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Synchrotron X-ray Microprobe Determination of Chromate Content Using X-ray Absorption Near-Edge Structure

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X-ray absorption near-edge structure (XANES) has been applied to the quantitative analysis of chromate (CrO_4^{2-}) content in oxides, silicate glasses, and simulated cementitious waste forms. The method uses the normalized area of a pre-edge peak (bound-state transition) in XANES spectra acquired with the synchrotron X-ray microprobe on beam line X26A at the National Synchrotron Light Source. The estimated accuracy of the technique is $\pm 5\%$ in terms of Cr^{6+} /total Cr. The minimum detection limit approaches 10 ppm Cr^{6+} using a 150- μm synchrotron X-ray beam. These results demonstrate the value of synchrotron-based microXANES for the nondestructive quantification of the first-row transition metal species present as tetrahedral oxyanions.

INTRODUCTION

The determination of the oxidation state and speciation of minor and trace elements in various matrices is important in the earth, material, and environmental sciences. In the environmental sciences, oxidation state and speciation play significant roles in the retention of toxic metals in solid hazardous and/or radioactive waste forms. In the earth sciences, the oxidation states of minor and trace elements in minerals from deep-seated volcanic rocks provide important clues on the physiochemical states of the interiors of solar system bodies and their petrogenetic histories. Oxygen fugacity affects many processes in planetary interiors, including melting pressure and temperature, and ultimately determines the compositions of the crust and mantle.¹ In material sciences, oxidation-state information is valuable in the development of corrosion-inhibiting coatings; see for example, refs. 2 and 3.

The focus of the present study is on environmental issues associated with low-level waste disposal. Studies on the leachability and transport of Cr and Tc from cementitious wastes through a soil column indicate that the oxidized, anionic species CrO_4^{2-} and TcO_4^- diffuse much more rapidly and are more mobile than the reduced species Cr^{3+} and Tc^{4+} .^{4,5} Therefore, control of the redox chemistry of the system is important because of the toxic, mobile nature of CrO_4^{2-} , and

quantification of the Cr species present is essential to predicting long-term performance of the waste form.

During microencapsulation of aqueous wastes in cement matrices, redox reactions likely occur at reactive sites within the microporous structure of the waste form, and the mechanisms involved in these redox reactions are largely unknown.⁶ Slag materials that are frequently added to the matrix provide sources of Fe^{2+} and sulfide compounds, which can readily reduce the mobile Cr^{6+} to less soluble Cr^{3+} .⁷ At the same time, fly ash is added as an effective heat sink during curing but also provides a source of manganese dioxide, one of the few naturally occurring oxidizers of Cr^{3+} to Cr^{6+} .⁸ Other studies have demonstrated that Cr^{3+} sorption to manganese dioxides and iron oxides occurs at specific sites via surface precipitation, rather than by a uniform distribution of Cr covering the entire surface.^{9,10} Obviously, quantitative spatial resolution of the Cr speciation in the cement microstructure is essential to understanding these redox mechanisms and designing effective waste forms for the management of Cr-containing waste effluents.

Studies of this type require determinations of oxidation state and speciation on heterogeneous materials, and therefore, spot analysis on as small a scale as possible is crucial. Conventional chemical methods for the determination of oxidation states in bulk solids usually require dissolution of the solid matrix; occasionally, separation of the various species is also required. Few nondestructive techniques for quantification of in-situ oxidation state have been developed, especially in systems where multiple oxidation states of a particular element can coexist. Optical spectrophotometry is one such technique, but the need for transparent materials and interferences from overlapping spectral features limit its applicability for natural materials.^{11,12} Diffuse reflectance spectrophotometry yields insufficient signal for trace elements. The Mössbauer technique is applicable to only a few elements, notably iron.

