

# Chromium speciation in mildly heated Cr(VI)-doped latosol soil

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Cr(VI) chemical reduction in natural organic matter (NOM)-bearing latosol soil was investigated under various heating conditions at  $\leq 378$  K. An enhanced Cr(VI) reduction rate has been observed for the reaction at 353–378 K. The effect of Fe(II) naturally occurring in the latosol soil on Cr(VI) chemical reduction is negligible compared with the effect of NOM. Cr(OH)<sub>3</sub> was quantitatively specified by X-ray absorption spectroscopy to be the key chromium species ( $\sim 80\%$ ) after  $\sim 90\%$  of Cr(VI) was chemically reduced by NOM at 353–378 K. This study indicates a potential strategy for using the heat extracted from industrial flue gas with a heat exchanger to chemically reduce Cr(VI) in NOM-bearing or organics-amended soils that contain Cr(VI).

**Keywords:** Cr XANES; Cr EXAFS; Cr(VI) chemical reduction; latosol.

## 1. Introduction

Chromium-contaminated soils can be optionally remedied by inorganic and organic substances through the chemical reduction of Cr(VI) that is mobile to much less mobile Cr(III). Cr(VI) and Cr(III) are the two most stable oxidation states of chromium in natural systems. The chemical reduction of Cr(VI) with organic and/or inorganic materials has been extensively studied (Kumpiene *et al.*, 2008).

Photocatalytic reduction of Cr(VI) with humic acid in the presence of TiO<sub>2</sub> is effective and there exists an optimum dosage of TiO<sub>2</sub> (Yang & Lee, 2006). Although Fe(III) cannot reduce Cr(VI) to Cr(III), its presence can enhance the photocatalytic reduction of Cr(VI) in the presence of citrate by the use of TiO<sub>2</sub> under light irradiation (Tzou *et al.*, 2005). The combined effectiveness of Fe(II) and magnetite suspensions on Cr(VI) reduction was determined to be lower than that of the linear sum of the individual components (Jung *et al.*, 2007). It was also demonstrated that Cr(III) and Fe(III), forming metal (oxy)hydroxides, were the primary products after Cr(VI) reduction with X-ray photoelectron spectroscopy (Jung *et al.*, 2007). A kinetic study of Cr(VI) reduction showed that pyrite, as a reducing agent under acidic conditions, is about two orders of magnitude faster than biotite (Chon *et al.*, 2006). Chon *et al.* (2006) proposed (Cr,Fe)(OH)<sub>3</sub> as the resulting precipitate after Cr(VI) reduction. They also found that waste Fe(0) metal was more efficient than a commercially available Fe(0) in reducing Cr(VI) (Lee *et al.*, 2003). Other than being associated with direct reduction of Cr(VI), an organic ligand such as *N*-hydroxyethyl-ethylenediamine-tri-

acetic acid was determined to enhance the Cr(VI) reduction with Fe(II) *via* electron transfer (Tzou *et al.*, 2003).

It was shown that mixed-valence Cr(III/VI) in an aqueous effluent from magnetite-containing soils in Cr-contaminated sites was reduced to Cr(III) when associated with the magnetite fraction, and was reduced to mixed Cr(III/VI) adsorbates or precipitated phase when associated with non-Fe(II)-containing minerals (Peterson *et al.*, 1997*a,b*).

The study of the influence of mineral surfaces on the Cr(VI) reduction by Fe(II), and the kinetic results in suspensions of mineral and soil at pH 5, showed that the mineral accelerated Cr(VI) reduction in the decreasing order  $\alpha$ -FeOOH =  $\gamma$ -FeOOH  $\gg$  montmorillonite > kaolinite = SiO<sub>2</sub>  $\gg$  Al<sub>2</sub>O<sub>3</sub>, where Al<sub>2</sub>O<sub>3</sub> did not seem to affect Cr(VI) reduction (Buerge & Hug, 1999). Buerge & Hug (1998) also investigated the influence of organic compounds on Cr(VI) reduction by Fe(II). It was found that downstream migration of Cr(VI) in the groundwater was limited owing to a redox mechanism involving Cr(VI) and Fe(II) that was a result of pyrite residues from old activities at the site (Loyaux-Lawniczak *et al.*, 2001). They also observed that vertical Cr(VI) migration into the groundwater was stopped by the very thick clay that naturally contained a large amount of iron (Loyaux-Lawniczak *et al.*, 2001). Batch and column techniques were used to evaluate *in situ* Cr(VI) reduction and immobilization by Fe(II) solutions within coarse-textured oxide-coated soil and aquifer systems (Seaman *et al.*, 1999).

