



## Reduction and immobilization of chromate in chromite ore processing residue with nanoscale zero-valent iron

Jingjing Du<sup>a</sup>, Jinsuo Lu<sup>b</sup>, Qiong Wu<sup>a</sup>, Chuanyong Jing<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

<sup>b</sup> School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

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### ABSTRACT

Chromite ore processing residue (COPR) poses a great environmental and health risk with persistent Cr(VI) leaching. To reduce Cr(VI) and subsequently immobilize in the solid matrix, COPR was incubated with nanoscale zero-valent iron (nZVI) and the Cr(VI) speciation and leachability were studied. Multiple complementary analysis methods including leaching tests, X-ray powder diffraction, X-ray absorption near edge structure (XANES) spectroscopy, and X-ray photoelectron spectroscopy (XPS) were employed to investigate the immobilization mechanism. Geochemical PHREEQC model calculation agreed well with our acid neutralizing capacity experimental results and confirmed that when pH was lowered from 11.7 to 7.0, leachate Cr(VI) concentrations were in the range 358–445 mg L<sup>-1</sup> which contributed over 90% of dissolved Cr from COPR. Results of alkaline digestion, XANES, and XPS demonstrated that incubation COPR with nZVI under water content higher than 27% could result in a nearly complete Cr(VI) reduction in solids and less than 0.1 mg L<sup>-1</sup> Cr(VI) in the TCLP leachate. The results indicated that remediation approaches using nZVI to reduce Cr(VI) in COPR should be successful with sufficient water content to facilitate electron transfer from nZVI to COPR.

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### 1. Introduction

Chromium contamination of soil, sediment, and water has received increasing attention because of its severe impact on public health. Common Cr exposure pathways include ingestion, inhalation, and dermal contact. The primary health impacts from Cr are damages to the gastrointestinal, respiratory, and immunological systems, as well as reproductive and developmental problems [1]. Recently, a study from the U.S. National Institute of Health suggested that drinking water containing hexavalent chromium Cr(VI), a human carcinogen with an inhalation exposure pathway, could lead to cancer [1]. Among various forms of Cr contamination, the chromite ore processing residue (COPR) possess a great environmental and health risk with persistent Cr(VI) release at appreciable concentrations [2,3]. In addition to inhalation and drinking, incidental ingestion of Cr-containing dusts is a potential important exposure route for nearby residents. Although the high-lime process responsible for such COPR generation was abandoned in the U.S. and the U.K. by the late 1960s, it is still being used in countries such as China and India [4,5]. About 1 million tonnes of COPR are produced each year in China and more than 6 million tonnes of COPR was stored in heaps [6]. The fact that Cr(VI) is

incorporated in the COPR solid matrix rather than on particle surfaces makes it a great challenge to reduce and immobilize Cr(VI) in COPR [7].

Stabilization/solidification (S/S) technology with Portland cement is commonly used for the treatment of soils contaminated with heavy metals including Cr [8]. The Cr leachability in S/S treated samples is determined by its oxidation state, and Cr(VI) is readily leachable. Meanwhile, the S/S additives are not effective in reducing Cr(VI) to Cr(III) [9]. Effective reductants should be added before cement addition to solidify the contaminated soils [10].

The Cr(VI) reductants generally include S-containing species [2,11–13], and ferrous iron [3,14]. The reduction using S-containing species was generally not satisfactory with respect to the residual Cr(VI) content in COPR. Although TCLP leachate Cr(VI) concentration was lower than 5 mg L<sup>-1</sup>, *in situ* XANES analysis demonstrated that the residual Cr(VI) content was as high as 610.2 mg kg<sup>-1</sup> [15]. On the other hand, ferrous iron has been most extensively studied and proven to be an effective reductant of Cr(VI) at acidic and neutral pH [16]. However, it cannot successfully remediate high-lime COPR because its mineralogical complexity prevents effective Cr(VI) availability for subsequent conventional chemical reduction [3,17]. In recent years nanoscale zero-valent iron (nZVI) has been developed and demonstrated to be an effective reductant for the immobilization of Cr(VI) in water and soils [18–21]. Nevertheless, limited research is conducted on the leachability and speciation of Cr in COPR in the presence of nZVI [22].

\* Corresponding author. Tel.: +86 10 6284 9523; fax: +86 10 6284 9523.  
E-mail address: [cyjing@rcees.ac.cn](mailto:cyjing@rcees.ac.cn) (C. Jing).

The objectives of this study were to (1) explore the Cr immobilization mechanism in COPR in the presence of nZVI, (2) evaluate the effects of nZVI dosage and water content on Cr(VI) reduction, and (3) identify the Cr speciation in COPR with multiple complementary techniques including X-ray absorption near edge structure (XANES) spectroscopy and X-ray photoelectron spectroscopy (XPS). The complete Cr(VI) reduction and immobilization with nZVI shed new light on COPR remediation.

