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# The coordination core and charge of Chromium in Metakaolin-geopolymers as revealed by X-Ray Absorption Spectroscopy

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## Abstract

Geopolymers obtained by mixing metakaolin powder with tannery wastewater and NaOH pellets are proposed as 3D aluminosilicate network to chemically entrap Cr(III) species. X-ray Absorption Spectroscopy studies show the absence of toxic Cr(VI). The analysis of EXAFS also reveals a Cr(III) first coordination shell formed by 6 oxygen and a second shell of 7/8 Al or Si atoms, indicating strong bonding with the aluminosilicate network.

## Highlights:

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Geopolymers prepared with as-received tannery wastewater

Zero-water technology

Cr(III) stabilization in aluminosilicate network

XAS/XANES signal at Cr edge shows Cr(III) 6-fold coordinated species

**Keywords:** x-ray absorption spectroscopy, tannery wastewater, geopolymer, chromium.

## Introduction

Recently the topics of circular economy, zero waste and zero water technology are becoming increasingly more important when adopting strategies for environmental impact reduction or safe waste disposal. Chromium is a metal which has a relatively low toxicity at its most common oxidation state, Cr (III), but its oxidation leads to the 100 fold more toxic state, the hexavalent form, Cr(VI)<sup>1</sup>. Many industries make use of large amount of soluble chromium salts, such as  $[\text{Cr}_2(\text{H}_2\text{O})_6(\text{OH})_4]\text{SO}_4$  (CAS#39380-78-4), used extensively in the tanning industry. The treatment of wastewater containing chromium in a complex matrix is being tackled using an alkali activated material exploiting its ability of solidification/stabilization<sup>2,3</sup>. Here, we propose a metakaolin(MK)-based geopolymer obtained by mixing the MK powders with Cr(III)-bearing wastewater and sodium hydroxide as alkali activator to treat via solidification.<sup>4</sup> Differently from what is already proposed in recent literature, on the use of geopolymer composites as adsorbents for removal of heavy metal ions from water<sup>5</sup>, we propose a chemical entrapment of Cr(III) within the 3D aluminosilicate network by introducing the wastewater directly in the preparation of the fresh paste.

The concern is that the extreme alkalinity of the solution could oxidize the trivalent chromium in its more hazardous hexavalent form. In this letter we use the sensitivity of the x-ray absorption spectroscopy (XAS) for the atomic species within the bulk of solid materials to demonstrate

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unambiguously the occurrence of Cr(III) in the geopolymer product. XAS can be applied to both solution<sup>6</sup> and solid samples<sup>7</sup> and was used as a fingerprint of the Cr(III) in spinel-based glass-ceramic matrix<sup>8</sup>.

## Experimental

Two different geopolymer formulations were prepared as described in a previous study<sup>4</sup> adding 14 wt% NaOH pellets to the as-received Cr(III)-bearing tannery wastewater. Formulation GeoCr5 contained 5 wt% of wastewater with respect to MK powder, Argical<sup>TM</sup> M1000, Imerys, France (Cr content referred to the MK = 0.6wt%), while GeoCr30 contained 30% (Cr content referred to the MK = 3.3wt%). This zero-water approach required addition of about 66 wt% of Na-silicate solution (SiO<sub>2</sub>/Na<sub>2</sub>O =3, 43 wt%, by Ingessil, Italy), referred to the weight of the wastewater, to obtain a homogeneous geopolymeric paste, Table 1.

Table 1. Composition of the geopolymer

Geopolymer	Water (g)	MK(g)	Na Silicate (ml)	NaOH (g)
Geochrom	10.2	51	34	7

The elemental analysis of the starting material is reported in the supplementary data.

The chromium content in the wastewater used is 5420 ppm, the complete composition is available for consultation in the supplementary data. The morphological homogeneity of the cured geopolymer was confirmed by SEM micrograph, see supplementary data, and composition homogeneity by EDS-analysis performed on several points.

Samples for the XAS data collection were prepared as pellets. 40 mg of GeoGr5 and 10 mg of GeoCr30 were mixed with 110 mg of cellulose (Merck 310697) and pelletized at 3 tons.

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X-Ray Absorption experiments were performed at Sincrotrone Elettra in Basovizza (Italy) at the XAFS beam line<sup>9</sup>. The storage ring operated at 2.0 GeV in top-up mode with a typical current of 300 mA. XAS data were collected at Cr K-edges in transmission mode. Data were collected from 5700 eV to 6735 eV at the Cr K-edges, with a constant k-step of 0.03 Å<sup>-1</sup> with 2 s/point acquisition time. Data analysis were performed by using the GNXAS package<sup>10</sup>. Details of the data collection and analysis in the Appendix **A**.

