

**Remediation of hexavalent chromium contamination in chromite ore  
processing residue by sodium dithionite and sodium phosphate  
addition and its mechanism**

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**Published in Journal of Environmental Management, Volume 192, pp 100-106, 2017.**

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## **Abstract**

Large amounts of chromite ore processing residue (COPR) wastes have been deposited in many countries worldwide, generating significant contamination issues from the highly mobile and toxic hexavalent chromium species (Cr(VI)). In this study, sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) was used to reduce Cr(VI) to Cr(III) in COPR containing high available Fe, and then sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) was utilized to further immobilize Cr(III), via a two-step procedure (TSP). Remediation and immobilization processes and mechanisms were systematically investigated using batch experiments, sequential extraction studies, X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). Results showed that  $\text{Na}_2\text{S}_2\text{O}_4$  effectively reduced Cr(VI) to Cr(III), catalyzed by Fe(III). The subsequent addition of  $\text{Na}_3\text{PO}_4$  further immobilized Cr(III) by the formation of crystalline  $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$ . However, addition of  $\text{Na}_3\text{PO}_4$  simultaneously with  $\text{Na}_2\text{S}_2\text{O}_4$  (via a one-step procedure, OSP) impeded Cr(VI) reduction due to the competitive reaction of  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_4$  with Fe(III). Thus, the remediation efficiency of the TSP was much higher than the corresponding OSP. Using an optimal dosage in the two-step procedure ( $\text{Na}_2\text{S}_2\text{O}_4$  at a dosage of  $12\times$  the stoichiometric requirement for 15 days, and then  $\text{Na}_3\text{PO}_4$  in a molar ratio (i.e.  $\text{Na}_3\text{PO}_4$  : initial Cr(VI)) of 4:1 for another 15 days), the total dissolved Cr in the leachate determined via Toxicity Characteristic Leaching Procedure (TCLP Cr) testing of our samples was reduced to 3.8 mg/L (from an initial TCLP Cr of 112.2 mg/L, i.e. at >96% efficiency).

**Keywords:** Cr(VI);  $\text{Na}_2\text{S}_2\text{O}_4$ ;  $\text{Na}_3\text{PO}_4$ ; COPR; remediation; reductive precipitation.

## 1. Introduction

Chromite ore processing residues (COPR) are hazardous industrial wastes which have been disposed in surface soils at many commercial and industrial sites in the USA, UK, China, Japan, India and in many other countries (Dhal et al., 2013). One of the biggest threats of COPR to the environment is the release of hexavalent chromium (Cr(VI)) ions, which are highly mobile and toxic, and are classified as a respiratory carcinogen in humans (IARC, 2010).

Many techniques, such as chemical reduction (Brose and James, 2013), leaching (Kanchinadham et al., 2013; Li et al., 2011; Wang et al., 2013), pyrolysis (Zhang et al., 2016), solidification & stabilization (Kameswari et al., 2015), electrokinetic methods (Hopkinson et al., 2009) and microbial or plant-based (phyto) remediation (Stewart et al., 2010; Wang et al., 2007, Lai et al., 2016, Habibul et al., 2016) have been employed to remediate or stabilize COPR at bench, pilot or full field-scale. Of these, chemical reduction has proven the most popular. A variety of chemical reductants, including Fe(II) (Chrysochoou et al., 2010; Di Palma et al., 2015; Jagupilla et al., 2009), nZVI (Du et al., 2012; Wang et al., 2014a; Wang et al., 2014b), amorphous FeS<sub>2</sub> (Li et al., 2016), calcium polysulfide (CaS<sub>x</sub>) (Chrysochoou and Johnston, 2015; Chrysochoou et al., 2012; Zhong et al., 2009; Dresel et al., 2008; Graham et al., 2006), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) (Feng et al., 2015) and sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) (Cheng et al., 2009; Fruchter et al., 2000; Istok et al., 1999; Khan and Puts, 2003; Su and Ludwig, 2005) have been utilized in laboratory and field studies to reduce Cr(VI) to Cr(III). The latter, sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>), is a widely used industrial chemical. The effective use of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, in combination with a pH buffer, to treat Cr(VI)-containing groundwater and vadose zone soils has been reported in a number of studies (Fruchter et al., 2000; Istok et al., 1999; Khan and Puts, 2003). The general mechanism of Cr(VI) treatment in Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> applications involves the conversion of Fe(III) present in the Cr-containing