## 2. Materials and methods

### 2.1. Sample preparation

COPR samples were collected from an industrial waste site at Jinan, China. The samples were passed through a 60-mesh (0.25 mm) sieve to remove large particles. The sieved samples were dried at 80 °C and stored in capped containers. The cement used in our experiment is the Portland cement, which was obtained from Anhui CONCH Cement Company. The water content listed in Table 1 was calculated using Eq. (1):

$$\text{Water\%} = \frac{m_{\text{water}} \text{ (g)}}{m_{\text{water}} \text{ (g)} + m_{\text{nZVI}} \text{ (g)} + m_{\text{COPR}} \text{ (g)}} \times 100\% \quad (1)$$

The nZVI particles were synthesized according to the method introduced by Wang and Zhang [23]. Briefly, solutions of ferric chloride (0.045 M) and potassium borohydride (0.25 M) were mixed with 1:1 v/v ratio. The formed nanoparticles were separated from the solution using vacuum filtration, and then washed with distilled water and 5% ethanol.

For the nZVI incubation treatment, 0% (Inc-0 as a control sample), 1% (Inc-1), 2% (Inc-2), 3% (Inc-3), 4% (Inc-4), 6% (Inc-6), and 10% (Inc-10) nZVI (wt. nZVI/wt. dry COPR) were mixed with 15 g COPR in a glove box (100% N<sub>2</sub>). The samples were incubated with saturated water content (28–36%) in wide mouth glass bottles in darkness for 180 d to study the durability and stability of the nZVI treatment. This water saturation was operationally achieved by adding DI water dropwisely till free water (unbounded with particles) was observed. At designed times, the samples were used in batch extraction tests to evaluate Cr(VI) leachability.

To explore a two-step COPR remediation route, *i.e.*, nZVI incubation followed by cement stabilization, sub-samples of Inc-0, Inc-2, Inc-6, and Inc-10 were mixed with 25% cement (wt. cement/wt. dry COPR) after incubated for 7 d. The cement treated samples denoted as CInc-0, CInc-2, CInc-6, and CInc-10 were stored in sealed sample bags and cured at room temperature for another 7 d.

To confirm the nZVI optimum dosage under constant water content, increasing amounts of nZVI from 0 to 10% were mixed with 15 g COPR. The samples named as WInc-0, WInc-2, WInc-6, and WInc-10 under the same water content (33%) were incubated in wide mouth glass bottles in darkness for 7 d.

To evaluate the effect of water content on the COPR stabilization using nZVI, various amount of water was added into Inc-6 sample to reach water content ranging from 23% to 33%. The samples were incubated for 7 d.

Conventional S/S treatment with Portland cement and nZVI were also employed as control and the treatment procedure was the same as our previous report [24]. Briefly, COPR samples were mixed with 10% cement (10% C), 25% cement (25% C), 2.5% nZVI (2.5% Fe), 6% nZVI (6% Fe), a series of combinations of 10% cement and 2.5% nZVI (LCLFe), 10% cement and 6% nZVI (LCHFe), 25% cement and 2.5% nZVI (HCLFe), and 25% cement and 6% nZVI (HCHFe), respectively. The mixtures were compacted according to ASTM D 1557-91 standard. The compacted specimens were stored in sealed sample bags and cured at room temperature for 28 d. Then, the solids were pulverized and used in batch extraction tests.

### 2.2. Experiments

Total metal contents were determined according to USEPA method 3050B [25] and analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES Optima 2000 DV, Perkin Elmer Co., USA) with a detection limit of 100 µg L<sup>-1</sup>. Alkaline digestion test was conducted to determine Cr(VI) content in solid samples following USEPA method 3060A [26]. The soluble Cr(VI) concentrations were determined using a Hach DR 2800 Spectrophotometer based on USEPA method 7196A [27] with a detection limit of 20 µg L<sup>-1</sup>. The Fe(II) concentration was measured using 3500-Fe B phenanthroline colorimetric method [28] with a detection limit of 50 µg L<sup>-1</sup>. XANES data were collected at the BL3C1 beamline at Pohang Light Source, South Korea for Cr speciation analysis. XPS, X-ray powder diffraction, and energy dispersive X-ray spectrometry for mineralogical analysis were performed. A complete description of data collection and analysis is provided in [supplementary material](#).

General acid neutralizing capacity (GANC) test was performed following the procedures described in a previous report [29]. Eleven single batch extractions were performed in parallel. After 48 h tumbling at a L/S ratio of 20, the equilibrium pH and soluble Cr concentration were measured. Toxicity characteristic leaching procedure (TCLP) was employed to determine the Cr(VI) leachability according to USEPA method 1311 [30]. A 0.1 M acetic acid solution with a pH of 2.88 was used as leachant. The COPR samples were extracted at a liquid to solid (L/S) ratio of 20 in capped polypropylene bottles on a rotary tumbler at 30 rpm for 18 h. After the extraction, the final pH of the leachate was measured and the liquid was separated from the solids by filtration through a 0.45 µm glass fiber filter. A Chinese leaching protocol, solid waste extraction procedure for leaching toxicity: sulfuric acid and nitric acid method (HJ/T299-2007) [31], was also employed and referred to HJ. Synthetic acid rain water was used as leachant in HJ by mixing sulfuric acid and nitric acid (60/40, w/w) at pH 3.20. COPR samples were extracted at a liquid to solid (L/S) ratio of 10 on a rotary tumbler at 30 rpm for 18 h. At the end of the leaching tests, pH and Eh were monitored and soluble metal concentrations were determined.

