

Report: Experiment 26-01-769 carried out at DUBBLE (ESRF)

Introduction

The valence state of Cr (speciation) is of primary importance because CrIII is considered to be virtually non-toxic and insoluble (at pH >4), while CrVI is toxic and easy soluble (in all the range of the pH values). The quantification of the later specie in different sampling media (soils, sediments, tailings ...) is challenging with respect to the short-and long-term prediction for toxicity risks and mobilization.

There are a large variety of methods used to measure the different species of chromium in solutions (i.e. water, leachates), e.g. by colorimetry or ion-chromatography, or in the solid state (i.e. soils, sediments) by XRD. The majority of the extraction methods consist in the leaching of the CrVI species in solution by using different techniques which are mainly operationally defined. Moreover due the low detection limit of XRD, carried out on extracted samples no accurate assessment can be made whether all the hexavalent chromium is transferred in solution.

An additional non-destructive technique for solid sampling media, which can be used to determine the relative amounts of CrVI and CrIII in sediments, is by XANES. Moreover this technique can provide information with regard to the oxidation state of an atom, and is not susceptible to matrix effects. The analysis is based on the fact that, CrVI pre-edge in the XANES spectra, differs in intensity and position compared to the CrIII species.

Samples and Experimental Method

Environmental remediation of Cr contaminated sites requires knowledge of the Cr speciation and the quantity of the hexavalent fraction in the contaminated samples. XANES may be used to supply both types of information with minimal sample processing and data analysis. Apart of the preparation of calibration standards, sample preparation is minimal, so changes with respect to the speciation of Cr are avoided. In literature, Cr speciation analysis by XANES is widely recognized and used. Synchrotrone-based technique of the XANES spectroscopy is the most adapted technique for fingerprinting the different Cr species present in solid samples, especially since the signal was interference free from matrix effects. Our experiment were carried out at DUBBLE at scanning energy 5850-6250 eV; first inflection point for CrVI is 5989 eV while CrVI pre-edge is 5998 eV; scanning step size is at 0.05 Å.

Preliminary Results

The calibration curve is the most important step in the use of the XANES method. The absence of a well calibrated Cr pre-edge and standards, implicates the accuracy of the measurements with regard to the speciation of CrVI in contaminated samples. The Cr pre-edge peak was calibrated by the examination of the pre-edge region of a series for model compounds containing known amounts of CrIII and CrVI. The normalized pre-edge mixtures of CrVI+CrIII in the calibration standards consisted of different components containing respectively 75, 50 or 25 % of CrVI versus CrIII, while the end members consisted of analytical grade Cr₂O₃ and K₂CrO₄ (results given in Fig. 1)

The selected sediments consisted of high total concentrations of chromium due to the activity of a former chemical plant that has been producing sodium chromate (Na₂CrO₄) and sodium dichromate (Na₂Cr₂O₇) for around 20 years. Before the XANES investigation the selected samples were characterized geochemically as well as mineralogically. They displayed variable amounts of total Cr concentrations 1130 to 66000 mg/kg occurring in two different valence states, i.e. approximately 75-90% present as CrIII, while 25-10% as CrVI. The data from the different leaching tests were also confirmed by XANES (Fig. 2) where maximally 25%CrVI was detected in the most polluted samples.

Moreover samples where natural attenuation processes and only CrIII species have been observed were analyzed by XANES, which indicated that the pre-peak characteristic for the CrVI species was absent as indicated in Figures 3 and 4.

From the XANES investigation it was clear that the intensity of the curve was affected by the total Cr concentration. Moreover the presence of CrVI species was accurately assessed by the presence of the Cr pre-edge. The use of this technique in fingerprinting the different Cr species was considered as an enormous success in the first experimental experience of our team. However the data reported here are just a fast summary of the data collected at DUBBLE while the main findings of our work will be completed within a research paper aiming for an international journal in order to address a wider scientific audience.

