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XAFS Analysis of Cr(VI) in Israeli fly-ash samples

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Cr XANES spectroscopy indicates that the Cr(VI) contents of the examined Israeli fly-ash samples constitute from 6 to 14% of the total Cr in the sample.

Introduction:

At the request of Dr. Y. Nathan, Geological Survey of Israel, Jerusalem, and Dr. O. Lulav, Israeli Coal Ash Board, Tel Aviv, a suite of five fly-ash samples was examined using Cr X-ray absorption fine structure (XAFS) spectroscopy. Dr. Nathan described the samples in an email communication, as follows:

Sample 1 - Jasr: the original road base material of Jasr (Jisr) el-Zarka

Sample 2 - FM2: 3 months composite industrial ash

Sample 3 - C 3-5: sample from the upper part of the southern embankment at the Electric Power plant ((Hadera), depth 1 – 1.5 m

Sample 4 - C 4-1: sample from the lower part of the southern embankment at the Electric Power plant ((Hadera), depth ~ 7.5 m

Sample 5 - D 9-11: sample from the road base material of Jasr-el-Zarka, one year after emplacement, depth ~ 2 m

Experimental:

The speciation of chromium in fly-ash samples from Israel has been examined using Cr K-edge X-ray absorption fine structure (XAFS) spectroscopy performed at the U.S. National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, NY. Due to possible concerns regarding resolution issues in the spectra obtained at NSLS, some additional experiments were also briefly conducted at the Stanford Synchrotron Radiation Laboratory, Stanford University, but the results were virtually identical to those obtained at NSLS.

The fly-ash samples were used at the synchrotron in their as-received forms without any additional preparation. A portion of the sample (~200 mg) was suspended in the X-ray beam at the synchrotron in an envelope made of ultrathin polypropylene. Data were collected from this sample in fluorescence geometry using an 11-element Ge detector, which was gated electronically to receive predominantly the X-rays fluoresced by chromium. A 6μ V filter was also employed to enhance further the signal/noise ratio. The Cr XAFS spectrum was collected as a function of energy over a range from 5,889 eV to 6,389 eV. Over the edge

(XANES) region, that is, from –10 eV to +40 eV with respect to the Cr K absorption edge at 5,989 eV, the data were collected at a stepping interval of 0.25 eV. For each sample, a chromium XAFS spectrum was recorded in each of the 11 channels of the detector and the set of 11 spectra were accumulated at least 4 times; hence, a minimum of 44 individual spectra were added together to obtain a spectrum of reasonable quality (Figure 1). The first major derivative in the XAFS spectrum of a thin chromium foil was assumed to occur at exactly 5,989 eV and the energy scales of the spectra of the fly-ash were adjusted accordingly.

Figure 1 shows the absorption spectrum obtained for sample "Jasr #1"; it is the plot of the ratio of the intensity of the fluorescent radiation (I_f), measured in the multi-element Ge detector, divided by the intensity of the incident radiation (I_0) as a function of energy. As is normally done (Koningsberger and Prins, 1988), the slope below and above the edge is removed mathematically and the resulting XAFS data are then normalized to the edge step so that the difference in absorption across the chromium K-edge at approximately 5,989 eV is unity. The resulting spectra (Figure 2) are the X-ray absorption near-edge structure (XANES) spectra. Normally, further analysis is then performed to generate the extended X-ray fine structure (EXAFS) spectrum, but in this case, the observed signal-to-noise ratio is too low and the L-edge absorption peaks due to neodymium and cerium (Figure 1) are too large and too close to the chromium K-edge to permit meaningful analysis of the Cr EXAFS structure.

Results and Discussion:
The Cr XANES spectra were least-squares fitted in the region from –8 eV to +8 eV using a mathematical function based on two peaks of lorentzian-gaussian shape and an arctangent curve for the background produced by the chromium absorption edge. Examples of the fitting are given in Figure 3. As discussed in more detail elsewhere (Huggins et al., 1999), the peak at about 1.5 – 2 eV represents a small, weakly allowed localized transition in Cr^{3+}, whereas the peak at 3.5 – 4 eV represents a composite peak for an even smaller Cr^{3+} transition peak and the much more intense peak due to Cr^{6+}. By measuring the relative heights of these two peaks for mixtures of known amounts of Cr^{3+} and Cr^{6+}, a calibration curve was developed that related the peak-heights to the fraction of the Cr present as Cr^{6+} in the sample. The inverse procedure can then be used to estimate the Cr(VI) contents of fly-ash and other samples. The results of this precedure for the five samples from Israel are shown in Table 1.