The adsorption diffuse layer model (DLM) was employed to describe the leachability of Cr and Cr(VI) in the GANC test. The chemical equilibrium computer program PHREEQC Version 2.18 with DLM adsorption option was used to simulate adsorption, precipitation, and aqueous reactions [32]. Default equilibrium constants in MINTEQA and LLNL database were used in the calculation. Details of the model parameters are presented in [Table S2 in the supplementary material](#).

## 3. Results and discussion

### 3.1. Characterization of COPR

#### 3.1.1. Total metal content

The metal contents in COPR are shown in [Table S1 \(supplementary material\)](#). The total Cr in COPR was 43.2 g kg<sup>-1</sup>. The Cr(VI) content determined using alkaline digestion was 15.9 g kg<sup>-1</sup>, which was approximately 37% of total chromium. The calcium and iron content was 191 and 62.3 g kg<sup>-1</sup>, respectively. The high calcium concentration and the high pH at 11.7 were the result of the high-lime processing of chromite ore for chromate production. COPR sample also contained magnesium (72.4 g kg<sup>-1</sup>), sodium (36.7 g kg<sup>-1</sup>), and potassium (4.7 g kg<sup>-1</sup>).

#### 3.1.2. GANC

Acetic acid was used to determine the GANC and the metal leachability. When the leachant acidity increased from 0 to

**Table 1**  
Physical and chemical properties, and leaching tests results for nZVI incubation samples.

Sample	Water, %	TCLP				HJ			
		pH	Eh (mV)	Cr(VI) (mg L <sup>-1</sup> )	Total Cr (mg L <sup>-1</sup> )	pH	Eh (mV)	Cr(VI) (mg L <sup>-1</sup> )	Total Cr (mg L <sup>-1</sup> )
COPR	15	9.1	–	330 ± 39	–	11.6	–	453 ± 36	–
Inc-0 <sup>a</sup>	28	9.2	190	309 ± 28	312 ± 12	11.5	36	451 ± 21	527 ± 42
Inc-2 <sup>a</sup>	31	8.9	87	64.3 ± 1.7	74.1 ± 4.7	11.1	23.7	84.0 ± 1.0	101 ± 25
Inc-6 <sup>a</sup>	34	7.5	–459	N.D. <sup>c</sup>	N.D. <sup>c</sup>	9.7	–435	N.D. <sup>c</sup>	N.D. <sup>c</sup>
Inc-10 <sup>a</sup>	36	7.2	–461	N.D. <sup>c</sup>	N.D. <sup>c</sup>	8.8	–455	N.D. <sup>c</sup>	N.D. <sup>c</sup>
Clnc-0 <sup>b</sup>	20	9.4	174	168 ± 6.1	201 ± 22	12.4	–87	229 ± 25	286 ± 33
Clnc-2 <sup>b</sup>	23	9.2	115	32.1 ± 2.2	40.3 ± 2.5	11.9	–131	40.6 ± 0.29	53.1 ± 1.7
Clnc-6 <sup>b</sup>	24	7.8	–325	N.D. <sup>c</sup>	N.D. <sup>c</sup>	10.7	–167	N.D. <sup>c</sup>	N.D. <sup>c</sup>
Clnc-10 <sup>b</sup>	24	7.5	–329	N.D. <sup>c</sup>	N.D. <sup>c</sup>	9.6	–323	N.D. <sup>c</sup>	N.D. <sup>c</sup>
WInc-0 <sup>a</sup>	33	8.8	231	308 ± 34	319 ± 29	11.3	111	364 ± 8.1	507 ± 16
WInc-2 <sup>a</sup>	33	8.6	210	92.1 ± 20	115 ± 17	10.5	104	102 ± 3.2	121 ± 9.3
WInc-6 <sup>a</sup>	33	7.3	–318	N.D. <sup>c</sup>	N.D. <sup>c</sup>	9.5	–304	N.D. <sup>c</sup>	N.D. <sup>c</sup>
WInc-10 <sup>a</sup>	33	7.2	–423	N.D. <sup>c</sup>	N.D. <sup>c</sup>	8.8	–368	N.D. <sup>c</sup>	N.D. <sup>c</sup>

<sup>a</sup> The samples were incubated for 7 d.

