# *In situ* XAFS studies of redox chemistry in hydrothermal chromium solutions

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## Introduction

An understanding of chromium redox chemistry in high-temperature aqueous solutions is of interest to a number of scientific disciplines (e.g., corrosion science and geochemistry) and hazardous waste processing. Our main motivation to study hydrothermal chromium solutions stems from the worldwide need to stabilize enormous quantities of radioactive aqueous waste streams for safe storage over long periods of time. These diverse waste streams often contain chromium in a wide range of concentrations and may also contain high concentrations of hydroxides, nitrates, and nitrites plus a host of other species. Proposed stabilization and pretreatment processes (e.g., vitrification) for these complicated waste streams involve temperatures in excess of 1000°C [1]. Chromium has been observed to exhibit unusual redox behavior during the early stages of waste calcination/vitrification. Hence, it is important to understand the chemical changes that occur during the transient heating stages of these high-temperature waste treatment processes before the water has been driven off. In this report we use the 1s-to-3d transitions in the pre-edge region of the Cr K-edge to monitor the chrome oxidation state in hydrothermal solutions as a function of temperature and pressure. To the best of our knowledge, the presented findings represent the first *in situ* observation of homogeneous aqueous inorganic redox chemistry at temperatures beyond the critical temperature of water (> 374°C).

## Methods and Materials

X-ray absorption fine structure (XAFS) experiments of high-pressure systems require window ports for the x-ray beam. The fraction of the x-ray beam intensity that is absorbed by the window material is significant and sets a limit on the range of low-Z elements that can be studied. The high flux available at the Advanced Photon Source was one key aspect that enabled us to study dilute aqueous chrome solutions to high temperatures and pressures. To maximize transmission we selected very thin (1/4 mm thick) single-crystal diamond wafers as window material to minimize beam intensity losses by the x-ray windows. Diamond is not only a superb optical material with the highest mechanical strength but is also chemically inert to the very aggressive media encountered in aqueous solutions at extreme conditions of pressure, temperature, and pH. The high-pressure/high-temperature XAFS flow cell that was used consisted of a Ti-6-4 body with an insert made from Pt/Ir, another suitable corrosion-resistant material. Solutions can be introduced into the cell at experimental conditions of pressure and temperature. Resistance heaters were used to heat the cell, and the temperature was controlled to within 0.1°C using a three-mode temperature controller. Pressures were measured to an accuracy of ± 1 bar using a calibrated pressure transducer. The optical path length was 2.5 mm.

Further details of the high-pressure/high-temperature XAFS flow-cell can be found elsewhere [2, 3]. The experiments were conducted at the beamline 20-ID, operated by the PNC-CAT. The beam energy was calibrated and monitored using suitable foils. For rejection of higher harmonics, the monochromator was detuned by 50%. Sodium hydroxide was used to adjust the room temperature pH value of the aqueous 0.02 molal Cr(III) nitrate solutions to 13.5. The solutions were prepared fresh, within a few hours before the experiments.

## Results and Discussion

Figure 1 shows the temporal spectral changes that were observed in the x-ray absoption near-edge structure (XANES) region of the Cr K-edge after the 0.02 molal $Cr(NO_3)_3$ solution was introduced into the cell at 400°C and 410 bar. The absorption edge background is subtracted in the spectra shown in Figure 1. The peak position of the feature near 5990.5 eV is tentatively assigned to the 1s-to-3d ($t_{2g}$) transition present in octahedral Cr(III) [4]. The feature near 5993 eV is increasing with time and corresponds to the position of a 1s-to-3d transition of tetrahedral Cr(VI) [4].

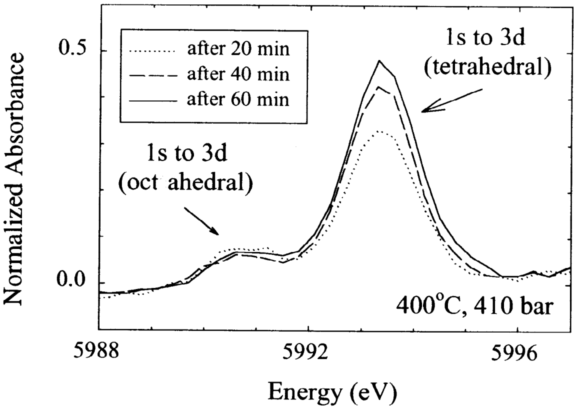

Figure 1: Temporal spectral changes observed in the pre-edge region of the Cr K-edge of a 0.02 molal $Cr(NO_3)_3$ solution at 400°C and 410 bar. The growing peak near 5993 eV indicates the oxidation of Cr(III) to $CrO_4^{2-}$ by the $NO_3^-$ under these conditions of pressure and temperature.

Hence, the temporal spectral changes of Figure 1 monitor the progression of the oxidation of Cr(III) to $CrO_4^{2-}$ by the nitrate. The oxidation of Cr(III) was observed to progress faster at 400°C and 410 bar if the solution also contained

0.06 molal $NaNO_2$, indicating an accelerating effect of the nitrite on the redox reaction kinetics. In both cases, the discharged solution was yellow in appearance (which is typical of chromate-containing aqueous solutions), a further confirmation of the presence of $CrO_4^{-2}$.

## Conclusions

The oxidation of Cr(III) to Cr(VI) by nitrate and nitrite was observed for the first time *in situ* in high-temperature aqueous solutions by monitoring the temporal changes in the pre-edge region of the Cr K-edge. The reaction rates are on the order of one hour at 400$^{o}$C and 410 bar, slow enough that one can follow the temporal progression of the redox reaction using XAFS spectroscopy. The presence of nitrite accelerates the reaction rates under the same experimental conditions of temperature and pressure. These findings are important to guide high-temperature stabilization processes of radioactive waste streams. Further work will obtain more refined kinetic information on these redox processes and identify the coordination structure of the reacting species.

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