Table 1: Results of least-squares fitting analysis of Cr XANES spectra of Israeli fly-ash

Sample (XAFS File ID)	Peak at 2 eV		Peak at 4 eV		%Cr(VI)*+
	Height	Pos'n, eV Width, eV	Height	Pos'n, eV Width, eV	
1. Jasr (CRASH.X912S)	0.041	1.2 2.6	0.145	3.5 2.6	14
2. FM2 (CRASH.X918S)	0.046	1.4 2.7	0.103	3.4 2.7	10
3. C4-1 (CRASH.X907S)	0.050	1.5 3.1	0.067	4.0 3.1	6
4. C3-5 (CRASH.X924S)	0.039	1.4 2.7	0.133	3.7 2.7	13
5. D9-11 (CRASH.X903S)	0.053	1.2 3.4	0.085	3.9 3.4	7

* Calculated from: Cr(VI) = (h_4 - h_2/3)*110 where h_2 and h_4 are the peak heights.
+ Estimated uncertainty is no more than ±3%

It is apparent that all five fly-ash samples show positive signs for the presence of Cr(VI), given the estimated uncertainty of ±3%. The samples do show some significant differences: for example, the two samples from the southern embankment at the Hadera (samples 3 and 4)

site differ significantly, as do the two Jasr samples (1 and 5). This may imply that the Cr^{3+}/Cr^{6+} ratio is being affected by the depth of burial or by its interaction with groundwater.

Conclusions:

The chromium speciation of a five Israeli fly-ash samples has been determined quantitatively from their Cr K-edge XANES spectra using the XAFS spectroscopic method recently developed at the University of Kentucky (Huggins et al., 1999). This method is based on a least-squares fitting procedure that relates the height of the pre-edge peak in the chromium XANES spectrum to the Cr(VI) content. Cr(VI) was detected in all five Israeli fly-ash samples, however, the determined values were relatively low, varying from as little as 6% to only as high as 14% of the total Cr in the sample. The estimated uncertainty in the Cr(VI) determination is no more than ±3%.

References:

Huggins, F. E., Najih, M. and Huffman, G. P., 1999. *Direct speciation of chromium in coal combustion by-products by X-ray absorption fine structure spectroscopy.* **Fuel (Special Issue, Proceedings, 1997 International Ash Utilization Symposium),** 78, 233-242.

