

Micro and conventional XAFS study of incinerated Cr-rich tannery sludge

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Abstract. μ -XRF, XAFS and μ -XAFS spectroscopies were implemented in order to investigate the effect of thermal annealing on the stability of a vitrified tannery waste. The two dimensional μ -XRF scans disclose the presence of Cr-rich and depleted regions where both Cr(III) and Cr(VI) are present. However the polymerization of the Cr-O-Cr chains is different in these two distinct regions. More specifically, the μ -XANES and μ -EXAFS results reveal that in the Cr-rich inclusions, the Cr(III)O₆ belong to Cr₂O₃, while in the Cr-depleted regions, different linkages among the Cr(III)O₆ octahedra are detected. The percentage of the different type of polymeric structure around Cr(III) in the two distinct regions was assessed using Cr-K-EXAFS and XANES spectroscopies. It is revealed that upon thermal annealing the number of Cr(VI) ions is preserved and participate in the formation of the glass matrix. Even though Cr(III) is a glass modifier, the local coordination of the Cr(III)-octahedra changes upon thermal treatment. The presence of Cr(VI) suggests the limited capacity of the vitrification process to inhibit Cr(III) oxidation, however, Cr(VI) is safely trapped into both the glass and glass-ceramic matrix.

1. Introduction

The common practice of land-based disposal of tannery wastes, where trivalent chromium [Cr(III)] is the dominant species, is responsible for the contamination of soils. Furthermore, the presence of naturally occurring minerals (e.g. Mn oxides) can promote the oxidation of Cr(III) to the more toxic Cr(VI), thus water pollution with Cr(VI) can also be related to the current disposal criteria for tannery wastes [1]. Chrome tanning produces two types of sludge, hair-burn and chrome: the former is produced during the mechanically scrapping and soaking of salt-cured hides and is mainly organic, while the latter is a chrome sludge, produced after sequentially cleansing and soaking of hair in a NaCl-H₂SO₄ solution, bathed for several hours in a basic Cr(SO₄)₃ solution and neutralized with NaHCO₃ [2].

Incineration of the Cr-sludge at extremely high temperatures is a process that minimizes the need for additional land disposal; during incineration, the toxic components are converted to harmless or less harmful compounds whereas the volume of waste is significantly reduced. However, the wastes produced during pre-treatment and in the combustion unit (ashes and other residues) may still be toxic and must be disposed in an environmentally sound manner. Stabilization via vitrification of incinerated tannery waste is a promising and cost effective method that leads to the formation of glass and vitroceramic products, capable of immobilizing the Cr(III) and Cr(VI) species [3]. The aim of this work is to investigate the feasibility of preparing glass and vitroceramic materials that immobilize safely chromate and chromite, whether the oxidation of Cr(III) has been provoked and if the presence



of Cr(III) and Cr(VI) species are involved in the building of the glass matrix (glass forming role of Cr(VI) and network modifying role of Cr(III)).

2. Experimental details

The studied tannery sludge originates from the industrial zone of Thessaloniki in northern Greece and was incinerated for 1.5 h at 500 °C in an oxygen-starved atmosphere under anoxic conditions. In this process Cr(III) is not oxidized to the highly toxic and mobile Cr(VI) and also nearly most of organic carbon is removed. The resulting chromium-loaded ash was rich mainly in Ca (% 16 mass%) and Cr (% 15.5 mass%) with few remaining organic content [4]. The Cr-loaded ash was then mixed with glass-forming oxides (SiO₂) and network modifiers (CaCO₃ and Na₂CO₃ in the form of CaCO₃ and Na₂CO₃ respectively) and melted in a platinum crucible at 1400 C for 2 h. The melt was then quenched in air on a refractory steel plate. The chemical composition of the studied glass is 10 wt% ash, 20 wt% CaO and a SiO₂/Na₂O ratio equal to 3.66. In an effort to produce vitroceramic products by controlled crystallization of the initial vitreous products, thermal treatment is applied at 880°C.