wastes or soils to Fe(II) by  $\text{Na}_2\text{S}_2\text{O}_4$ , and the subsequent reduction of Cr(VI) to Cr(III) by Fe(II) to form the  $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$  solid (Su and Ludwig 2005). However, these authors note the limitations of  $\text{Na}_2\text{S}_2\text{O}_4$  in treating COPR in systems with low available (specifically, dithionite-reducible) iron, and that  $\text{Na}_2\text{S}_2\text{O}_4$  application in such systems may actually enhance Cr release. The effect of  $\text{Na}_2\text{S}_2\text{O}_4$  on the remediation of COPR with high available iron remains largely unexplored, and the mechanisms involved in the remediation of COPR by  $\text{Na}_2\text{S}_2\text{O}_4$  are not precisely defined.

In addition, even in systems where Cr(VI) is effectively reduced to form Cr(III)-containing solid phases, the stability of the reduction products can significantly affect the long-term remediation efficiency of chemical reduction techniques (Zhang et al., 2014). The reduction product of Cr(VI) by  $\text{Na}_2\text{S}_2\text{O}_4$  is  $\text{Cr}(\text{OH})_3$  (Istok et al., 1999; Su and Ludwig, 2005).  $\text{Cr}(\text{OH})_3$  is amorphous, pH-dependent, and can be chelated by low molecular weight organic compounds (e.g. citric acid) (Bartlett, 1991; James et al., 1997). Under certain conditions (e.g. in the presence of strong oxidants such as manganese oxides),  $\text{Cr}(\text{OH})_3$  could be re-oxidized to Cr(VI), and subsequently re-released into the environment, impacting the long-term effectiveness of the remediation (Dhal et al., 2013). Research by Mustafa et al. (2005) and Gomm et al. (2007) illustrates however that the addition of phosphate species to Cr(III) (present as the trivalent chromium ion or chromium hydroxides) resulted in formation of highly stable and insoluble Cr phosphate minerals under ambient conditions. Therefore, the addition of phosphate minerals could be expected to further transform Cr(III) into phosphatic mineral forms, making the reduction products more stable, less extractable and less toxic. This was illustrated in a preliminary study by Feng et al., (2015) who report the successful use of combined sodium thiosulphate and sodium phosphate addition to reduce and immobilize Cr(VI), although the specific reaction mechanisms involved were not examined in this paper.

Herein, we develop a new two-step COPR remediation technique using a combination of a more effective reductant,  $\text{Na}_2\text{S}_2\text{O}_4$ , and  $\text{Na}_3\text{PO}_4$ , and assess the resulting Cr(VI) reaction processes and products. Three sets of aqueous batch experiments were conducted to explore the mechanisms involved in the remediation of COPR by  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Na}_3\text{PO}_4$ . Furthermore, sequential extraction tests, and X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis, were also employed to assess the resulting Cr(VI) reaction products and mechanisms.

## **2. Materials and methods**

### **2.1. Materials**

#### **2.1.1. Chemicals**

Details on chemical reagents used can be found in the Supporting Information. All solutions were prepared using deionized (DI) water with a resistivity of 18 M $\Omega$ -cm obtained from a Milli-Q system (Millipore, Millford, MA).

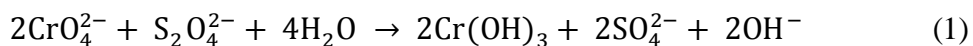
#### **2.1.2. COPR materials**

COPR samples used in this study were collected from a COPR disposal site in Yima, Henan province, China (34.796 N, 111.877 E), where the Zhenxing Chemical Plant was previously located. Information on analytical methods used for characterization of COPR materials can be found in the Supporting Information.

## **2.2. Methods**

### **2.2.1. Remediation of COPR by $\text{Na}_2\text{S}_2\text{O}_4$ alone**

The theoretical redox reaction between Cr(VI) and  $\text{S}_2\text{O}_4^{2-}$  under anaerobic and alkaline conditions (Su and Ludwig, 2005) is:



Based on the reaction stoichiometry of Eq. 1 and the initial concentration of Cr(VI) (2956 mg/kg) in the COPR assessed, solutions with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> dosage of once (1×), twice (2×), four times (4×), eight times (8×), twelve times (12×), sixteen times (16×) and twenty times (20×) the stoichiometric requirement were mixed with COPR at the L:S ratio of 1:1, respectively. The concentration of total dissolved Cr (including dissolved Cr(III) and Cr(VI)) in the leachate following application of the Toxicity Characteristic Leaching Procedure (described below, TCLP Cr) was analyzed after 1, 3, 7, 15 and 30 days of treatment, respectively. The optimal stoichiometric ratio of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to Cr(VI) and the optimal treatment time were obtained when the TCLP Cr concentration reached a minimum.

