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IN SITU X-RAY ABSORPTION SPECTROSCOPY STUDY OF RADIOLYSIS-INDUCED REDOX IN CHROMIUM NITRATE AQUEOUS SOLUTION UNDER SUPERCRITICAL CONDITION

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Abstract

The radiolysis-induced redox in a chromium aqueous solution was observed based on synchrotron X-ray absorption spectroscopy (XAS) measurements. The *in situ* Cr *K*-edge XAS spectra were acquired for a chromium nitrate aqueous solution with the concentration of Cr(III) at 1000 ppm from room temperature up to 500 °C. The radiolysis in this fluid sample within a Bassett-type hydrothermal diamond anvil cell (HDAC) caused the oxidation of Cr(III) to Cr(VI) at 300 °C, and the reduction of Cr(VI) to Cr(III) at 500 °C. The two components of the pre-edge peaks of the *K*-edge spectra were fitted using an established fitting model and applied to identify the presence of Cr(VI) in the solution. The influence of the high basicity ligand, *i.e.* Cl^-, on the electronic environment of the Cr centre is also discussed.

1. Introduction

The coolant of the Canadian supercritical water-cooled reactor (SCWR) will enter the reactor core at 350 °C and exit at 625 °C. The ability to control the coolant water chemistry in order to minimize corrosion and radionuclide transport is regarded as a key point to the long-term viability of the SCWR.[1-3]. The candidate fuel cladding alloys for all Generation IV SCWR concepts are steels. Accordingly, a detailed understanding of the speciation and solubility of the elements of various stainless steel alloys is essential. In particular, the interaction between supercritical water and the oxides formed on the surface of the alloys is of considerable interest. As the Canadian SCWR is expected to use stainless steel alloy as the fuel cladding and their alloys derive their corrosion resistance from the formation of a protective chromium oxide film, it is important to investigate chromium chemistry in SCW.

Synchrotron-based X-ray absorption spectroscopy (XAS) is a well-recognized technique to probe the structural and coordination environmental information which indicate the metal-metal and/or metal-water interaction in aqueous solutions.[4, 5] It provides a spectroscopic tool to monitor *in situ* chemical changes occurring in hydrothermal aqueous solutions at elevated temperatures and pressures and has thus been employed in the study of many aqua metal ions.

In this study, XAS spectra were used to monitor the redox behaviour of chromium in aqueous solution from room temperature up to 500 °C. The 1s-to-3d photoelectron transition features in the pre-edge region of the Cr *K*-edge are fitted into two components using an established fitting model.[6] The tetrahedral component is utilized to infer the existence of Cr(VI) in the hydrothermal solution as a function of temperature and pressure. The influence of the basicity of the aqueous environment of the chromium ion on the radiolysis-induced redox chemistry is also discussed.

2. Experiment

A $Cr(NO_3)_3$ standard aqueous solution with the concentration of 1000 ppm Cr in nitric acid was purchased from Sigma-Aldrich (lot number BCBF5917V). For testing the influence of a coordinating ligand, LiCl was added to the Cr standard solution to yield a sample with a molar ratio of $Cl^-/NO_3^- \approx 1:1$.

The synchrotron XAS measurements were made on the solution sample loaded in a Bassett-type hydrothermal diamond anvil cell (HDAC). The HDAC consists of an upper diamond anvil with a flat culet face and a lower diamond anvil with a 300 μm-diameter cylindrical sample recess situated in the center of the culet face. No gasket was used between the anvils to avoid possible contamination and to avoid non-isochoric behavior of the fluid sample due to gasket corrosion and deformation under high pressure-temperature conditions. The lower anvil has two milled grooves leading to the sample recess. These grooves reduce the attenuation of the incident x-rays and the signal fluorescence. The sample was loaded into the recess of the lower diamond and sealed, together with a vapor bubble, against the upper diamond anvil (see Figure 1). Sample pressure upon heating was estimated using the equation of state of water.[7]