X-ray absorption spectroscopy (XAS) is an attractive technique for in-situ oxidation state and speciation analyses.¹³⁻¹⁵ Recent studies of X-ray absorption near-edge

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structure (XANES) demonstrate that oxidation states can be inferred from the precise energy of the X-ray absorption edge and associated absorption resonances. For example, Waychunas et al.¹⁶ reported that the Fe K absorption edge energy was systematically higher for ferric-bearing minerals compared to ferrous minerals. Sutton et al.¹⁷ demonstrated that trace levels of Cr²⁺ and Cr³⁺ in olivine [(Fe,Mg)₂SiO₄] could be determined qualitatively from the energies of Cr K absorption edge features. Both reports indicate that the observed energy shift with increasing charge on the metal is typically +2 eV per unit increase in oxidation state. Because the precise energies of these features also depend on matrix effects, quantitative application of this method requires matrix-matched standards containing the element in known oxidation states.

XANES spectra for K-edge transitions typically consist of a characteristic increase in X-ray energy as the 1s core electrons are promoted to the continuum. In the case of transition metals with empty d orbitals (*nd*⁰ configuration, where *n* is an integer), the XANES spectra of the K edge are sometimes characterized by a pre-edge absorption resonance due to electronic transitions from the 1s core state to primarily the *nd* molecular orbital state. For example, this transition is partially allowed in the case of CrO₄²⁻ due to mixing of the 3d metal state of the Cr with 2p orbitals of the O ligands. This mixture of the final state is possible due to the absence of a center of inversion or by a reduction (break) of the inversion symmetry due to the lattice vibrations.¹⁸ These pre-edge features are also observed in the case of Ti⁴⁺, V⁵⁺, and Mn⁷⁺¹⁹ and, in theory, should be observed for heavier transition metals such as Tc⁷⁺ and Re⁷⁺.

Such a pre-edge resonance serves as a fingerprint for the presence of species lacking an inversion center²⁰⁻²² and also, in principle, can provide quantitative information. Kendig et al.² used the pre-edge peak intensity to determine the proportion of Cr⁶⁺ in chromate conversion coatings. To date, however, there is no report on the use of the pre-edge peak to obtain quantitative information concerning mixtures of oxidation states in materials containing metals at trace levels.

In this paper we demonstrate the use of the intensity of the Cr K pre-edge XANES peak for quantitative analysis of tetrahedral-coordinated chromium with trace-level detectability and microscale spatial resolution. This method relies on a calibration curve of pre-edge peak area versus known mixtures of CrO₄²⁻ and Cr³⁺ in different matrices. The calibration curve was then used to quantify the amount of Cr⁶⁺ in simulated waste forms used for the immobilization of radioactive and/or hazardous materials.

SAMPLES

Oxide Standards. Oxide standards consisted of pellets containing known oxidation states of Cr prepared in finely ground NaCl (Aldrich Chemical Co., Inc., Milwaukee, WI). Cr⁶⁺ standards were made from Na₂CrO₄·4H₂O (Aldrich, 99.99% pure), while Cr³⁺ standards were prepared using Cr₂O₃ (Aldrich, 99.999% pure). In addition, standards containing known proportions of

Table I. Simulated Waste Solution Composition

component	wt %	component	wt %
H ₂ O	71	NaAl(OH) ₄	3.3
NaNO ₃	14.1	Na ₂ SO ₄	1.7
NaNO ₂	3.5	NaCl	0.11
NaOH	3.8	Na ₂ C ₂ O ₄	0.28
Na ₂ CO ₃	1.5	Na ₃ PO ₄	0.12

Table II. Slag-Bearing, Dry Cement Composition

component	wt %
portland type II cement	6
blast furnace slag (ground and granulated)	47
class F fly ash	47

Cr⁶⁺ and Cr³⁺ were prepared by mixing known weights of Na₂CrO₄·4H₂O and Cr₂O₃. The mixture proportions were 78%, 39%, and 24% expressed as 100Cr⁶⁺/total Cr. Standards containing a range of total Cr concentrations were also prepared by dilution of the pure compound or the mixture with NaCl. The total Cr content of these standards ranged from less than 0.2 to 10 wt %. After the Cr compounds and NaCl were ground and mixed, 300-mg samples were pressed into 13-mm-diameter, 0.3-mm-thick disks using a Wilmad evacuable press under vacuum at a pressure of 8 metric tons.