## **Results and discussion**

The sensitivity of the XAS probe for the atomic species allowed to gain a clear understanding of the local structure arrangements and charge of chromium in a selected Cr-bearing geopolymer. The relevant information is provided by both XANES and EXAFS portions of the XAS spectrum. Figure 1 displays the normalized K-edge XANES curves relative to both samples GeoCr30 and GeoCr5 compared to reference oxides of chromium. Not only the edge energy of both samples is nearly coincident to the Cr(III) oxide reference sample but also its general shape of the curves. Unlike the Cr(VI) oxide reference sample, both geopolymer samples do not display the typical and very intense pre-edge peak A. This transition is used as fingerprint of the Cr(VI) in the environment<sup>11</sup>. Overall, the XANES data suggest the occurrence of the Cr(III) in both geopolymeric samples, yet within a very similar geometric environment. This is also corroborated by the linear combination fitting analysis (see Appendix A) of samples GeoCr5 and GeoCr30 and using Cr(III) and Cr(VI) oxides.

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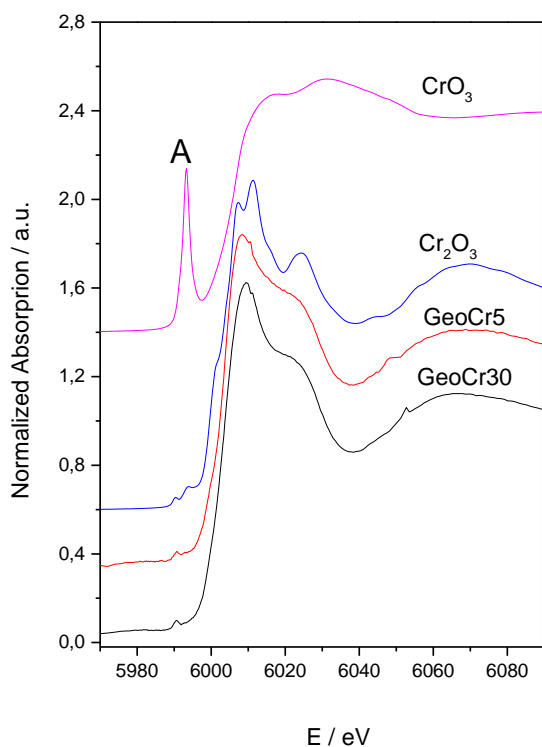


Figure 1. XANES spectra at Cr K-edge of geopolymers GeoCr5 and GeoCr30. Cr(III) and Cr(VI) oxides are also displayed for reference.

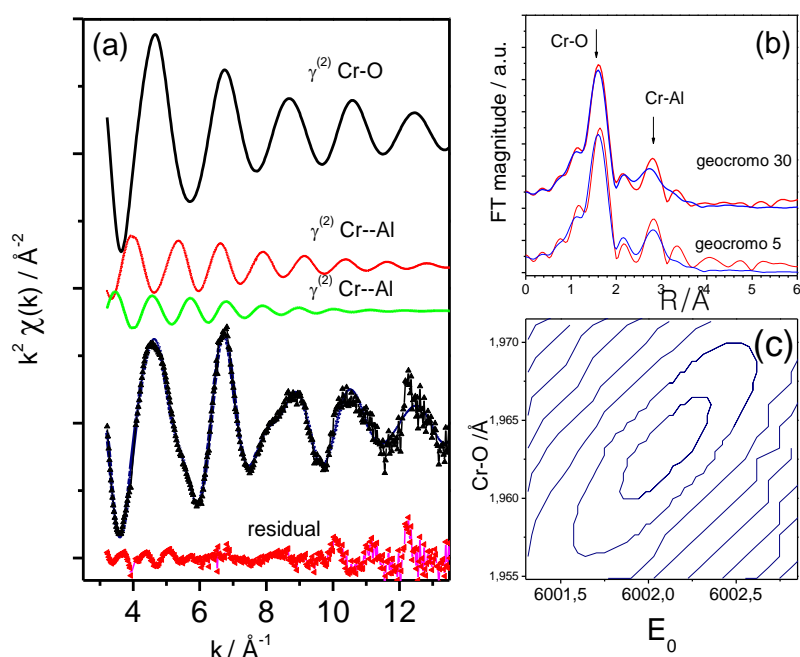
The analysis of the extended portion of the XAS spectrum, EXAFS, provides the local structural information of chromium, i.e. its coordination core site. Figure 2b displays the comparison of the Fourier Transform (FT) curves relative to the EXAFS signals for both samples GeoCr30 and GeoCr5. FTs suggests a scattering contribution (first atomic shell) at around 1.9 Å and a possible second atomic shell at less than 3 Å. More details can only be achieved through an accurate EXAFS data analysis. Figure 2a reports the details of the EXAFS analysis in terms of single scattering path to the total theoretical EXAFS, and the comparison to the experimental one, for sample GeoCr30 as

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an example. Table 2 presents the relevant structural information as obtained by the best fitting, together with their respective statistical errors. They were obtained by correlation maps for the highly correlated parameters (Fig. 2c).