The time taken for direct Cr(VI) reduction without metal oxide catalysis by organic compounds containing alcoholic, carbonyl and carboxylic functional groups could have half-

lives as long as years in some cases (Elovitz & Fish, 1994). Deng & Stone (1996) investigated the kinetics of Cr(VI) reduction by low-molecular-weight (<200 a.m.u.) organic compounds containing various functional groups in the presence and absence of mineral oxides in liquid solutions. The organic compounds used to reduce Cr(VI) *via* surface oxide catalysis included  $\alpha$ -hydroxyl carboxylic acids and their esters,  $\alpha$ -carbonyl carboxylic acids, oxalic acids and substituted phenols (Deng & Stone, 1996). Both  $\alpha$ -FeOOH and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had an appreciable catalytic effect, although not as potent as TiO<sub>2</sub>, on Cr(VI) reduction by these low-molecular-weight organic compounds (Deng & Stone, 1996). They suggested that additional research determining whether larger-molecular-weight organic compounds such as humic substances participating in surface-catalyzed reduction is needed in this area (Deng & Stone, 1996). Jardine *et al.* (1999) demonstrated that natural organic matter (NOM) could effectively reduce Cr(VI) by batch mixtures of dissolved NOM and Cr(VI) in the absence of solid-phase substances, and the rate of reduction of aqueous-phase Cr(VI) was quite slow with a time scale of months to reach ~50% Cr(VI) reduction.

In a previous study (Wei & Hsieh, 2006) it has already been demonstrated that Cr(VI) can be effectively immobilized in a latosol soil by treating the samples at temperatures of 378–1373 K. However, after treatment at 773 and 1373 K, soils lost some important properties such as organic matter content and porosity. Further, the effect of iron compounds present in the soil matrix was not clarified. Thus, the aim of the present study is to use the XAS technique to (i) investigate the technical feasibility of reducing Cr(VI) to Cr(III) in soil slurry at temperatures of 303–378 K that may be readily reached with the heat extracted from industrial flue gases with a heat exchanger, and (ii) examine the contribution of the reducing capacity of Fe(II) toward Cr(VI) in soil.

## 2. Experimental

### 2.1. Chemicals

All chemicals are reagent grade, listed as follows:

(i) CrO<sub>3</sub>, HNO<sub>3</sub> 69%, H<sub>2</sub>SO<sub>4</sub> 98% and 1000 mg Cr(III) L<sup>-1</sup> chromium standard solution: Merck; (ii) HCl 37%, H<sub>2</sub>O<sub>2</sub> 30%, HF 48%, NaOH 1.0 N and 1,5-diphenylcarbohydrazide: Riedel-de-Haën; (iii) CrO<sub>3</sub> 99.9% and Cr<sub>2</sub>O<sub>3</sub> 99.995%: Aldrich; (iv) FeS<sub>2</sub> (pyrite), FeS (pyrrhotite), FeO (wüstite),  $\alpha$ -FeOOH (goethite),  $\gamma$ -FeOOH (lepidocrocite),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite),  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) and Fe<sub>3</sub>O<sub>4</sub> (magnetite): Alfa Aesar.

Humic-acid-bound Cr(III) (denoted as HA-Cr) was also prepared by the following procedure: 3.00 g of humic acid (Sigma-Aldrich, Switzerland) was mixed for 1 h in 40 ml of deionized water with 0.120 g of Cr(III) that was in the form of Cr(NO<sub>3</sub>)<sub>3</sub>, and the solid phase of the resulting slurry was separated by centrifugation. The solid phase was then sequentially extracted five times, each time for 1 h with 10 ml de-ionized water under magnetic stirring. After each extraction the solid and liquid phases were separated and the

chromium concentration in each liquid was determined. The chromium content in the last liquid phase only represented 0.080 wt% of the remaining chromium in the last solid phase (being regarded as HA-Cr) which contained 21503 mg of Cr per kilogram of solid.

### 2.2. Equipment

The equipment used was as follows:

(i) Hot air rapid drying oven: RHD 120 L, maximum 573 K, Risen Co., USA. (ii) Mixing device: type 34R4BFCI-5R, Associated Design and Manufacture Co., Virginia, USA. (iii) Microwave digester: MDS-2000, CEM Co., North Carolina, USA. (iv) Flame atomic absorption spectrophotometer (FAAS): Z-6100, Hitachi, Japan. (v) Elemental analyzer: Vario EL CHNOS elemental analyzer, Elementar Analysensysteme GmbH, Germany. (vi) Inductively coupled plasma atomic emission spectrometer (ICP-AES): ICAP 9000, Jarrell-Ash, USA. (vii) Inductively coupled plasma mass spectrometer (ICP-MS): SCIEX ELAN 5000, Perkin Elmer, USA. (viii) X-ray fluorescence (XRF) spectrometer: X-ray spectrometer system 3063M, Rigaku, Japan. (ix) X-ray powder diffractometer (XRPD): X-ray diffractometer D-500, Siemens, Germany. (x) XAS: wiggler C (BL-17C), National Synchrotron Radiation Research Center (NSRRC), Taiwan.