Borosilicate Glasses. A suite of alkali borosilicate glasses (Savannah River Laboratory glass frit 131, wt %: 57.1 SiO₂, 14.5 B₂O₃, 17.4 Na₂O, 5.6 Li₂O, 1.0 TiO₂, 0.5 ZrO₂, 0.5 La₂O₃, 2.0 MgO, and 1.0 Cr) synthesized under various controlled oxygen fugacities by H. Schreiber (Virginia Military Institute) were also used as standards. The oxidation states of Cr in these glasses were determined previously by conventional chemical procedures and optical spectrophotometry.¹² The uncertainty in the Cr ion concentrations is estimated to be ± 0.03 wt % (H. Schreiber, personal communication). The specimens were circular disks about 5-mm diameter and several hundred micrometers thick.

Simulated Waste Forms. Cement samples were prepared by making a slurry of dry cementitious materials with a solution of composition described in Table I. This solution was doped with 1000 ppm CrO₄²⁻ prior to formation of the slurry. The slurry was allowed to solidify under 100% humidity for a minimum of 28 days. The cementitious material used for the non-slag-bearing sample was portland type II cement, while the composition of the dry materials used to prepare the slag-bearing cement is listed in Table II. In both cases, the solidified material was fractured to obtain small pieces of cement approximately 0.1 mm thick. In addition to the solid samples, some of the cements were ground and mounted as powders to obtain a more controlled and uniform sample thickness.

ANALYTICAL TECHNIQUE

XANES spectra were obtained at the National Synchrotron Light Source at Brookhaven National Laboratory using the X-ray fluorescence microprobe on beam line X26A.²³⁻²⁶ Briefly, the X-ray microprobe beamline consisted of a primary aperture, a monochromator, a focusing mirror, and a four-jaw slit assembly. The intensity of the incident beam was monitored with an ion chamber, and the resulting Cr Kα fluorescence signal was detected using a Si(Li) energy-dispersive detector (150-eV resolution at Mn Kα) at 90° to the incident X-ray beam and within the horizontal plane of the synchrotron. An optical microscope was used for viewing the sample and to position the sample (mounted on a motorized target assembly with 1-μm precision) in the X-ray beam.

The monochromator was a silicon (111) channel-cut crystal mounted on a rotating shaft which in turn was attached to a

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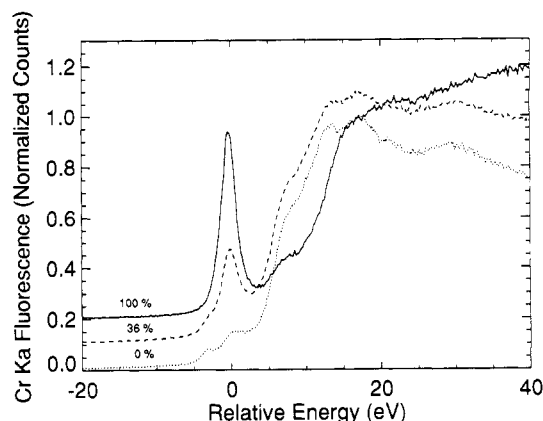


Figure 1. XANES spectra for mixtures of Na_2CrO_4 and Cr_2O_3 showing Cr K α normalized counts versus energy relative to the pre-edge peak energy. The spectra are labeled with the percentage of total chromium that is Cr^{6+} in each mixture. Counts are normalized to the "above-edge" intensity, and the spectra are offset vertically for clarity. The height of the peak at 0 eV increases monotonically with Cr^{6+} content.