### 2.2.2. Remediation of COPR by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> combined with Na<sub>3</sub>PO<sub>4</sub>

Na<sub>3</sub>PO<sub>4</sub> was introduced to further immobilize Cr(III) after the reduction of Cr(VI) by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (via a two – step procedure, TSP). In order to simplify the addition process, the effect of a one-step procedure (whereby Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> were added simultaneously, OSP) was also investigated.

The optimal Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> dosage was determined according to the optimal stoichiometric ratio of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to Cr(VI) (see 2.2.1 above). In the OSP experiments, the solutions with the optimal dosage of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and the designated dosage of Na<sub>3</sub>PO<sub>4</sub> were added to COPR at a 1:1 liquid to solid (L:S) ratio, and the molar ratios of Na<sub>3</sub>PO<sub>4</sub> to the initial Cr(VI) in COPR (MR<sub>P/Cr</sub>) were 0.5:1, 1:1, 2:1 and 4:1, respectively. TCLP Cr and pH were analyzed after treating for 30 days.

In the TSP experiments, COPR was firstly mixed with the optimal dosage of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and treated for 15 days; afterwards, the designated dosage of Na<sub>3</sub>PO<sub>4</sub> (MR<sub>P/Cr</sub> were 0.5:1, 1:1, 2:1 and 4:1, respectively) was added, and then reacted for a further 15

days. After the TSP experiments (total 30 days), TCLP Cr and pH were analyzed.

### 2.2.3 Mechanisms of Cr(VI) reduction

To investigate the mechanisms involved in the reduction of Cr(VI) in COPRs by  $\text{Na}_2\text{S}_2\text{O}_4$ , aqueous batch experiments using  $\text{K}_2\text{CrO}_4$  as the Cr(VI) source and  $\text{Na}_2\text{S}_2\text{O}_4$  as the reductant were conducted. Previous studies (Istok et al. 1999; Fruchter et al., 2000; Khan and Puts, 2003; Su and Ludwig, 2005) illustrated that Fe(III) species could promote more effective Cr(VI) reduction by  $\text{Na}_2\text{S}_2\text{O}_4$  via a catalytic process. To further analyze the effect of Fe(III),  $\text{Fe}(\text{OH})_3$  (analytical chemical reagent grade) was introduced to the reaction system. When adding  $\text{Na}_3\text{PO}_4$ , Fe(III) species may react with  $\text{PO}_4^{3-}$  with the formation of  $\text{FePO}_4$ .  $\text{FePO}_4$  is insoluble, stable and crystalline (Shen et al. 2001), and so should not effectively catalyze the reduction of Cr(VI). To investigate the effect of  $\text{Na}_3\text{PO}_4$  on the reduction process, batch experiments were also carried out in the presence of  $\text{FePO}_4$ .

Based on Eq. 1, 60  $\mu\text{M}$  (3120 mg/L) Cr(VI) was reacted with  $\text{Na}_2\text{S}_2\text{O}_4$  solution with a concentration of 0, 30, 60, 120, 240 and 360  $\mu\text{M}$  (namely 0 (0 $\times$ ), 1 (1 $\times$ ), 2 (2 $\times$ ), 4 (4 $\times$ ), 8 (8 $\times$ ), and 12 (12 $\times$ ) times the stoichiometric relationship of  $\text{Na}_2\text{S}_2\text{O}_4$  to Cr(VI)) in a total volume of 40 mL for 24 h on a shaker at 200 rpm at 25 °C. To investigate the effect of  $\text{Fe}(\text{OH})_3$  and  $\text{FePO}_4$ , another two groups of reactions were conducted with 10  $\mu\text{M}$   $\text{Fe}(\text{OH})_3$  and  $\text{FePO}_4$ , respectively. For all reactions, solution pH was controlled by 0.10 M borate buffer with an initial pH of 9.0 (the pH of COPR). The influence of the buffer on the reduction process was negligible (Kim et al., 2001). After reaction, the samples were filtered through 0.22  $\mu\text{m}$  membrane filters for further analysis of dissolved Cr.