### 2.3. Latosol soil

The top surface layer (0–15 cm depth) of a latosol soil was collected from central Taiwan. It was dried, ground and sieved to <50 mesh. The appropriate equivalent of the soil pedon is fine-silty, mixed, hyperthermic, Typic Kandiodult (Wei, 1995; Wei & Hsieh, 2006) and the soil pH value was determined (US EPA, 1995a) to be 3.85. Its major component elements were measured by XRF, and they were Si, Al, Fe, K, Na, Ca, Ti, Mg and Zn. Expressed in oxide form (wt%), the latosol soil consists of 64.3% SiO<sub>2</sub>, 15.5% Al<sub>2</sub>O<sub>3</sub>, 3.23% Fe<sub>2</sub>O<sub>3</sub>, 1.11% Na<sub>2</sub>O, 1.84% K<sub>2</sub>O (Wei & Hsieh, 2006), 0.08% MgO, 0.02% MnO<sub>2</sub>, 0.56% TiO<sub>2</sub>, 0.23% CaO and 0.01% ZnO. It is free of heavy-metal contamination (*i.e.* thus termed Neat-L) and the content of Cr, Pb, Cu, Cd and Ni compounds were all in non-detectable amounts [Cr  $\leq$  0.012 mg kg<sup>-1</sup> (Wei & Hsieh, 2006), Pb  $\leq$  0.022 mg kg<sup>-1</sup>, Cu  $\leq$  0.084 mg kg<sup>-1</sup>, Cd  $\leq$  0.002 mg kg<sup>-1</sup> and Ni  $\leq$  0.1 mg kg<sup>-1</sup>], as analyzed with an ICP/MS after HF/HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> digestion in a microwave digester. The mixed-acid-containing HF was used to digest latosol soil because of its high content of SiO<sub>2</sub> (US EPA, 1995b). The soil is also characterized by a 8.35  $\pm$  0.47% loss of ignition (LOI) (Wei & Hsieh, 2006). Its XRD-detectable crystalline phases are silicon oxide and muscovite [KAl<sub>2</sub>Si<sub>3</sub>AlO<sub>10</sub>(OH)<sub>2</sub>]. The surface area of the latosol soil was 6.5 m<sup>2</sup> g<sup>-1</sup> based on the N<sub>2</sub>-adsorption method. The soil sample is rich in NOM as indicated by the 3.11% organic carbon. The total carbon in the soil sample is 3.95%.

### 2.4. Cr(VI)-doped latosol soil sample

To study the reduction capacity of the NOM-bearing latosol soil, the latosol soil was artificially doped with Cr(VI) to

prepare a 40000 mg Cr (kg soil)<sup>-1</sup> sample. Soil contaminated with chromium at 52200 mg of Cr (kg soil)<sup>-1</sup> has been found in a pesticide processing plant in Central Taiwan (ROC EPA, 2005). The Cr-doped latosol sample was prepared by end-to-end mixing (30 ± 2 r.p.m.) of 0.75 L 0.513 M CrO<sub>4</sub><sup>2-</sup> solution with 0.5 kg latosol soil for two days (Wei & Hsieh, 2006). The slurry was then divided into two parts. The first part of the slurry was air-dried for 12 days at 303 K (*i.e.* this sample is termed L-303), and then each portion of this dry sample was heated in an oven at 333, 353 or 378 K for three days (*i.e.* these samples are termed L-303–333, L-303–353 and L-303–378, respectively) to study the effect of low-temperature heating on the extent of Cr(VI) chemical reduction in dry Cr-doped latosol soils. (ii) The second part of the slurry was directly oven-heated at 353 K for two days to dryness, and then this dry sample was further heated at 378 K for one day (this sample is termed L-353–378). The extent of Cr(VI) reduction in the last sample was compared with that of all samples made from the first part of the slurry to determine the influence of the direct heating at 353 K on Cr(VI) reduction.