The theoretical signal matches well with the experimental one in Fig. 2a, demonstrating the reliability of the data analysis. Even though the first shell signal due to the Cr-O interaction is the most intense and important signal, there is a non-negligible contribution due to the second atomic shell, which is seen to be due to a Cr - Al interaction (not direct bonding). As reported in Table 2 Cr(III) was found to be 6-fold coordinated by oxygen in the first shell in both investigated geopolymers, with distances of 1.963(4) Å and 1.960(6) Å, respectively for sample GgeoCr30 and GeoCr5. This distance is shorter respect to the Cr<sub>2</sub>O<sub>3</sub> reference samples. Also, the EXAFS bond variance values suggested a very strong bonding between chromium and oxygen.



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Figure 2. EXAFS best fit result. (a) Sample GeoCr30. Single individuals multiple scattering signal and comparison of the total theoretical to the experimental. The residual signal is indicated at the bottom. (b) Comparison of the experimental and theoretical Fourier Transform (FT) curves for samples A and B. (c) Examples of correlation maps for the parameter errors determination. The figure indicates the highly correlated variables, the  $E_0$  and Cr-O distance.

The second shell is actually composed by two interactions, both due to Cr - - Al, one at around 2.82-2.84 Å, the other at longer distances, 3.20-3.22 Å. These contributions can be postulated arising from the Cr-O-Al(Si) atomic triplet with an oxygen bridge. The coordination number (CN) of those scattering contributions were let floating during the minimization, and the best fit released an overall value of ~ 7-8 for both investigated samples. This value is affected by a large error as the CN variable is strongly correlated with the Debye Waller factor  $\sigma^2_{\text{Cr-Al}}$  and the reduction factor  $S_0^2$ . This, in addition to the noise of the measurements makes the CN quotation not clearly determined. Anyway, a CN of  $7-8 \pm 1$  may suggest a  $\text{CrO}_6$  structural units (evidenced by the more reliable first coordination shell) trapped within the aluminosilicate network.

Table 2: EXAFS Best fit parameters at the Cr K-edge. Errors in parenthesis have been determined by contour plots (see Figure 3c).

	<b>GeoCr30</b>	<b>GeoCr5</b>
Cr-O /Å	1.963(4)	1.960(6)
$\sigma^2_{\text{Cr-O}} / \text{Å}^2$	0.0011(4)	0.0011(4)
CN <sub>Cr-O</sub>	6 FIX	6 FIX
Cr-Al /Å	2.82(1)	2.84(2)
$\sigma^2_{\text{Cr-Al}} / \text{Å}^2$	0.006(2)	0.007(2)
CN <sub>Cr-Al</sub>	3.9(5)	4.0(4)
Cr-Al /Å	3.22(2)	3.206(15)
$\sigma^2_{\text{Cr-Al}} / \text{Å}^2$	0.011(3)	0.005(2)

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CN <sub>Cr-Al</sub>	3.9(5)	3.2(5)
E <sub>0</sub> / eV	6002.1(3)	6002.0(3)
S <sub>0</sub> <sup>2</sup>	0.71 FIX	0.71 FIX

## Conclusions

Summarizing XANES-EXAFS analyses on 3D bulk structure of Cr-bearing geopolymer indicate: i) the existence of only Cr(III) species in the samples after geopolymerization and, ii) structurally speaking, the chromium site is found to be octahedrally coordinated by oxygen as the first shell forming a CrO<sub>6</sub> figure, and iii) an interaction of the Cr with the 3D aluminosilicate network suggested the occurrence of Cr-O-Al bridges, rather than a segregation as pure oxide Cr<sub>2</sub>O<sub>3</sub>.

The low leachability of both geopolymers indicates that a zeolitic cage is likely formed around the Cr(III) species, thus achieving a chemical entrapment<sup>12,13</sup>.

## Acknowledgements

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## Appendix A. Supplementary data

Metakaolin XRF chemical analysis and XRD characterisation. Tannery waste water characterization. Cured geopolymer characterization (SEM). Linear Combination Fitting (LCF) analysis of the XANES spectrum for samples GeoCr30 and GeoCr5 and details of the x-ray absorption data collection and analysis (8 pages).

Supplementary data to this article can be found online at ...

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