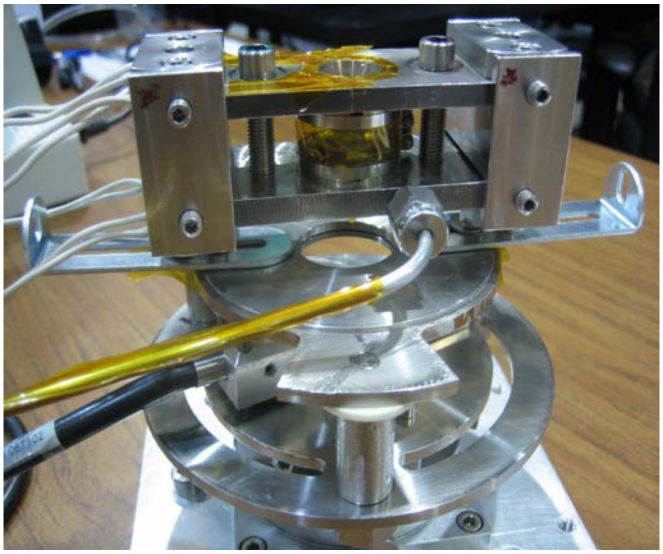

Figure 1 The Bassett-type hydrothermal diamond anvil cell (HDAC).

Cr *K*-edge (5989.0 eV) XAS measurements were carried out on the Cr aqueous solution sample at the PNC/XSD beam line 20-ID-B of the Advanced Photon Source (APS), Argonne National Laboratory. The sample pressure varied from vapour pressure (close to atmospheric) at 25 °C to ~ 200 MPa at 500 °C. A 4-element Vortex detector, placed horizontally at 90^o orientation to the incident micro-focused (ca. 4-5 μm dia.) x-ray beam, was used to measure the fluorescence XAS spectra. The synchrotron was operated at 7.0 GeV and 100 mA maximum fill current. The incident x-ray beam flux was $1x10^{11}$ photons/second. Cr *K*-edge calibration was accomplished using Cr metal foil.

The pre-edge features of the XAS data were analyzed using the following steps. Firstly, all XAS spectra were normalized by setting the *K*-edge step height to 1. The background curves were then obtained by fitting the data near the pre-edge features with third-order polynomials. After the background subtraction, the pre-edge peaks were fitted into two components with multi-Gaussian functions.[6]

3. Results and discussion

The *in situ* Cr *K*-edge XAS spectra measured for the Cr(III) standard solution at different temperatures are shown in Figure 2. In order to provide a reference, the spectrum for $Cr(NO_3)_3$ is also presented. As has been reported previously,[8, 9] the pre-edge region of the Cr K-edge is composed of two components at the transition position near 5990 eV and 5993 eV respectively. The feature near 5990 eV is due to the 1s-to-3d transition of the X-ray induced photoelectron of the Cr(III) aqua ion in octahedral coordination. The feature near 5993 eV is consistent with a 1s-to-3d photoelectron transition of the tetrahedrally coordinated chromium complex, indicating the existence of Cr(VI) in the sample.[10] The pre-edge peaks of the Cr *K*-edge X-ray absorption near edge structure (XANES) increase significantly when the sample is heated from room temperature to 300 ^{o}C, indicating the occurrence of radiolysis-induced chemical reactions. The intensity of the pre-edge feature of the Cr *K*-edge increased to a peak value at 400 ^{o}C and started to decrease when the temperature of the sample was increased from 400 ^{o}C to 500 ^{o}C, and when cooled from 500 ^{o}C to 300 ^{o}C. These observations indicate that the radiolysis induced reaction is temperature dependent and reversible. The pre-edge region of the Cr *K*-edge XAS spectra before the background subtraction are also shown in Figure 2(b).