#### **2.2.4 The detection of TCLP Cr**

The concentration of dissolved Cr (including dissolved Cr(III) and Cr(VI)) was determined at different experimental durations in COPR samples using the Toxicity Characteristic Leaching Procedure (TCLP), to evaluate the remediation effect on Cr(VI) in COPR. TCLP was conducted according to EPA method 1311, and the total dissolved Cr in the TCLP leachate was determined according to EPA 6010C using ICP–OES.

The concentration of Cr(VI) in the TCLP leachate (TCLP Cr(VI)) was not determined and analyzed in our research. Method EPA 7196, the recommended method for Cr(VI) determination, uses 1,5-diphenylcarbohydrazide as a chromogenic reagent which reacts with Cr(VI) to form a magenta complex that is measured at a wavelength of 540 nm. However, this method gives false negatives for Cr(VI) determination in the presence of  $\text{Na}_2\text{S}_2\text{O}_4$ , even at concentrations as low as 0.0025 M (Su and Ludwig, 2005). This phenomenon appears to be caused by the chemical reduction of Cr(VI) to Cr(III) by dithionite at the required pH of less than 2. Thus, only TCLP Cr was determined.

#### **2.2.5. Sequential extraction tests**

The sequential extraction procedure developed by Tessier et al. (Tessier et al., 1979) was used to quantify the fraction of five operationally defined Cr species in treated and untreated COPR samples. Detailed extraction procedures can be found in Supporting Information.

#### **2.2.6. X-ray diffraction analyses**

Mineralogical analyses of the untreated and treated COPR samples were conducted by X-ray diffraction (XRD, DMAX-2400, Rigaku, Japan), using Cu-K $\alpha$  radiation (40 kV, 30 mA) at a scanning rate of 4°/min from 10° to 70°. Crystalline phases were identified by comparing the intensities and the positions of the Bragg peaks



with the PDF data files of the Joint Committee on Powder Diffraction Standards (JCPDS).

### **2.2.7. X-ray Photoelectron Spectroscopy analyses**

Information on the chemical binding of chromium on the surface of untreated and treated COPR samples was obtained using X-ray Photoelectron Spectroscopy (XPS). Samples were finely ground prior to analysis. The XPS analyses were carried out using an axis ultra spectrometer (Kratos, UK), equipped with a monochromatized Al anode X-ray source ( $h\nu = 1486.7$  eV) at a power of 225 W (15 mA, 15 kV). To compensate for surface charge effects, binding energies were calibrated by using the C 1s hydrocarbon peak at 284.8 eV. The data were fitted using a Shirley baseline and Gaussian-Lorentzian peak shape. The narrow scanned spectra in the range of 567 – 596 eV were used to identify the redox state of chromium. Detailed fitting methods can be found in Supporting Information.

## **3. Results and discussion**

### **3.1 Characteristics of COPR**

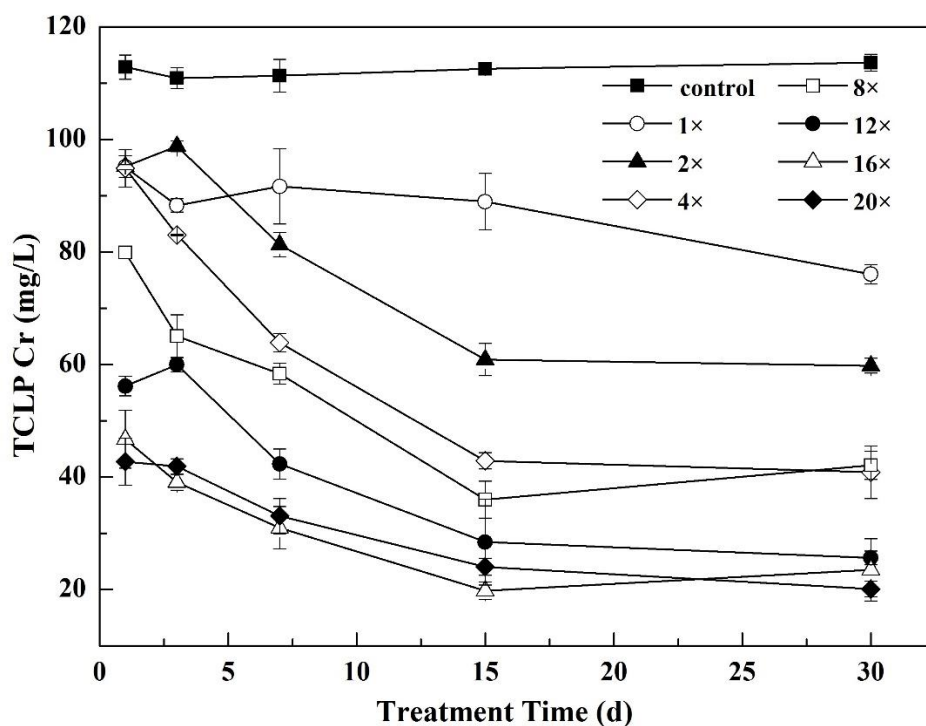
The physical and chemical characteristics of the tested COPR are shown in Table 1. The COPR had a pH of  $9.07 \pm 0.20$ , and is classed as a sandy loam with lower clay content (6.4%). The concentration of total Cr in the COPR was 16917 mg/kg, while Cr(VI) was 2956 mg/kg, approximately 17.5% of the total Cr. The TCLP Cr of the COPR was 112.2 mg/L, which exceeded the EPA regulatory limit (TCLP Cr  $\leq 5$  mg/L) by over 20 times. The concentration of Fe in the COPR was 63306 mg/kg, indicating that it can be classed as a high-Fe COPR.