230-mm "sine bar". The energy of the monochromator was adjusted and scanned by driving the end of the sine bar with a 0.1- μm -precision, Klinger stepping translator. The usable range of the monochromator was between 4 and 20 keV with an energy bandwidth of about 10^{-4} ($\Delta E/E$). The focusing mirror, an 8:1 ellipsoidal surface, was used to increase the photon flux/area incident on the sample by a factor of 40.²⁷ An added advantage of using the mirror was in harmonic rejection since the third harmonic (18 keV with the monochromator tuned to the fundamental at the Cr K absorption edge) occurred above the energy cutoff of the mirror [the second-order diffraction is forbidden from the Si(111) planes]. Optimal energy resolution of the monochromator was found empirically to be obtained by using a primary vertical aperture of less than 0.4 mm. A 0.2-mm aperture (0.3 mrad opening angle) was used. The mirror produced a beam $150 \times 350 \mu\text{m}$, and this was reduced to $150 \times 180 \mu\text{m}$ using the four-jaw slit assembly. A minimum beam size of about $30 \mu\text{m}$ was attainable, but the larger beam was used to improve sensitivity.

The XANES spectra were obtained by scanning the monochromator in 0.2-eV steps from 80 eV below the edge to 500 eV above the edge and recording the Cr K α fluorescence intensity at each energy. Typically, each energy step in the standard Cr XANES spectra was counted for 1 s live time, which yielded several thousand counts per pixel above the edge and a total scan time of approximately 1 h. The waste forms contained 400–500 ppm Cr and were counted for longer times with larger monochromator steps to obtain acceptable statistics in a reasonable time.

DATA ANALYSIS

XANES spectra of standard oxides containing pure and mixed Cr oxidation states are shown in Figure 1. As can be seen, samples containing CrO_4^{2-} exhibit the distinct absorption peak prior to the main Cr K absorption edge. Spectra were plotted relative to the energy of this pre-edge maximum. All spectra showed additional features near the absorption edge due to multiple scattering resonances and electron transitions to other bound valence states (e.g., ref 28). The energies and intensities of these features contain information on the bonding character of the Cr site. Previous studies have demonstrated that the energies of these features increase with increasing oxidation state.^{18,17,20} However, for transition metals in coordination geometries that lack a center of inversion, the pre-edge peak intensity is more useful for

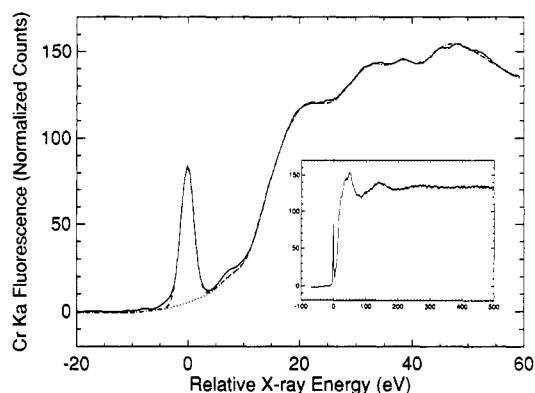


Figure 2. XANES spectrum (solid line) of pure Na_2CrO_4 (hexavalent Cr standard) showing Cr K α normalized counts versus energy relative to the pre-edge peak energy. Dotted line is a spline fit of the baseline. Peak area was defined as the area of a fitted Gaussian peak (dashed line) normalized to the average counts per channel between 400 and 500 eV above the pre-edge peak (inset).

quantitative determinations than shifts in XANES energies primarily because the energies of the spectral features superimposed on the edge depend more on interatomic distances²⁰ and are, therefore, more matrix dependent. In the present work, the pre-edge peak energy was the same for all measurements to within 0.2 eV (one monochromator step). The intensity of the pre-edge peak in the XANES spectra of the mixed oxide standards increased with increasing proportion of hexavalent chromium (Figure 1).