Koningsberger, D.C., and Prins, R., 1988. X-ray Absorption. Principles, Applications, Techniques of EXAFS, SEXAFS and XANES. Wiley, NY.
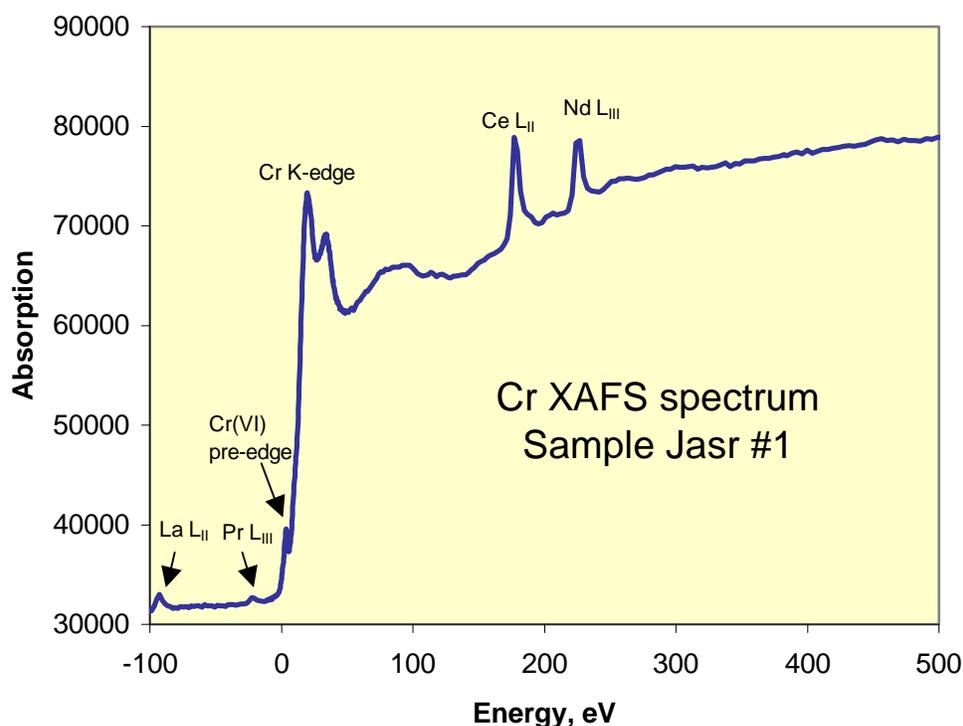
Figure 1: Chromium XAFS spectrum of a fly-ash sample from Israel (sample Jasr #1). Note the L-edge absorptions for La, Ce, Nd and Pr that limit the extent of the useful EXAFS region for Cr. The Cr XANES region, however, is unaffected.
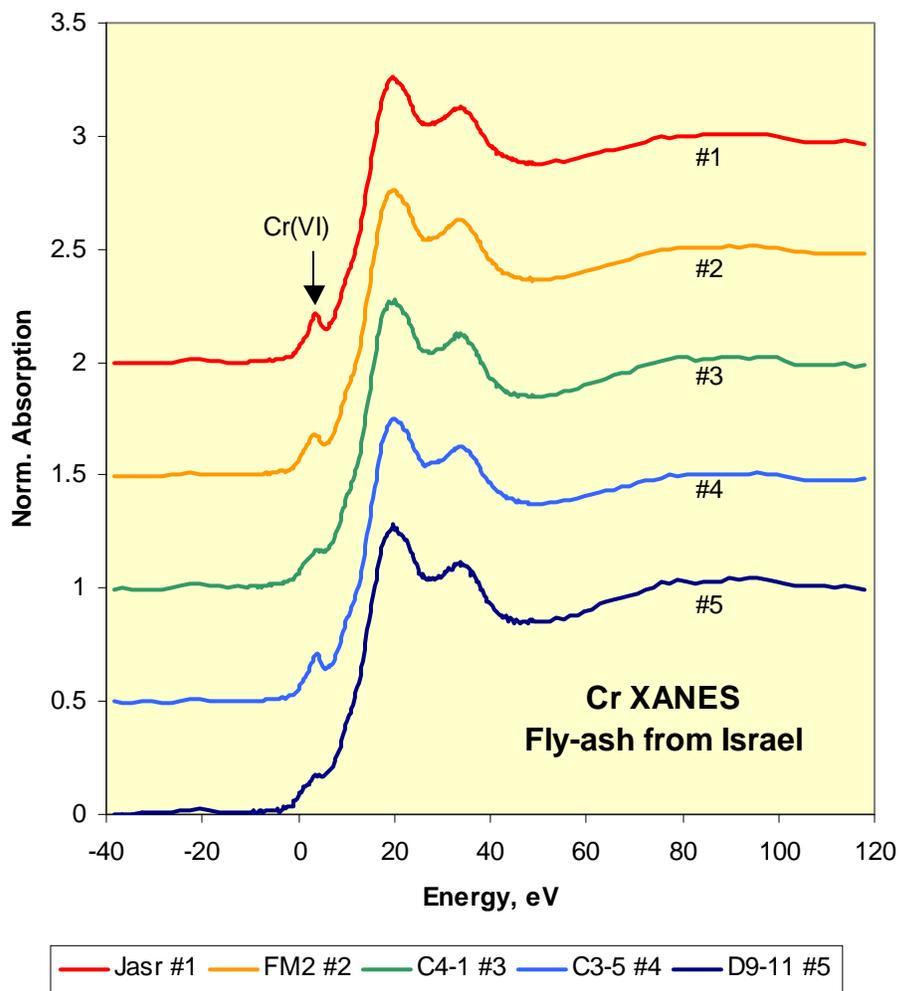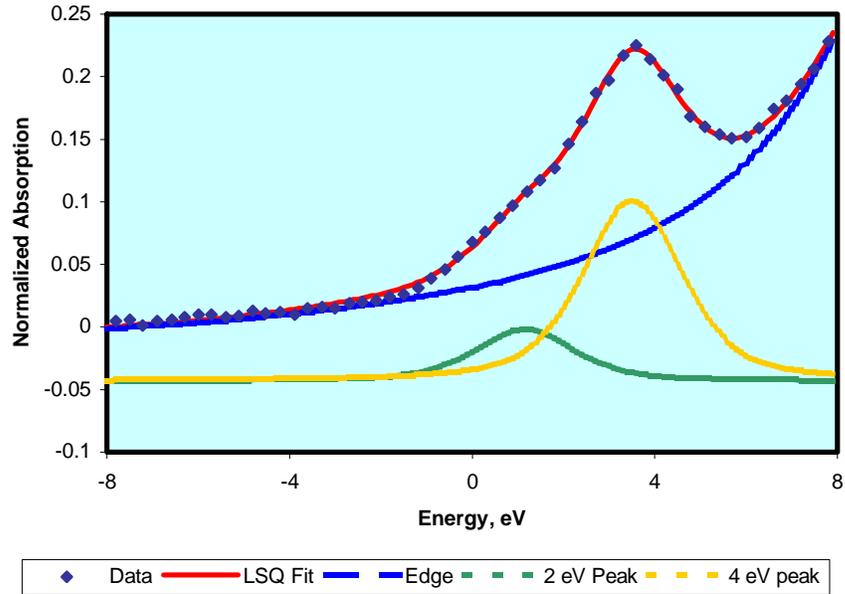
4