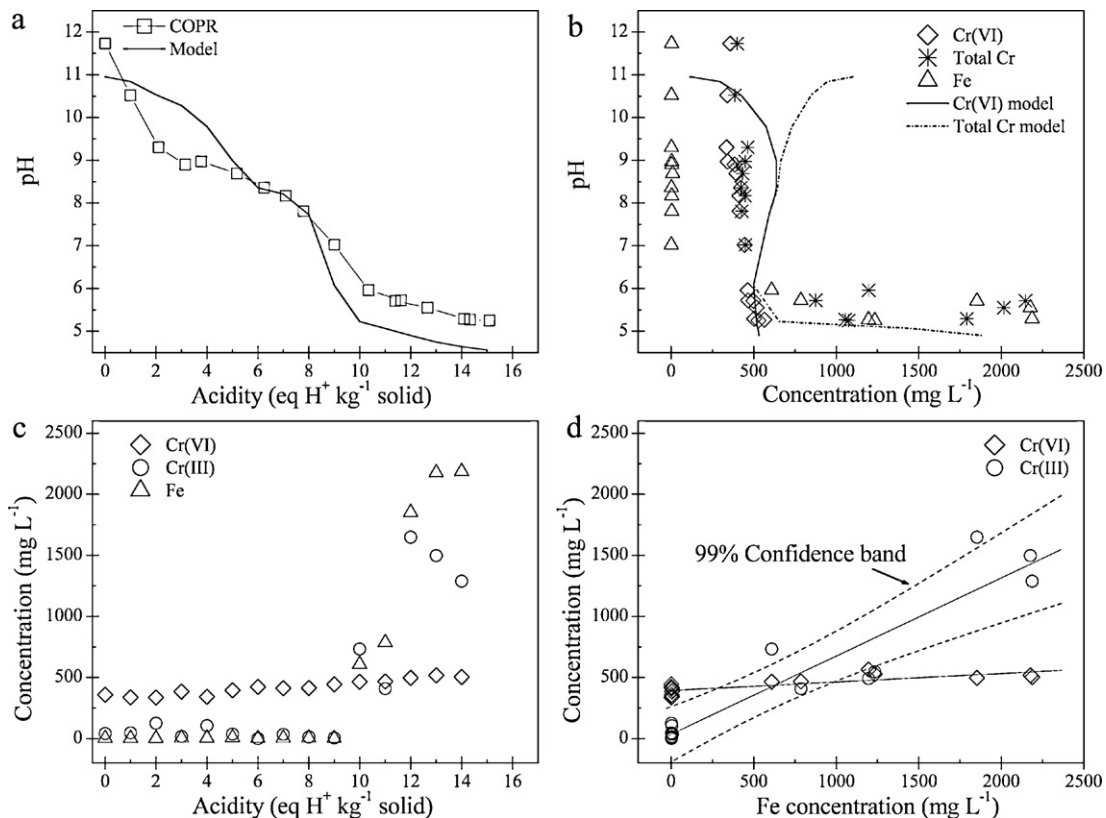
<sup>b</sup> The samples were incubated for 7 d and mixed with 25% cement for another 7 d.

<sup>c</sup> The concentration was below the detection limit.

15 eq H<sup>+</sup> kg<sup>-1</sup>, the solution pH decreased from 11.7 to 5.3 (Fig. 1a). Approximately 2 eq H<sup>+</sup> kg<sup>-1</sup> acidity was needed to attain pH value at about 9. The GANC results from PHREEQC calculation are also presented in Fig. 1, which fits reasonably well with the experimental data. Both observed and model calculated results showed that when pH was lowered from 11.7 to 7.0, Cr(VI) concentrations slightly ascended from 358 to 445 mg L<sup>-1</sup> which contributed over 90% of dissolved Cr (Fig. 1b). Upon pH further declined to less than 6, Cr(III) and Fe concentrations were elevated exponentially while Cr(VI) concentration was slightly increased up to about 500 mg L<sup>-1</sup>. The sharp increase of Cr(III) and Fe leachability occurred when acidity was higher than 9 eq kg<sup>-1</sup> (Fig. 1c). The correlation of Cr(III)

and Cr(VI) concentrations with the concentration of Fe is shown in Fig. 1d. The correlation coefficient of a linear regression model was 0.80 (slope = 0.07,  $p = 1.05 \times 10^{-4}$ ) for Cr(VI) and 0.95 (slope = 0.64,  $p = 8.04 \times 10^{-9}$ ) for Cr(III). The dashed lines in Fig. 1d show the 99% confidence limits. The amount of Cr released was positively related to the amount of Fe dissolved from COPR.

GANC results showed that about 42–65% Cr(VI) were available in aqueous phase upon pH decreased from 11.7 to 5.3 (Fig. 1b and c). On the other hand, about 50% Cr(VI) were associated with solid phase in a wide pH range. This high percentage of solid association might be the major challenge for effective Cr(VI) reduction and COPR remediation [7].



**Fig. 1.** GANC results and the PHREEQC model calculation for COPR sample. The changes of equilibrium pH with increasing leachant acidity (a); changes of Cr(VI), Cr(III), and Fe concentrations as a function of acidity (b); changes of Cr(VI), total Cr, and Fe concentrations as a function of equilibrium pH (c); changes of Cr(VI) and Cr(III) concentrations as a function of Fe concentration (d).

### 3.2. Immobilization of Cr(VI) by nZVI

#### 3.2.1. Cr(VI) immobilizing efficiency

The nZVI addition significantly reduced the Cr(VI) leachability as determined by TCLP and HJ (Table 1). For example, the Cr(VI) concentration in TCLP leachate decreased from 330 mg L<sup>-1</sup> in untreated COPR sample to 64 mg L<sup>-1</sup> with 2% nZVI addition (Inc-2). The pH in the TCLP leachate of untreated COPR sample was slightly reduced to 9.1 because of the high GANC of COPR (Fig. 1a). A remarkable Cr(VI) immobilization was achieved with 6% and 10% nZVI addition, where the Cr(VI) leachate concentration was below the detection limit (20 μg L<sup>-1</sup>). Our experimental observations agree well with thermodynamic calculations as shown in the pe–pH diagram in Fig. S2 and confirm that Cr(III) should be the stable Cr species with 6% and 10% nZVI addition.

