The analysis of the fractured zones of this sample, for which cement phases undergone limited interaction with waters, shows that a fraction of Cr is present at the 6+ oxidation state.

Conclusion

Cr(III) and Cr(VI) were found in the cement samples; generally Cr(III) was the major species (more than 80% in most cases). In the altered parts the Cr(VI)/Cr(tot) ratio evolved from the border to the unaltered core of the material. The mechanisms and conditions of Cr oxidation are not totally understood, especially in terms of O₂ fugacity, but these observations suggest that a diffusive phenomenon exists in different areas and that Cr could be oxidised over very long leaching time scales under high pH-low O₂ fugacity conditions. This study demonstrated the possibility of in situ determination of Cr speciation not only at extremely low concentrations but also with a small beam spot: 1 µm. The Cr speciation map reveals for the first time the highly heterogeneous spatial distribution of Cr(VI) vs. Cr(III). To our knowledge, such an in-situ characterization at the micron scale had never been reported for cement samples.