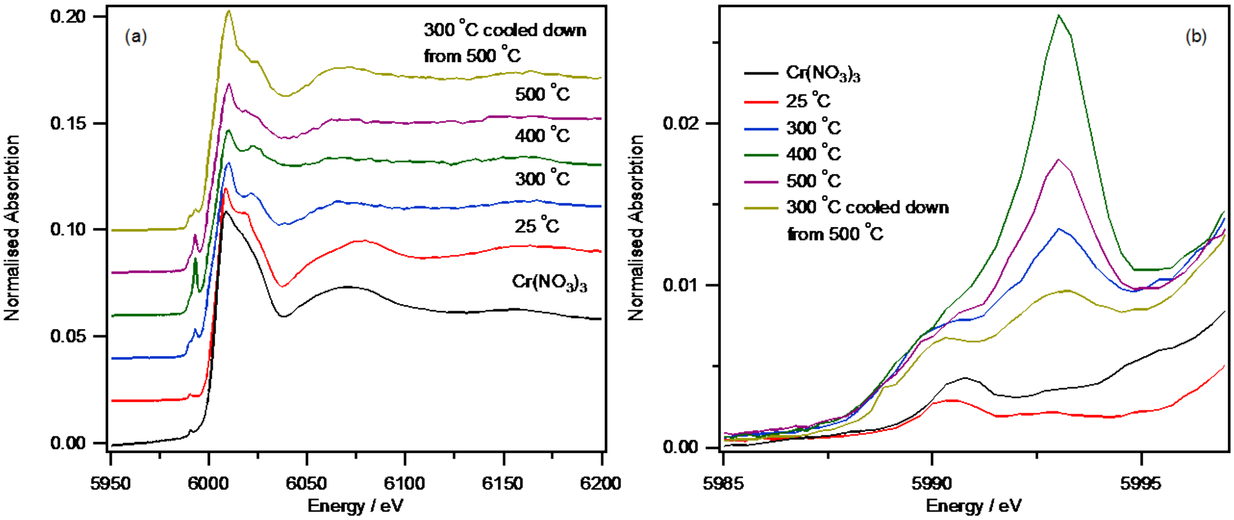

Figure 2 (a) Cr K-edge XAS spectra of $Cr(NO_3)_3$ and the aqueous solution at different temperatures. (b) The pre-edge peaks before background substraction.

Figure 3a shows a more detailed analysis of the background-subtracted pre-edge feature. It illustrates the change of the concentration of the Cr(VI) component in the solution as a function of temperature. The increase in intensity of the 5993 eV pre-edge feature when the sample is heated from room temperature to 400 ^{o}C is indicative of the oxidation of Cr(III) to Cr(VI). However, the reduction of Cr(III) to Cr(VI) occurs when the sample is heated from 400 ^{o}C up to 500 ^{o}C and cooled down from 500 ^{o}C to 300 ^{o}C.

The fitting data of the two temperature-dependent components (see Table 1) of the XANES pre-edge region also suggests that the energy of the tetrahedral-symmetry 1s-to-3d transition component feature (A2) is shifted to higher energy values when the temperature of the sample was increased from room temperature to 400 °C. The maximum value is observed at 400 °C and this shifts to lower energies when heated to 500 °C and during cooling to 300 ºC. (see Figure 3b).