Our previous study suggests that cement can be successfully used for Cr(III) immobilization in soils [33]. We therefore hypothesized an approach to reduce the nZVI dosage by a two-step route: reducing Cr(VI) in COPR with nZVI and subsequently immobilizing the waste with cement. The results show that 25% cement addition after nZVI incubation (CInc-2) lowered Cr(VI) and total Cr concentrations in TCLP leachate from 64.3 and 74.1 mg L<sup>-1</sup> in Inc-2 sample, respectively, to 32.1 and 40.3 mg L<sup>-1</sup> (Table 1). Although cement addition resulted in approximately 50% additional decrease in leachate Cr concentrations, more than 30 mg L<sup>-1</sup> of Cr(VI) in CInc-2 sample was leached out which was far beyond the current regulatory limit of 5 mg L<sup>-1</sup> for a nonhazardous waste characterized by the US EPA. The results signifies that cement as one of the most commonly used S/S-treatment binders was ineffective in Cr(VI) immobilization in COPR samples. In order to achieve complete Cr(VI) reduction and immobilization, sufficient nZVI should be added. Once Cr(VI) in COPR was reduced, cement addition may increase the strength of the solid waste to be used for construction purpose [24].

#### 3.2.2. Effect of nZVI dosage

The effect of nZVI dosage on Cr(VI) reduction in COPR was investigated under a constant water content at 33% with increasing nZVI dosage from 0 to 10% (Table 1). The concentration of Cr(VI) in TCLP leachate was 92.1 mg L<sup>-1</sup> with 2% nZVI addition, and substantially decreased to below the detection limit with 6% and 10% nZVI addition. The results indicated that Cr(VI) reduction were positively related with the nZVI dosage. A minimum addition of 6% nZVI was required to achieve a complete Cr(VI) reduction in COPR, which is in agreement with the results obtained under slightly different water content (23–33%).

#### 3.2.3. Control experiment

To gain insight of COPR immobilization using nZVI, control experiments were performed by concurrently mixing COPR, nZVI, and cement under a series of concentrations. As shown in Table 2, co-addition of nZVI and cement could reduce the Cr(VI) leachability, however, more than 100 mg L<sup>-1</sup> of Cr(VI) was still detected in TCLP and HJ leachate. The results of control experiments indicate that simultaneous addition of nZVI and cement could not remediate COPR, which is contrary to incubation results with the same amount of nZVI. Cao and Zhang reported a reduction capacity of 69–72 mg Cr(VI) g<sup>-1</sup> nZVI, which was obtained from the mass balance calculation of dissolved Cr(VI) concentration in a slurry of 2 g COPR with 40 mL water [22]. The resulting high reduction capacity is indicative of an effective electron transfer between Cr(VI) and nZVI in their slurry experiments. In stark contrast, the electron transfer was not successfully established in S/S-treated samples with such low water content in the range of 14.2–21.3% due to water consumption by cementitious reactions. Furthermore, the presence of cement could prevented the effective Cr(VI) and nZVI availability

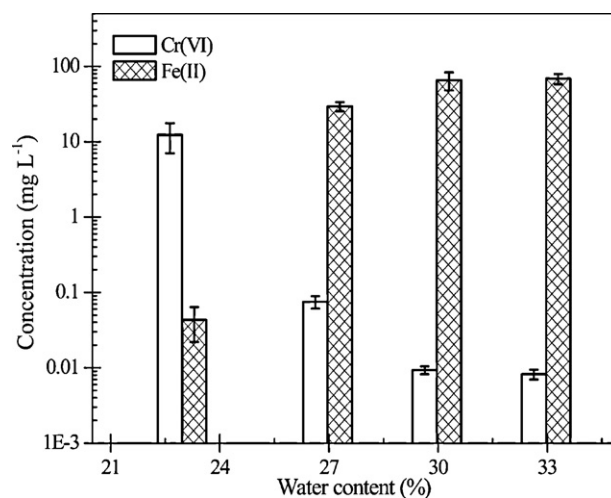


Fig. 2. Cr(VI) and Fe contents determined with TCLP method from the Inc-6 (6% nZVI + COPR) sample at water content 23%, 27%, 30%, and 33%. The samples were incubated for 7 d.

for the redox reaction, thus resulting in poor Cr(VI) remediation performance. In addition, because the Cr(VI) reduction favors at low pH range as illustrated in the pe–pH diagram (Fig. S2), the high pH values as a result of cement addition (10.6–12.1, Table 2) may also be responsible for the ineffective Cr(VI) reduction. The contrast between incubation and S/S treatment samples necessitates further investigations such as water content effect.