**Table 1.** Characteristics of tested COPR

Parameter	COPR	Parameter	COPR
Sand (%)	74.20	Cr(VI) (mg/kg)	2956 ± 289
Silt (%)	19.36	Cr(total) (mg/kg)	16917 ± 1403
Clay (%)	6.44	TCLP Cr (mg/L)	112.2 ± 3.8
pH	9.07 ± 0.20	Fe(total) (mg/kg)	63306 ± 3498

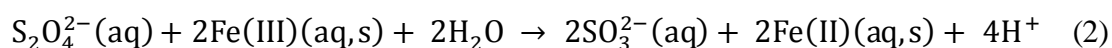
### 3.2. Remediation of COPR by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> alone

The change in TCLP Cr of the COPR during the 30-day treatment period is shown in Fig. 1. No decrease of TCLP Cr was observed in control experiments, indicating that Cr was stable under our experimental conditions. In the first 15 days, TCLP Cr decreased with time regardless of the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> dosage (although the greatest decreases were seen at higher dosages), which demonstrated the effective reduction of Cr(VI) to Cr(III) by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was significantly more effective at reducing TCLP Cr over the 30 day period than either Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or Na<sub>2</sub>SO<sub>3</sub> (Figure S1, Supporting Information).

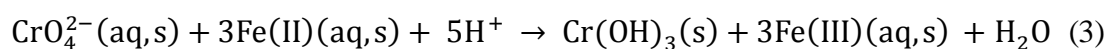


**Fig. 1.** TCLP Cr of COPRs treated by different dosages of  $\text{Na}_2\text{S}_2\text{O}_4$  at different experimental duration.

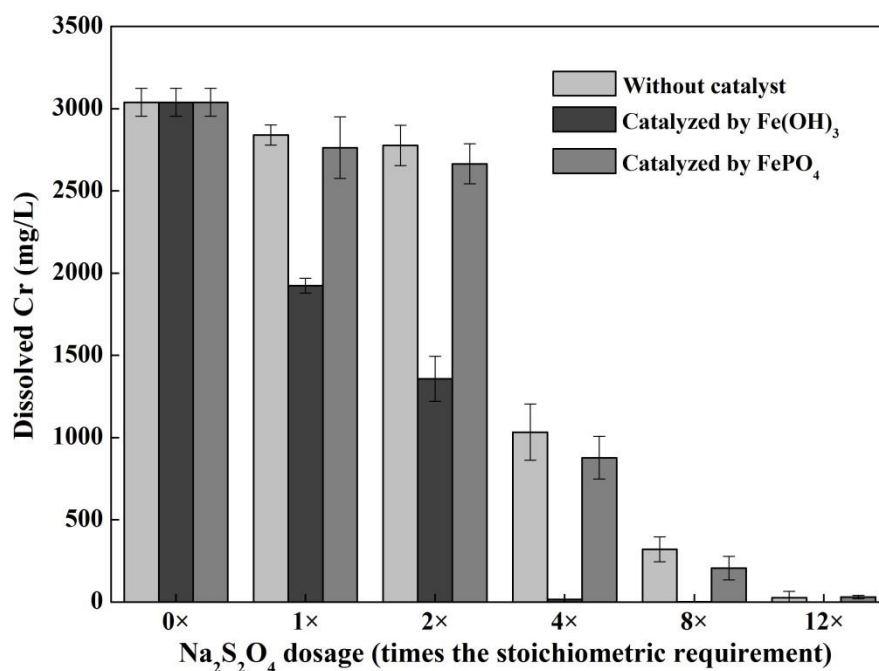
Cr(VI) in COPR could be reduced by  $\text{Na}_2\text{S}_2\text{O}_4$  through two processes: direct (non-catalytic) reduction (i.e. via Eq. 1, section 2.2.1) and catalytic reduction via Fe(III). Istok et al. (Istok et al., 1999) initially proposed that  $\text{Na}_2\text{S}_2\text{O}_4$  could reduce Cr(VI) to Cr(III) via a catalytic process in the presence of Fe(III) (Eq. 2-3), which was confirmed by subsequent studies (Fruchter et al., 2000; Khan and Puts, 2003; Qafoku et al., 2003; Su and Ludwig, 2005; Qafoku et al., 2007; Qafoku et al., 2010). Briefly,  $\text{S}_2\text{O}_4^{2-}$  reacts with available Fe(III) species in COPRs, which may include structural Fe(III) in aluminosilicates, iron-bearing minerals (e.g. iron oxides, siderite and iron sulfides), surface adsorbed Fe(III) species and dissolved Fe(III) species, reducing Fe(III) to Fe(II) as described by Eq. (2).