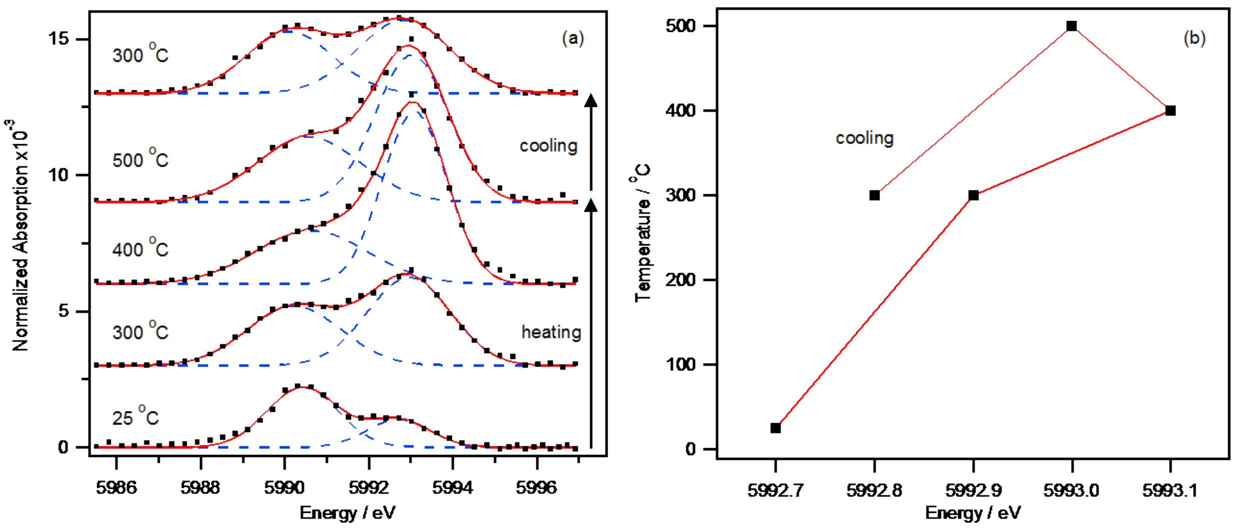

Figure 3 (a) The pre-edge peaks after the background subtraction. The dotted lines show the two fitted components and the solid lines show the envelope of the peaks. (b) The energy of the tetrahedral 1s-to-3d transition component plotted against the temperature. Note: the point labelled 'cooling' is derived from the spectrum acquired when the sample was cooled from 500 °C to 300 °C.

Table 1 Data from fitting of the XANES pre-edge peaks. Note: '300 cooling' is derived from the spectrum acquired when the sample is cooled down from 500 °C to 300 °C. '300 with Cl$^-$' is the data for the solution with Cl$^-$ as ligand at 300 °C.

T	A1				A2				A2/A1
(°C)	Area	Centre (eV)	Width (eV)	Height	Area	Centre (eV)	Width (eV)	Height	
$Cr(NO_3)_3$	0.0063(5)	5990.6(1)	1.4(1)	0.0035	0.0013(5)	5992.7(4)	1.2(2)	0.0009	0.21
25	0.0047(2)	5990.4(5)	1.7(1)	0.0022	0.0019(2)	5992.7(1)	1.5(2)	0.0010	0.40
300	0.0146(7)	5990.2(5)	2.2(1)	0.0052	0.0191(6)	5992.9(3)	2.0(1)	0.0077	1.31
400	0.0199(6)	5990.6(1)	2.7(2)	0.0059	0.0368(5)	5993.1(1)	1.5(1)	0.0192	1.85
500	0.0154(3)	5990.6(2)	2.5(2)	0.0050	0.0245(3)	5993.0(3)	1.7(1)	0.0113	1.59
300 cooling	0.0117(5)	5990.1(5)	2.1(1)	0.0045	0.0148(5)	5992.8(4)	2.2(7)	0.0054	1.26
300 with Cl$^-$	0.0198(3)	5990.5(2)	2.8(2)	0.0057	0.0241(2)	5992.8(1)	2.0(1)	0.0098	1.22

The coordination environment and metal oxidation state have a determinative effect on the configuration and electronic occupation of the molecular orbitals of a metal complex.[11-13] This is manifested in p-d orbital hybridization or mixing and ligand-to-metal-ion charge transfer effects on the metal complex site, which can be directly probed by XANES. The coordination and the interaction effects (i.e. through orbital overlap and electron donation) of the ligand directly affect the chemical properties of the metal complex. The temperature-dependent energy shift exhibited in Figure 3 (and from the data in Table 1) predominantly reflects the temperature-dependent radiolysis-induced oxidation/reduction reactions involving the chromium ion.

Figure 4a compares the Cr *K*-edge of the Cr standard solution with and without Cl^- as a coordinating ligand at 300 ^{o}C. A shoulder is observed at approximately 6025 eV in the spectrum obtained for the Cr standard solution with Cl^-. As expected, the Cl^- ligand coordinated with the Cr centre leads to a solution with more species which includes Cr(III) and Cr(VI) aqua ions, as well as Cr chloroaqua and chlorochromate complexes, such as $Cr(III)(OH_2)_5Cl^{2+}$ and $Cr(VI)O_3Cl^-$, respectively, and/ or higher Cl^- coordination number complexes. The change of the speciation in the solution leads to a shift of the Cr *K*-edge to lower energy and an observed shoulder before the K-edge feature.