#### 3.2.4. Effect of water content

To assess the effect of water content on Cr(VI) reduction, COPR samples were incubated with 6% nZVI and increasing water content of 23, 27, 30, and 33%. The Cr(VI) and Fe(II) concentrations in TCLP leachate are shown in Fig. 2. The leachate Cr(VI) concentrations decreased from 12.3 mg L<sup>-1</sup> to less than 0.02 mg L<sup>-1</sup> with the increasing water content from 23% to 33%, meanwhile, Fe(II) concentrations increased from 0.04 mg L<sup>-1</sup> to 68.5 mg L<sup>-1</sup>. The change of Cr(VI) and Fe(II) concentrations as a function of water content corresponded to the drop of redox potential (Fig. S2), which favors the Cr(VI) reduction. The results validated our hypothesis that increasing water content lead to an effective electron transfer from nZVI to Cr(VI).

#### 3.2.5. Batch tests

The change of Cr(VI) contents in solid samples as a function of incubation time is shown in Fig. 3. To facilitate the effective electron transfer between Cr(VI) and nZVI, the mixtures of COPR and nZVI were incubated under saturated water content (31–36%) for a period of six months. With the nZVI ratio elevated to above 4%, the Cr(VI) content in COPR diminished to less than 0.01 g kg<sup>-1</sup> within 24 h and remained unchanged thereafter. The Cr(VI) content in Fig. 3 was determined using alkaline digestion method which might underestimate the Cr(VI) content because the residual nZVI might reduce the liberated Cr(VI) during digestion [34]. Therefore, *in situ* method such as XANES should provide complementary evidence in accurate determination of Cr speciation.

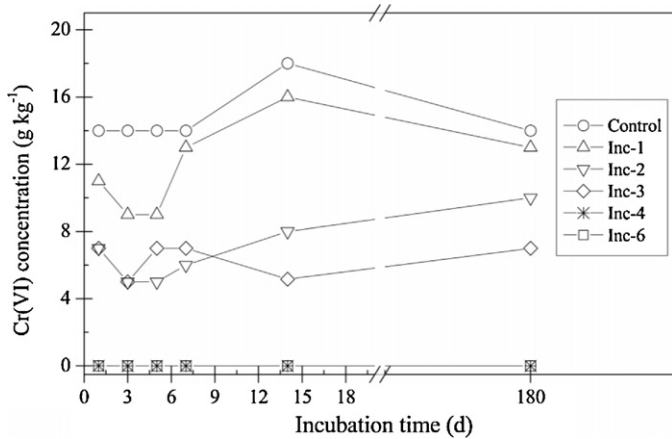
#### 3.2.6. XANES spectroscopy

The XANES analysis was performed to investigate the effectiveness of Cr(VI) reduction in COPR, and the spectra including standard reference samples are shown in Fig. 4. The XANES spectrum for Cr(VI) showed a well-defined pre-edge peak over a 5 eV interval starting at approximately 5992 eV. The Cr<sub>2</sub>O<sub>3</sub> standard showed a broad peak starting at 5998 eV. The distinct pre-peak feature of Cr(VI) allows for Cr speciation in solid samples through a robust

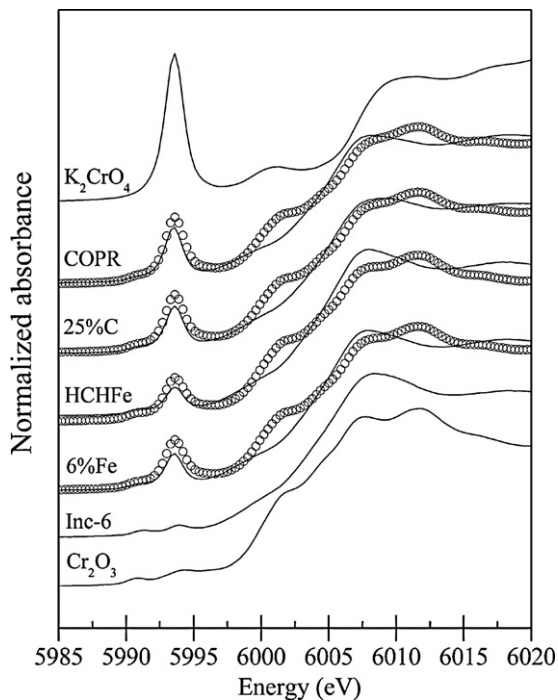
**Table 2**  
Physical and chemical properties, XANES and leaching tests results for S/S treated COPR samples.