To investigate the effect of organic matter on Cr(VI) reduction, an organic-matter-free sample was prepared by destroying and/or removing the LOI from latosol soil at 1173 K for 2 h in an oven before the Cr(VI) doping, and then the same procedure as that used for preparing the L-353–378 sample was followed to prepare the Cr(VI)-doped de-LOI latosol soil (termed DOL-353–378). The DOL-353–378 sample only contained 0.036% organic carbon, compared with 3.11% in the latosol soil; the de-LOI process removed ~99% of the carbon from latosol soil.

## 2.5. XAS analyses

The speciation and local structure around chromium in all Cr(VI)-doped latosol soil samples, and in reference compounds including CrO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Cr metal, Cr(OH)<sub>3</sub>, CrO<sub>3</sub> solution (denoted as HCrO<sub>4</sub><sup>-</sup>) and a humic-acid-bound Cr(III) (denoted as HA-Cr), were investigated using the synchrotron-based XAS technique on the wiggler C (BL-17C) at NSRRC in Taiwan.

The electron storage ring operated at 1.5 GeV with a beam current of 100–200 mA and an energy span of 4–15 keV for the monochromator during the data collection period. The energy resolution was 2.0 × 10<sup>-4</sup>. XAS spectra of the Cr *K*-edge (5989 eV) of the Cr(VI)-doped latosol soil samples were recorded in fluorescence mode (termed F-mode) at room temperature, while those of chromium references were recorded in transmission mode (termed T-mode). For Cr XAS recording, the scanned energy range was 5789–6989 eV. It was divided into three regions with various energy step sizes and scanning times for each scanned point: (i) 5789–5969 eV with 7.5 eV per step for 1 s (6.0 eV and 2 s for the F-mode), (ii) 5969–6029 eV with 0.4 eV per step for 1 s (0.3 eV and 2 s for the F-mode) and (iii) 6029–6989 eV with 0.06 Å<sup>-1</sup> per step for 2 s (0.06 Å<sup>-1</sup> with 4 s for the F-mode). The 5979–6059 eV range of the XAS spectra was selected as XANES spectra

after the processes of energy calibration with Cr(0) metal and normalization.

Data analysis was performed using *WinXAS 3.0* software (Ressler, 1998). With this software it was possible to simulate sample XANES spectra to quantify Cr species fractions based on their fingerprints in the near-edge region by linearly combining a set of reference XANES spectra. The quality of XANES fitting was evaluated by a 'residual' parameter which is mathematically defined as the ratio between the sum of the absolute values of the offsets of the simulative XANES from the normalized absorption of the experimental XANES and the normalized absorption of the experimental XANES (Ressler *et al.*, 2000). To determine the oxidation state of iron compounds that accounted for 3.23% of the latosol soil, XAS experiments were also performed on iron at the Fe *K*-edge (7112 eV). Reference compounds used were FeS<sub>2</sub>, FeS, FeO, Fe<sub>3</sub>O<sub>4</sub>, γ-Fe<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub>, γ-FeOOH and α-FeOOH.

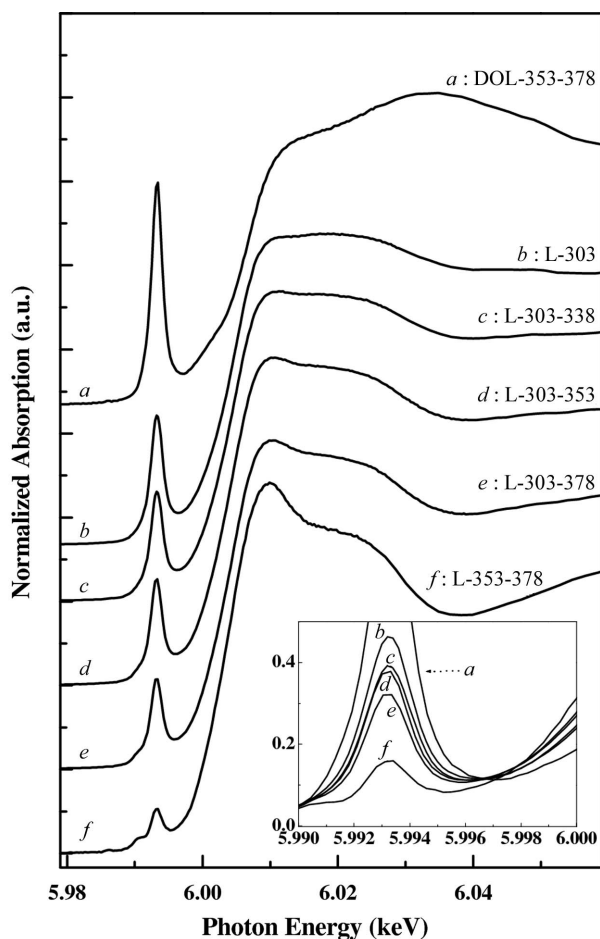
For Fe XAS T-mode recording, the range of scanned energy was 6912–8112 eV. The respective energy step size and scanning time at each point was 7.5 eV and 1 s (7.0 eV and 2 s for the F-mode) in the 6912–7092 eV range, 0.4 eV and 1 s (0.35 eV and 2 s for the F-mode) in the 7092–7152 eV range and 0.06 Å<sup>-1</sup> with 2 s (0.06 Å<sup>-1</sup> with 4 s for the F-mode) in the 7152–8112 eV range. The segments in the 7102–7182 eV range of the XAS spectra were selected as XANES spectra after the processes of energy calibration with Fe(0) metal and normalization.