Figure 2: Chromium XANES spectra of five Israeli fly-ash samples. Each spectrum is normalized to unit edge-step and offset by 0.5 absorption units.
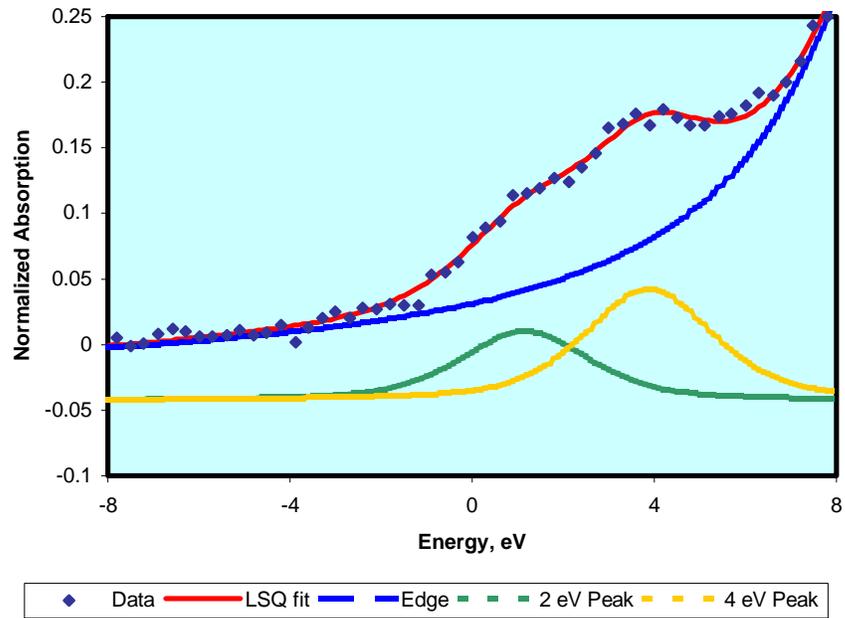
1. Jasr Ash

5. D9-11

Figure 3: Detail of least-squares fitting of chromium XANES spectra of fly-ash samples. Upper spectrum contains largest fraction of Cr(VI), whereas the lower spectrum contains smallest fraction of Cr(VI). Both spectral portions are fitted to two peaks and an arctangent function representing the absorption edge.