XAFS measurements were conducted at the KMC2 beamline at the synchrotron radiation facility BESSY in Berlin. The beamline is equipped with a double-crystal monochromator and capillary optics that allow the reduction of the beam diameter down to 4.8µm. Two dimensional µ-XRF scans allows for the detection of variations in the distribution of Cr in samples that developed annealing-induced inhomogeneities. Thus, combination of µ-XRF with µ-XAFS spectra recorded from selected sample spots permit the investigation of the local bonding environment of Cr, as a function of the Cr-varying distribution. Both XAFS and µ-XAFS spectra were recorded in the fluorescence yield mode using an energy dispersive (Röntec) detector and Cr₂O₃, Cr(OH)₃ and CrO₃ powders were used as references.

3. Results and Discussion

3.1. µ-XRF

A representative 300 µm² 2D-map of the studied thermally treated glass depicting the varying distribution of Cr is shown in Fig. 1(a). It is characteristic that in the Cr-rich regions, the Cr-content is 5 to 10 times higher compared to the Cr-depleted regions. The analysis of the µ-XRF spectra (figure 1(b)) recorded from the two distinct spots shown by arrows in Fig.1(a) reveal that the Cr/Ca concentration ratio differs: in the Cr-rich (Cr-high) inclusions the Cr/Ca ratio is three times higher than the respective in the Cr-poor (Cr-low) regions (0.35 and 0.11, respectively).

3.2. Cr-K-µ-XANES and Cr-K-XANES

In an effort to correlate modifications in the oxidation state and the bonding environment of Cr as a result of its inhomogeneous distribution, Cr-K-µ-XANES spectra were recorded from spots high- and low-Cr concentration. Similar to all 3d-transition metals, a pre-edge absorption occurs in the XANES spectra from both regions (shown in figure 2(a)), the characteristics of which are modulated by the Cr-valence: a prominent pre-edge peak occurs for Cr(VI) species, caused by transitions from an 1s state to empty d-orbital and though forbidden for octahedral Cr(III), a small pre-edge peak is present due to 3d(t_{2g}) and 3d(e_g) electronic transitions, respectively. As shown in figure 2(a), both the intensity and energy position of the pre-edge peak, which is a measure of the proportion of Cr(VI) in mixed valence samples, is not significantly altered [5]. However, the structure above the absorption edge (E_{abs}) is modified between the two regions: in the Cr-rich region, the spectrum resembles the respective in Cr₂O₃ while weak structure exists in the Cr-depleted region. The same conclusion can be drawn for the XANES spectra of the glassy and annealed sample: the intensity and energy position of the pre-edge peak are similar; however the changes in the structure above the E_{abs} are prominent. These findings imply the presence of both Cr(III) and Cr(VI) species and thus linear combination fitting (LCF) was applied in order to evaluate the changes in the Cr(III)/Cr(VI) ratio as a function of both Cr-concentration and annealing process.