Fig. 4. Standard curve for CrIII versus CrVI in weight ratios

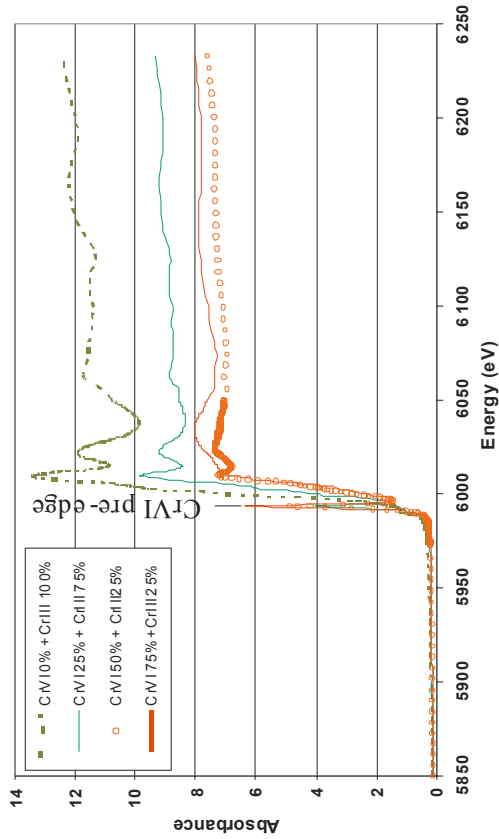


Fig. 2. Samples containing maximally 25% CrVI (visible in the presence of the pre-peak edge, indicated with arrow) are indicated

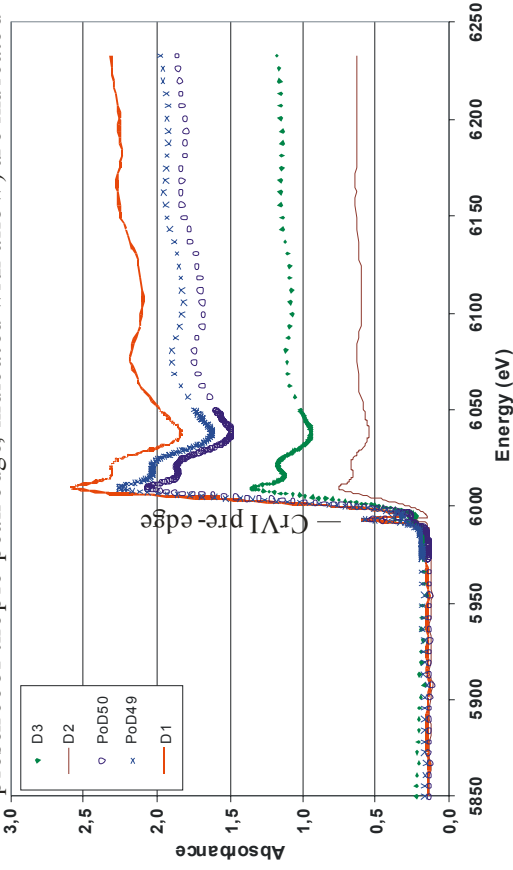


Fig. 3. In these samples due to natural attenuation processes the disappearance of the CrVI pre-edge is clearly observed

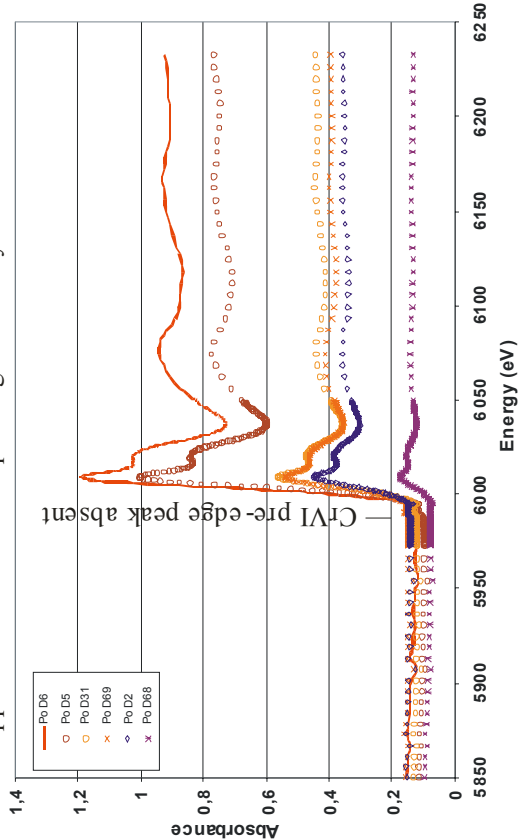


Fig. 4. In these samples CrIII is the only species which was detected from the XANES spectra