Sample	pH	Water (%)	TCLP			HJ			XANES Cr% <sup>a</sup>
			pH	Cr(VI) (mg L <sup>-1</sup> )	Cr% <sup>a</sup>	pH	Cr(VI) (mg L <sup>-1</sup> )	Cr% <sup>a</sup>	
COPR	11.7	17.0	9.1	330 ± 39	52	11.6	453 ± 36	36	39 ± 1
10%C	11.0	14.7	8.9	342 ± 35	55	11.6	583 ± 33	47	–
25%C	12.1	14.2	9.0	314 ± 26	57	11.9	466 ± 24	43	33 ± 1
LCLFe	11.8	19.7	8.8	183 ± 21	34	11.6	261 ± 23	25	–
LCHFe	11.8	21.3	9.1	118 ± 24	25	11.8	132 ± 12	14	–
HCLFe	12.0	16.3	9.5	211 ± 17	43	12.0	222 ± 19	23	–
HCHFe	12.1	17.6	9.4	101 ± 25	23	12.0	112 ± 18	13	22 ± 2
2.5%Fe	10.6	21.0	8.8	205 ± 18	36	12.0	321 ± 27	28	–
6%Fe	11.3	20.3	9.0	126 ± 21	25	11.4	217 ± 16	21	27 ± 2

<sup>a</sup> Cr% stands for the percentage content of Cr(VI) in the leachable total Cr.



**Fig. 3.** Changes of Cr(VI) contents determined with alkaline digestion method as a function of incubation time. Control (untreated COPR); Inc-1 (1% nZVI + COPR); Inc-2 (2% nZVI + COPR); Inc-3 (3% nZVI + COPR); Inc-4 (4% nZVI + COPR); Inc-6 (6% nZVI + COPR).

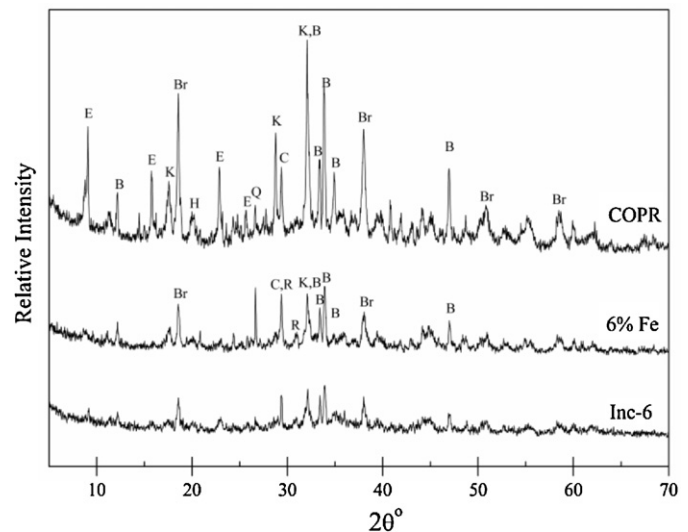


**Fig. 4.** Experimental observed (solid line) and linear combination fitted (dotted line) chromium K-edge XANES spectra for K<sub>2</sub>CrO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, COPR, and treated samples. 25% C: S/S treatment with 25% cement; HCHFe: S/S treatment with 25% cement and 6% nZVI; 6% Fe: S/S treatment with 6% nZVI; Inc-6: incubation with 6% nZVI.

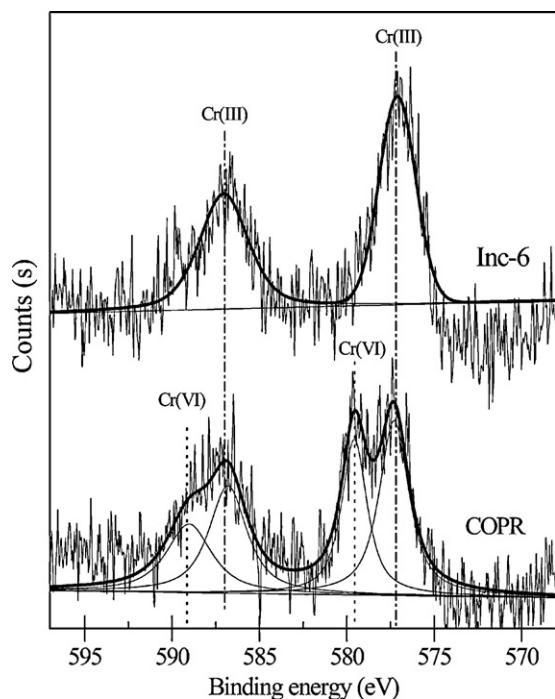
fitting procedure using a least-square linear combination (LC) of the standards. The results of LC fitting are listed in Table 2. Approximately 39% of total Cr was present as Cr(VI) in untreated COPR, which was in agreement with the result of alkaline digestion. The conventional S/S treatment could only lower the Cr(VI) content from 39% for the untreated COPR sample to 22% with 6% nZVI and 25% cement addition (HCHFe). In contrast, no Cr(VI) pre-peak was observed in the Inc-6 sample (Fig. 4), which suggests complete Cr(VI) reduction in this nZVI incubation sample.

### 3.2.7. X-ray powder diffraction (XRPD) analysis

XRPD patterns of untreated and treated COPR samples are shown in Fig. 5. The mineral assemblage of untreated COPR in this study was consistent with COPR mineralogy reported previously [35,36]. Cr(VI)-bearing minerals identified in the untreated COPR included hydrocalumite and katoite hydrogarnet, which are demonstrated hosts for Cr(VI) in COPR samples through anionic substitution [35,37]. The diminished peak intensity of katoite in treated samples indicated that the mineral substantially dissolved. No new Cr(III) and iron phases were detected in nZVI treated samples by XRPD, indicating the formation of amorphous rather than crystalline materials. The same amorphous Cr(III) products were reported by Graham et al. using CaS<sub>x</sub> as reductant for the COPR treatment [13].