The application of LCF using the experimental spectra of the Cr_2O_3 and CrO_3 reference samples does not yield satisfactory results in most of the samples. Nevertheless, if the experimental spectrum of a $\text{Cr}(\text{OH})_3$ sample is used, the fitting quality is significantly improved (colored dotted lines in figure 2(a)). Even though in both Cr_2O_3 and $\text{Cr}(\text{OH})_3$ compounds Cr is trivalent, the $\text{Cr}(\text{III})\text{O}_6$ octahedra link in different modes: in the former case they share one face, two edges and three corners while in the latter case, two Cr-octahedra share two edges and link to four adjacent polyhedra. Thus, the use of $\text{Cr}(\text{OH})_3$ in LCF does not indicate the presence of Cr-oxyhydroxides but rather the modification in the polymerization of the Cr-O-Cr chains. As listed in table 1, Cr(VI) species are always detected: the same amount of Cr(VI) exists in both the Cr-depleted and Cr-rich regions, while upon annealing of the glassy sample, a change in the percentage of Cr(VI) is not detected. However, as listed in table 1, Cr(III) belongs only to Cr_2O_3 inclusions in the Cr-rich region. In the Cr-depleted region, 53.1 % of the Cr(III) ions connect in a network similar to the structure of Cr_2O_3 while 29.5 % of $\text{Cr}(\text{III})\text{O}_6$ follow the polymeric structure of $\text{Cr}(\text{OH})_3$. In the glassy sample, the Cr-octahedra connect via edges and corners as in $\text{Cr}(\text{OH})_3$, while upon annealing the polymerization of the Cr-O-Cr chains changes completely. Thus, it is concluded that the Cr(VI) concentration is not affected by the varying distribution of Cr in the annealed sample, however changes in the type of linkage among the Cr-octahedra are induced. Upon thermal treatment of the glass, reduction of Cr(VI) is not detected while the Cr(III)-groups change their polymerization

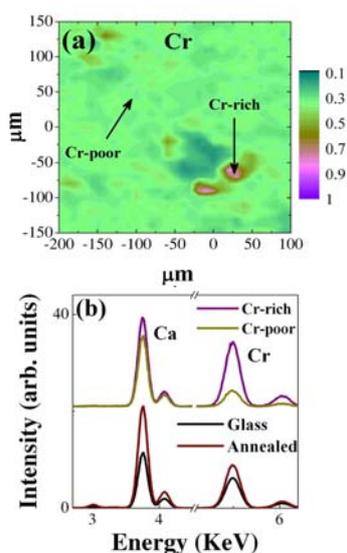


Figure 1. (a) 2D μ -XRF scans of the annealed glass showing the inhomogeneous distribution of Cr. The color bar represents the normalized intensity. (b) μ -XRF spectra recorded from the Cr-rich and Cr-depleted regions and XRF spectra of the glassy and annealed sample.

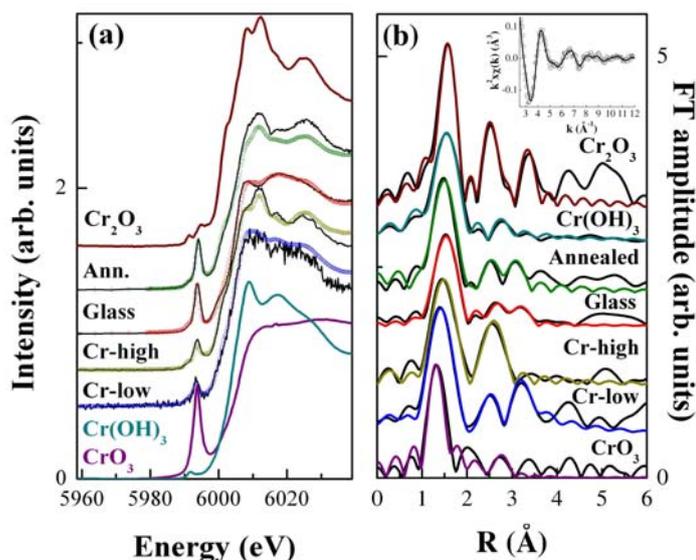


Figure 2. (a) Cr-K- μ -XANES spectra recorded from the Cr-rich and Cr-depleted regions of the annealed sample and Cr-K-XANES spectra of the glassy and annealed sample. The results of the linear combination fit (LCF) are shown in colored dotted lines. (b) Fourier Transforms (FT) of the $k^2 \times \chi(k)$ Cr-K- μ -EXAFS spectra recorded from the Cr-rich and Cr-poor regions of the annealed sample and Cr-K-EXAFS spectra of the glassy and annealed samples. A representative $k^2 \times \chi(k)$ EXAFS spectrum and the fitting is shown in circles and in a black line, respectively.