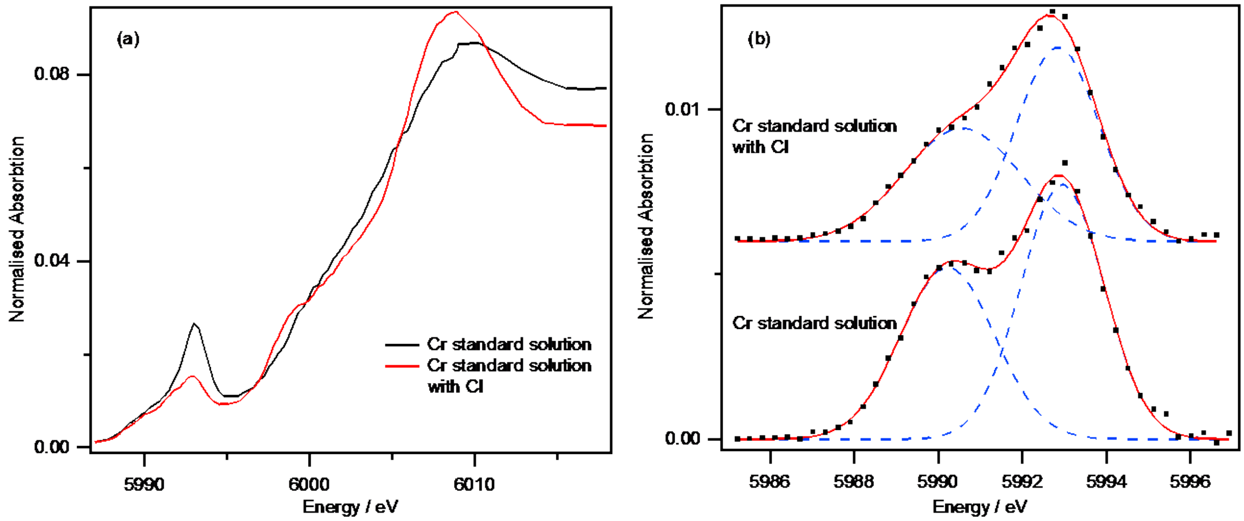

Figure 4 (a) XAS spectra of the Cr standard solution with and without Cl^- as ligand at 300 ^{o}C. (b) The pre-edge peaks after the background substruction.

It is evident that the effect of the high basicity ligand, *i.e.* Cl^-, is a slight lowering of the degree of radiolysis induced oxidation of Cr(III) to Cr(VI) (see Figure 4b). As indicated from the data shown in Table 1, the oxidation reaction rate is 93% in the Cl-bearing solution relative to the Cl^- free solution.

4. Conclusion

We have employed the XAS technique to characterize the radiolysis-induced redox of a Cr standard solution in an HDAC at different temperatures. The oxidation of Cr(III) to Cr(VI) occurred at temperature above 300 ^{o}C and achieved a peak value at 400 ^{o}C. The reduction of Cr(VI) to Cr(III) was observed at 500 ^{o}C and during the cooling down process. The fitted 1s-to-3d photoelectron transition in the tetrahedral symmetry component of the pre-edge feature was used as an indication of the proportion of Cr(VI) species in the solution. The effect of a high basicity ligand (Cl^-) on the electronic environment of the Cr centre was to suppress (by 7%) the oxidation of the Cr(III) ion relative to a Cl-free solution.

The radiolysis-induced production of Cr(VI) species may have implications on GEN IV materials as most alloys being considered for use as a fuel cladding in an SCWR derive their corrosion resistance from the formation of a protective Cr(III) oxide film. The conversion of Cr(III) to Cr(VI) may compromise this protective film and the integrity of the fuel cladding.

5. Acknowledgements

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