## 3. Results and discussion

### 3.1. Effect of temperature on Cr(VI) reduction

The Cr(VI) pre-edge is characterized by a strong absorption peak at ~5993 eV owing to the transition of a Cr 1s core electron to its 3d orbital. This transition is allowed owing to the lack of a center of inversion symmetry in the CrO<sub>4</sub><sup>2-</sup> tetrahedral structure (Bajt *et al.*, 1993; Sutton *et al.*, 1993; Peterson *et al.*, 1997a). The pre-edge region of Cr(III), which is dramatically different from that of Cr(VI), is characterized by two small-intensity peaks. The normalized area or height of the pre-edge peak of chromium has been determined to be quantitatively proportional to the ratio Cr(VI)/total-Cr (Bajt *et al.*, 1993; Sutton *et al.*, 1993; Peterson *et al.*, 1997a).

As shown in Fig. 1, the height of the pre-edge peak of Cr XANES spectra from samples heated at various temperatures were superimposed and compared with each other. This shows the dependence of Cr(VI) chemical reduction on heating conditions. Obviously, air-drying the Cr(VI)-doped latosol soil slurry at 303 K to dryness (L-303) reduced Cr(VI) to the lowest extent. Further application of heat at 333, 353 and 378 K for three days to the L-303 sample caused a decrease of the Cr pre-edge height (or area). Higher temperatures resulted in lower peak intensity, but the extent of the decrease was not dramatic. This indicates that heating the dry sample L-303 at 333, 353 and 378 K for three days has limited effect on a further Cr(VI) reduction. Fig. 1 indicates that the pre-edge intensity of the DOL-353–378 sample is much greater



**Figure 1**  
Cr XANES of heated samples. The pre-edge peaks have been magnified in the inset for clarity.

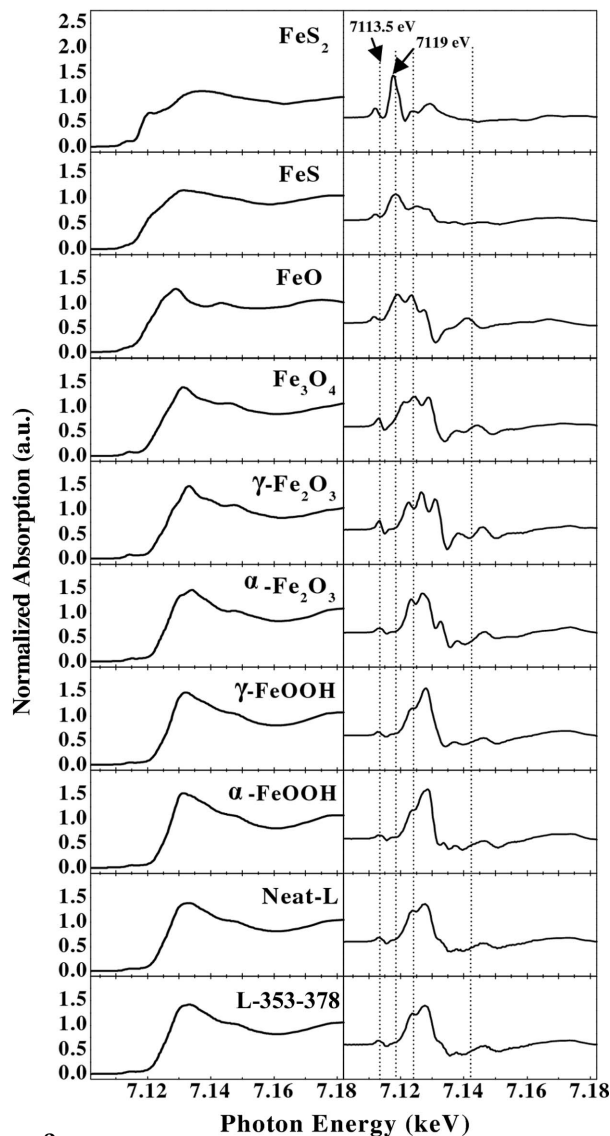
than all the other samples owing to the lack of organic matter to chemically reduce Cr(VI).