3.3. Cr-K- μ -EXAFS and Cr-K-EXAFS

Taking into consideration the results from the μ -XANES analysis, the Cr-K- μ -EXAFS spectra were fitted assuming that in the Cr-rich and Cr-depleted regions, the Cr(III)- and Cr(VI)-polyhedra link via

edges and corners, i.e. form Cr(III)O₆ octahedra that share edges and corners and Cr(VI)O₄ tetrahedra that share only corners. Curve fitting was carried out simultaneously in the R- and k-space using FEFF. The Fourier Transforms (FTs) of the k²-weighted Cr-K-μ-EXAFS spectra recorded from the high- and low-concentration-Cr-regions are shown in figure 2(b) and the analysis results are listed in table 1. In very good agreement with the Cr-K-μ-XANES results, it is found that approximately 25 (±8) % of Cr exists as Cr(VI) in both the Cr-rich and Cr-depleted regions where it is tetrahedrally coordinated and the Cr-O bondlength is equal to 1.60-1.62Å. However, even though the number of the Cr(III)O₆ is equal (within the error bar) in both regions, they link to the glass matrix in a different manner. Cr(III) belongs to Cr₂O₃ inclusions in the Cr-rich regions while in the Cr-depleted regions the polymerization of the Cr-O-O chains is modified: approximately 75% of Cr-polyhedra connect to adjacent polyhedra as in Cr₂O₃ while the rest link only via edges and corners, in a less compact structure, similar to Cr(OH)₃. The analysis of Cr-K-EXAFS spectra of the glassy and annealed sample reveal that upon annealing, the percentage of Cr(VI) does not change. In analogy with the μ-XAFS results, the polymerization of the Cr(III)O₆ chains is modified due to thermal treatment: Cr(III) links to adjacent Cr-polyhedra as in Cr(OH)₃ in the vitreous sample while after annealing, the Cr(III) are mainly involved in a linkage as in Cr₂O₃.

Table 1. LCF results of the μ- & conventional Cr-K-XANES of all studies samples. μ- & conventional Cr-K-EXAFS results of all studies samples.

	XANES LCF (%) (±5)			EXAFS				
	CrO ₃	Cr ₂ O ₃	Cr(OH) ₃	Cr(III)O ₆ (%) (±8 %)	Cr ₂ O ₃ (%) (±12 %)	R _{Edge} Cr(III) (±0.02 Å)*	R _{corner} Cr(VI) (±0.03 Å)*	R _{corner} Cr(III) (±0.04 Å)*
Cr-rich	11.2	88.8	-	73.1	75.5	2.90	3.31	3.46
Cr-poor	17.4	53.1	29.5	74.2	69.2	2.86 & 2.94	-	3.41 & 3.53
Glass	49.4	-	51.6	58.4	-	3.01	3.28	3.51
Annealed	37.9	49.5	17.6	49.6	72.6	2.86 & 2.95	-	3.45 & 3.52
CrO₃				0	-		3.34	-
Cr(OH)₃				100	-	2.98	-	3.50
Cr₂O₃				100	100	2.90	-	3.44

*R_{edge} and R_{corner} are the inter-atomic distances in the higher shells.

4. Conclusions

The effective stabilization via vitrification of Cr-rich tannery waste was investigated using micro- and conventional XAFS spectroscopies. Cr(VI) is present before and after thermal treatment, however it acts as glass former, and thus is safely immobilized into the glass matrix. The percentage of Cr(VI) is not affected by either Cr-concentration or thermal treatment. The Cr-inclusions formed after thermal treatment are rich in Cr₂O₃ while in the Cr-depleted regions, the bonding geometry of Cr(III) changes due to the different configuration of the Cr(III)O₆ polyhedra in space. In the vitreous sample, the polymerization of the Cr(III)-chains resembles the respective in Cr(OH)₃ while upon annealing the existing Cr(III)O₆ units preferentially link as in Cr₂O₃.

Acknowledgments

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