The basic data processing approach was to (1) subtract the pre-edge baseline, (2) fit the pre-edge peak, (3) derive the area of the fitted peak, and (4) normalize the area to the average intensity 400–500 eV above the absorption edge (Figure 2). The baseline of the spectrum in the pre-edge region was estimated with a spline fitting procedure. After this baseline was subtracted, the pre-edge peak area was determined by the area of a fitted Gaussian function (Figure 2). The pre-edge region for the pure Cr_2O_3 actually consisted of two peaks (Figure 1). These pre-edge peaks likely arise from t_2 and e_g symmetry bands separated by ligand-field splitting.²⁹ Optical data of the ligand-field splitting in chromium oxides showed a splitting of 2.1 eV,³⁰ which is in reasonably good agreement with the 2.8 eV splitting observed in the XANES spectra. In the present work, only the peak at the same energy as the pre-edge peak in the totally hexavalent sample was used. The high-energy normalization was used to correct for differences in Cr concentration and precise analytical parameters such as incident flux and counting time. Spectra were flat in this region so results were insensitive to the precise normalization region used.

Calibration curves and associated errors were calculated using standard weighted linear regression formulae³¹ on the peak areas for the standards. The uncertainty associated with each measurement of the normalized pre-edge peak area was taken to be the statistical error only, and the fraction of Cr^{6+} in the standards was assumed to be known exactly. The Cr^{6+} content in the cementitious (unknown) specimens and associated uncertainties were then calculated using the calibration regression line and the errors in slope and intercept. All quoted errors are 1 standard deviation.

RESULTS AND DISCUSSION

The normalized areas for the five oxide standards and the three borosilicate standards show excellent linear correlation

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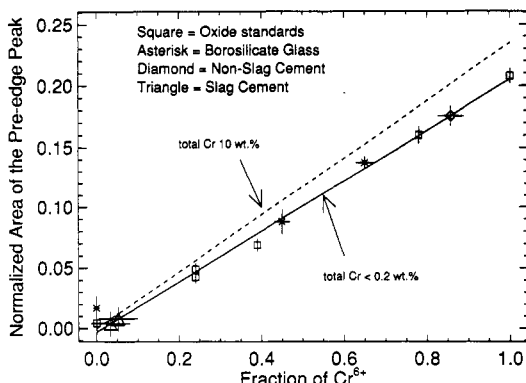


Figure 3. Linear regression of the area of the hexavalent pre-edge peak (Gaussian fit after baseline subtraction normalized to the "above-edge" intensity) versus known hexavalent Cr content for five mixtures of Cr_2O_3 and Na_2CrO_4 containing less than 0.2 wt % total Cr and for three borosilicate standards (solid line). Pre-edge peak areas for waste forms are superimposed on the calibration trend. The height of each bar represents the statistical error in the pre-edge peak area. The width of each bar is derived from the uncertainty in the calibration curve parameters. The dashed line is a similar linear regression plot based on oxide standard mixtures of 10 wt % total Cr and the three borosilicate standards (data points omitted from figure for clarity). The similarity of the two lines demonstrates that self-absorption effects are small.

with the known fraction of Cr^{6+} in the standards (Figure 3). Distortions of fluorescence XANES spectra have been reported for concentrated bulk specimens,^{32–34} so the possibility of self-absorption effects was examined by comparing the calibration curves generated by standards of different total Cr content. Figure 3 shows the resulting regression lines for the most dilute oxide standards (less than 0.2 wt % total Cr; solid line) and the most concentrated (10 wt % total Cr; dashed line). Each line includes the borosilicate data (total Cr 1%). The calibration curves were very similar. The "dilute standards" line has a slope of 0.208 ± 0.007 and an intercept of -0.0031 ± 0.0037 . The slope of the "concentrated standards" line is 0.235 ± 0.006 with an intercept of -0.0001 ± 0.0046 . Thus the intercepts of the two lines are virtually identical and equivalent to zero while the slopes overlap at the 2 standard deviation level. This suggests that self-absorption effects are small within the concentration range of interest here.