Furthermore, a comparison of the pre-edge intensity between L-353–378 and all other samples (Fig. 1) reveals that the rate of Cr(VI) chemical reduction by NOM was greatly enhanced when the sample was dried at 353 K before heating at 378 K (*i.e.* the L-353–378 sample). Note that when drying the Cr(VI)-containing soil slurry at 353 K in the oven, as compared with air-drying at 303 K, the kinetic rate constant of the redox reaction at 353 K is greater than that at 303 K according to the Arrhenius equation.

### 3.2. Effect of Fe(II) on Cr(VI) reduction

Because previous studies have reported that Fe(II) can reduce Cr(VI) in laboratory or field soil remediation experiments (Peterson *et al.*, 1997a,b; Buerge & Hug, 1998, 1999; Seaman *et al.*, 1999; Loyaux-Lawniczak *et al.*, 2001), and because the content of iron compounds (represented in oxide form) in our latosol soil was determined to be 3.23%, possible Cr(VI) chemical reduction by Fe(II) in latosol soil was investigated.

Fig. 2 presents a comparison of eight reference spectra and two sample spectra (Neat-L and L-353–378). The curves in the



**Figure 2**  
Fe K-edge XANES and its first derivative of eight iron reference compounds, latosol soil (termed Neat-L) and the L-353–378 sample. The dotted lines running through each panel in the right-hand column are intended for an easier comparison among the derivative spectra.

left-hand column represent XANES and their corresponding derivative spectra are presented in the right-hand column (see Fig. 2). For the derivative spectra, the Fe(II) reference compounds (*i.e.* FeS<sub>2</sub>, FeS and FeO) present a characteristic peak at 7119 eV, whereas the Fe(III) compounds show no distinctive features. Further, the small peak at 7113.5 eV observed for Fe(III) reference compounds, Neat-L and L-353–378 is slightly shifted to a lower photon energy by ~1.5 eV (*i.e.* located at 7112 eV) for Fe(II) references (FeS<sub>2</sub>, FeS and FeO). Note that a previous study reported that the photon energy of the average pre-edge centroid position of Fe(II) compounds was  $1.4 \pm 0.1$  eV lower than that of Fe(III) compounds (Wilke *et al.*, 2001). Based on this information, the present study infers that Fe in both Neat-L and L-353–378 samples is mainly present as Fe(III). In addition, as can be seen in Fig. 2, the XANES spectra of Neat-L and L-353–378

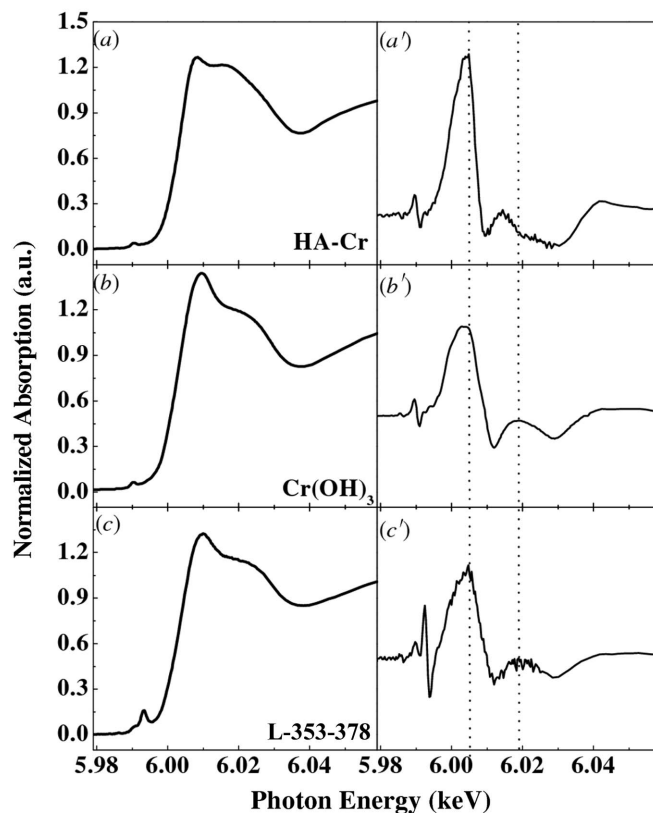
samples are almost identical to each other and so are their corresponding derivative spectra. This suggests that the thermal treatment did not change Fe speciation. In conclusion, the amount of Fe(II) in the soil samples can be considered negligible.