**Fig. 5.** The XRPD patterns for the untreated and treated COPR. 6% Fe: S/S treatment with 6% nZVI; Inc-6: incubation with 6% nZVI. B: brownmillerite; Br: brucite; C: calcite; E: ettringite; K: katoite; Q: quartz; R: rustumite.



**Fig. 6.** XPS survey of chromium 2p, for the untreated COPR sample and 6% nZVI incubated sample (Inc-6).

### 3.2.8. Analysis of Cr(VI) reduction by XPS

To confirm the Cr(VI) reduction in the sample incubated with 6% nZVI (Inc-6), surface sensitive XPS analyses were performed. Detailed XPS surveys on Cr 2p region with mathematical curve fitting by using a least-squares fit of Gaussian–Lorentzian line shape are shown in Fig. 6. Four Cr photo-electron peaks were observed for the untreated COPR sample where two  $2p_{3/2}$  peaks were centered at 577.3 and 579.6 eV and two  $2p_{1/2}$  peaks at 586.9 and 589.0 eV. The binding energies of the Cr  $2p_{3/2}$  peak at 577.3 eV and the Cr  $2p_{1/2}$  peak at 586.9 eV were consistent with reported values for  $\text{Cr}_2\text{O}_3$ ,  $\text{CrOOH}$ , and  $\text{Cr}(\text{OH})_3$  which was in the energy range 576.2–577.5 eV for  $2p_{3/2}$  and 586.7–587.0 eV for  $2p_{1/2}$ , respectively [38–40]. Furthermore, the magnitude of the spin-orbit splitting (SOS) between these two peaks was 9.6 eV, which was the characteristic of Cr(III) with reported SOS of 9.7–9.9 eV [41]. The binding energy of the  $2p_{3/2}$  peak at 579.6 eV was comparable to reported values for Cr(VI) which range from 579.0 to 579.8 eV [42]. The SOS for Cr(VI) was 9.4 eV, in agreement with the reported range 9.2–9.4 eV [39,43].

A comparison of peak area between Cr(III) and Cr(VI) indicated that Cr(VI) accounted for about 43% of total Cr on the surface of COPR particles. Further analysis of XPS spectrum for the sample incubated with nZVI suggested that the reduction of Cr(VI) to Cr(III) was complete. The two peaks located at 577.1 and 586.9 eV signified that only Cr(III) exists in the Inc-6 sample. In addition, the SOS between  $2p_{3/2}$  and  $2p_{1/2}$  (9.9 eV) demonstrated the presence of Cr(III) compounds [43].

Appreciable amounts of Cr(VI) were on the surface of COPR particles as evidenced by the surface sensitive XPS analysis (Fig. 6). Once nZVI attached to the COPR surface, nZVI would transfer electrons to Cr(VI) in proximity. However, a large amount of Cr(VI) was incorporated in the solid matrix which was not available to nZVI. Because the solid matrix comprised of metal oxides and  $\text{SiO}_2$  is not conductive, effective electron transfer could not be achieved in the absence of water. Based on our experimental results with 6% nZVI addition (Table 2), the Cr(VI) content was reduced from 39% in COPR to 27% under 20.3% water content. When the water content was increased to about 33% (Inc-6 in Fig. 4), all Cr(VI) was

reduced to Cr(III). The results suggested that the redox reaction mainly occurred in the solid/liquid interface with water facilitating the electron transfer.

## 4. Conclusions

Effective COPR remediation technique presents a great challenge. To explore Cr(VI) immobilization in COPR using nZVI, COPR samples were obtained from a waste site in China containing  $43.2 \text{ g kg}^{-1}$  total Cr. The Cr(VI) content was 37% of total Cr determined using alkaline digestion, which was in agreement with the XANES analysis (39%). XPS analysis suggested that more Cr(VI) (43%) was detected in the COPR surface than in the bulk. Results of GANC experiment and PHREEQC calculation showed that when pH was lowered from 11.7 to 7.0, leachate Cr(VI) concentrations slightly increased from 358 to  $445 \text{ mg L}^{-1}$  which contributed over 90% of dissolved Cr. Conventional S/S treatment with nZVI and cement could reduce the TCLP Cr(VI) concentration from  $330 \text{ mg L}^{-1}$  for the untreated COPR sample to around  $100 \text{ mg L}^{-1}$ . The Cr XANES analysis showed that over 22% of total Cr was in the Cr(VI) form in S/S-treated samples which contributed to the high Cr(VI) leachability. Results of alkaline digestion, XANES, and XPS demonstrated that incubating COPR with nZVI under water content higher than 27% could result in a nearly complete Cr(VI) reduction and less than  $0.1 \text{ mg L}^{-1}$  leachate Cr(VI). The results implied that remediation approaches using nZVI to immobilize Cr(VI) in COPR should be successful with sufficient water content to facilitate electron transfer between Cr(VI) and nZVI. The results shed new light on nZVI application in COPR remediation.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.02.049.

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