The fraction of Cr^{6+} in the waste forms was inferred by using both calibration lines in Figure 3. Using the dilute standards line, the fraction of Cr^{6+} in the two slag-bearing cements was 0.05 ± 0.04 and 0.03 ± 0.04 compared to 0.86 ± 0.03 for non-slag-bearing cement (Table III). Using the calibration curve for concentrated standards, the results were 0.03 ± 0.06 and 0.02 ± 0.06 for the slag-bearing cement and 0.75 ± 0.05 for the nonslag-bearing cement. Thus, when solutions containing chromate are solidified in a simple portland cement matrix, the Cr^{6+} content indicated by XANES is $80 \pm 5\%$. These results are significant because they suggest that the raw material (non-slag-bearing cement expected to have 100% Cr^{6+} initially) experiences some in-situ reduction to Cr^{3+} as a result of aging. In addition, if modifiers such as fly ash and slag are introduced to the matrix, trace quantities of Cr^{6+} are completely reduced to Cr^{3+} consistent with previous studies that document the reduced leachability of Cr from slag/fly ash-based cement matrices.^{4,5} Observations of this type have important implications for

Table III. Chromium K XANES Pre-Edge Peak Areas

Cr^{6+} content (% of total Cr)	total Cr (wt %)	normalized peak area
Mixed Oxides		
100	0.02	0.208 ± 0.006
100	2.0	0.219 ± 0.004
100	10.0	0.240 ± 0.003
78	0.17	0.160 ± 0.007
78	1.5	0.174 ± 0.004
39	0.11	0.069 ± 0.005
39	1.1	0.097 ± 0.004
39	10.5	0.100 ± 0.005
24	0.09	0.050 ± 0.005
24	0.09	0.043 ± 0.005
0	0.08	0.004 ± 0.010
0	1.0	0.019 ± 0.010
0	10.9	0.021 ± 0.010
Glasses		
65	1.0	0.138 ± 0.005
46	1.0	0.088 ± 0.010
0	1.0	0.017 ± 0.010
Cements		
nonslag unknown	0.05	0.176 ± 0.003
slag unknown	0.05	0.004 ± 0.010
slag unknown	0.05	0.008 ± 0.010

the mobility of toxic metals in specific waste forms. The first-order conclusion is that Cr will be more mobile in the non-slag, cement-based material since Cr exists as the chromate oxyanion. The trivalent species (cationic form) is less soluble in the alkaline cement matrix and will also tend to adsorb to clays, thereby retarding its transport. The proposed speciation of Cr^{3+} in the reducing system is a $\text{Cr}(\text{OH})_3$ precipitate.³⁵

The speciation of other toxic elements in wasteforms could be studied by XANES and applications to radioactive elements, in particular, are under investigation. An important target element is technetium (^{99}Tc , $t_{1/2} = 2 \times 10^5$ years), an abundant fission product from commercial nuclear operations. In oxic systems, its speciation has been inferred to be dominated by the tetrahedral oxyanionic species TcO_4^- , which is easily reduced to Tc^{4+} in many systems.³⁶ Diffusion kinetics appear to be controlled by changes in oxidation state,³⁷ and the temperature dependence of redox changes are being studied.

CONCLUSIONS

The area of the chromate pre-edge peak in XANES spectra is linearly correlated with chromate content and is virtually matrix independent. The weight fraction of Cr^{6+} in samples with greater than about 10 ppm total Cr can be determined with about 5% accuracy using this method, and applications to other metals in noncentrosymmetric coordination (e.g., Ti and V) should be possible. Chromium in low-level waste forms was demonstrated to be predominately a hexavalent, tetrahedral oxyanion in non-slag-bearing cements and a trivalent cation in slag-bearing cements. These results provide a direct confirmation of the Cr speciation in the cementitious matrix previously inferred from leaching studies.

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