Because most iron in the latosol soil was in the form of Fe(III), and because previous reports have shown that Cr(VI) reduction by organic compounds and by NOM in the absence of oxide catalysis proceeds at a rate as slow as months to years (Elovitz & Fish, 1994), it is reasonable to infer that the fast Cr(VI) reduction by the NOM in latosol soil was probably due to the catalysis effect exhibited by the intrinsic oxide surfaces. The latosol soil contains  $\alpha$ -FeOOH,  $\gamma$ -FeOOH, hematite, muscovite, kaolinite and SiO<sub>2</sub> as the main inorganic oxide constituents, and all of them have been previously demonstrated to accelerate Cr(VI) chemical reduction (Deng & Stone, 1996; Peterson *et al.*, 1997a,b; Buerge & Hug, 1998, 1999; Seaman *et al.*, 1999).

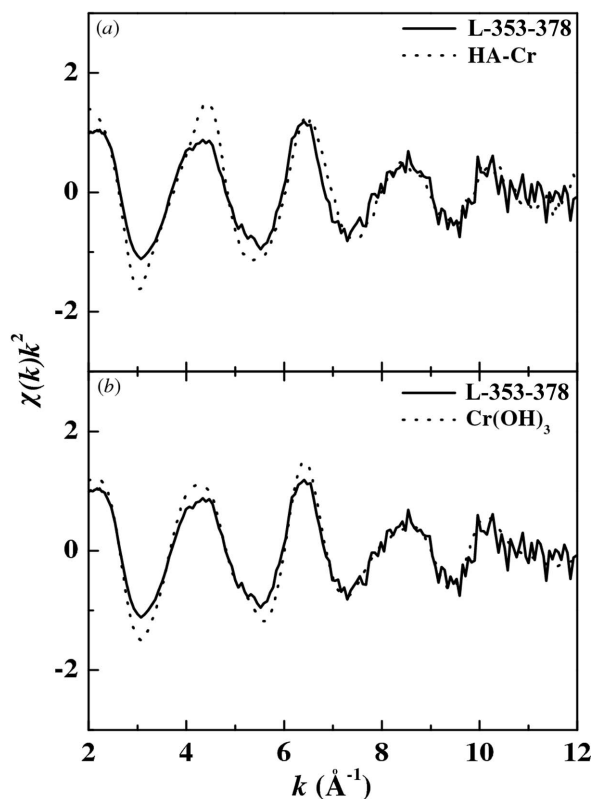
### 3.3. Speciation of chromium in the L-353-378 sample

Some research studies have suggested that Cr(VI) reduction in soils or aquifer systems by humic substance or organic compounds resulted in the formation of mobile Cr(III) that then readily precipitated as Cr(OH)<sub>3</sub> (James & Barlett, 1983; Jardine *et al.*, 1999) or as a solid solution Fe<sub>x</sub>Cr<sub>1-x</sub>(OH)<sub>3</sub> (James & Barlett, 1983), or chelated by organic compounds which were adsorbed to oxide surfaces (James & Barlett, 1983; Jardine *et al.*, 1999). Therefore, in order to speciate Cr after the reduction by NOM in sample L-353-378, in the present study the Cr XANES spectrum and its first derivative from L-353-378 are compared with those from Cr(OH)<sub>3</sub> and HA-Cr (Fig. 3). Fig. 3 indicates that the Cr XANES and its first derivative from L-353-378 are quite similar to Cr(OH)<sub>3</sub>, except for the pre-edge region because L-353-378 still contains a minor amount of Cr(VI). In Fig. 4, the Cr EXAFS spectrum of L-353-378 is superimposed onto that of HA-Cr (Fig. 4a) and the Cr(OH)<sub>3</sub> reference (Fig. 4b). Clearly, L-353-378 has a greater similarity to Cr(OH)<sub>3</sub> than to HA-Cr. Therefore, based on XANES and its first derivative, as well as on EXAFS, there is evidence that L-353-378 most probably contains Cr(OH)<sub>3</sub> as the major chromium species after the Cr(VI) chemical reduction.

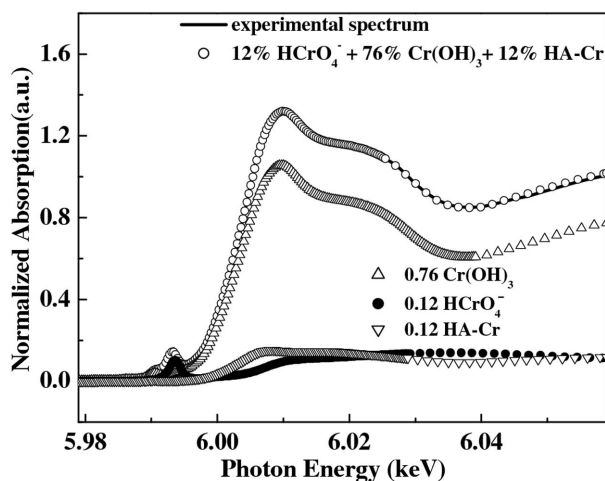
The determination of the ratio Cr(OH)<sub>3</sub>/total-Cr in L-353-378 is presented in Fig. 6 after Cr(OH)<sub>3</sub> was inferred as the key chromium species. An attempt to quantitatively determine the Cr(OH)<sub>3</sub> percent requires proper selection of chromium reference compounds. At an earlier stage of the present study, the XANES spectrum from L-353-378 was simulated with various linear combinations of CrO<sub>3</sub>, Cr(OH)<sub>3</sub> and HA-Cr in different percents; however, the least-square simulation based on a combination of these three references was unsuccessful. Thus, CrO<sub>3</sub> powder was replaced by a CrO<sub>3</sub> water solution of ~pH 4 [*i.e.* this solution is denoted as HCrO<sub>4</sub><sup>-</sup> because it contains HCrO<sub>4</sub><sup>-</sup> as the main Cr(VI) species at ~pH 4 based on a thermodynamic equilibrium calculation, although it was not exactly 100% HCrO<sub>4</sub><sup>-</sup> (Krajnc *et al.*, 1995)]. The reason



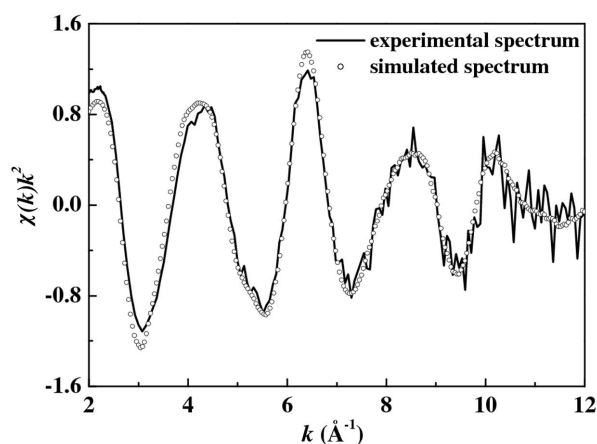
**Figure 3** Comparison of Cr XANES and its first derivative from the L-353-378 sample with that of Cr reference compounds.



**Figure 4** Cr EXAFS from the L-353-378 sample superimposed onto that from humic-acid-bound chromium (HA-Cr) (a) and Cr(OH)<sub>3</sub> (b).



**Figure 5**  
Result of fitting Cr XANES from the L-353–378 sample with Cr reference compounds. Note that humic-acid-bound chromium is here denoted as HA-Cr.



**Figure 6**  
Simulation of the Cr EXAFS spectrum from L-353–378 with a linear combination of the set of reference compounds based on the weight percents resulting from the Cr XANES fitting of L-353–378 as indicated in Fig. 5.

for using the  $\text{HCrO}_4^-$  reference was that there can be still some  $\text{HCrO}_4^-$  sorbed to the soil. Fig. 5 demonstrates that L-353–378 can be satisfactorily simulated with a linear combination of XANES spectra of 12%  $\text{HCrO}_4^-$ , 76%  $\text{Cr}(\text{OH})_3$  and 12% HA-Cr. The residual value for the simulation is 0.560. Fig. 6 indicates that the EXAFS from the L-353–378 can be well simulated with this linear combination too. This result is consistent with that based on the comparisons among XANES/first derivative (Fig. 3) and among EXAFS (Fig. 4); all these data indicate that  $\text{Cr}(\text{OH})_3$  is the major chromium species in L-353–378.

#### 4. Conclusions

Low-temperature treatment of Cr(VI)/NOM-containing latosol soil in the present study may have the potential to be

engineered into an effective remedial strategy toward immobilizing Cr(VI) in high content (e.g. 4.0 wt%) in NOM-containing inorganic matrices such as sediments, sludges, wastes and soils. The heat at 353–378 K is readily accessible from the flue gas stream of an industrial boiler or furnace; it may be accomplished by using a heat exchanger across the hot flue gas stream. For the Cr(VI)-containing inorganic matrices devoid of NOM, the Cr(VI) reduction can be achieved in the heated batch slurry with an addition of NOM that can be easily found in the environment.

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