Then,  $\text{CrO}_4^{2-}$  reacts with Fe(II) (produced by  $\text{S}_2\text{O}_4^{2-}$ ) and is precipitated as a solid hydroxide (e.g.,  $\text{Cr}(\text{OH})_3$ ), following the reaction described in Eq. (3).



To further examine the Cr(VI) reduction process, aqueous batch experiments (using  $\text{K}_2\text{CrO}_4$  as the Cr source) were conducted both in the presence and absence of added  $\text{Fe}(\text{OH})_3$  at pH 9.0. Results (Fig. 2) showed that in the absence of  $\text{Fe}(\text{OH})_3$ , Cr(VI) removal efficiency was 6.5%, 8.6%, 66.0%, 89.4% and 99.1% for stoichiometric ratios of  $\text{Na}_2\text{S}_2\text{O}_4$  to Cr(VI) ( $\text{SR}_{\text{S/Cr}}$ ) of 1 $\times$ , 2 $\times$ , 4 $\times$ , 8 $\times$  and 12 $\times$ , respectively, which demonstrated that reduction of Cr(VI) occurred in the absence of  $\text{Fe}(\text{OH})_3$ , especially when  $\text{SR}_{\text{S/Cr}}$  exceeded 4 $\times$ . In the presence of added  $\text{Fe}(\text{OH})_3$ , Cr(VI) removal efficiency increased sharply to 36.7% (1 $\times$ ), 55.3% (2 $\times$ ), 99.4% (4 $\times$ ) and 99.9% (8 $\times$  and 12 $\times$ ) for each  $\text{SR}_{\text{S/Cr}}$ , respectively. Due to the abundant Fe (63306 ppm) present in the COPRs examined and the faster reaction kinetics of the catalytic process (Beukes et al., 1999; Hug et al., 1997; Su and Ludwig, 2005), it is reasonable to deduce that the reduction of Cr(VI) in the COPRs was enhanced by the Fe(III) catalytic process.



**Fig. 2.** Removal efficiencies of Cr(VI) in aqueous solution under different conditions and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> dosage.

Considering reaction kinetics, further decrease in TCLP Cr was insignificant after the first 15 days of treatment (Fig. 1), and so the optimum treatment time was set to 15 days. TCLP Cr decreased with increasing  $SR_{S_{Cr}}$  up to a  $SR_{S_{Cr}}$  of 12 $\times$ , after which it remained relatively constant with increasing stoichiometric ratios of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to Cr(VI). A  $SR_{S_{Cr}}$  of 12 $\times$  was therefore chosen as the optimal dosage for the removal of Cr(VI) in COPR.

Although the introduction of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was shown to be effective in Cr remediation, the TCLP Cr of the treated COPRs still exceeded the EPA regulatory limit (5 mg/L) (Fig. 1). Due to the near-complete (> 99%) reduction of Cr(VI) by 12 $\times$  Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in aqueous batch experiments both in the presence and absence of Fe(OH)<sub>3</sub> (Fig. 2), the high TCLP Cr concentration most likely derives from the dissolution of Cr(III) during TCLP extraction (Chrysochoou et al., 2010; Dermatas et al., 2006). Further

immobilization of Cr(III) was required to meet the EPA standard.

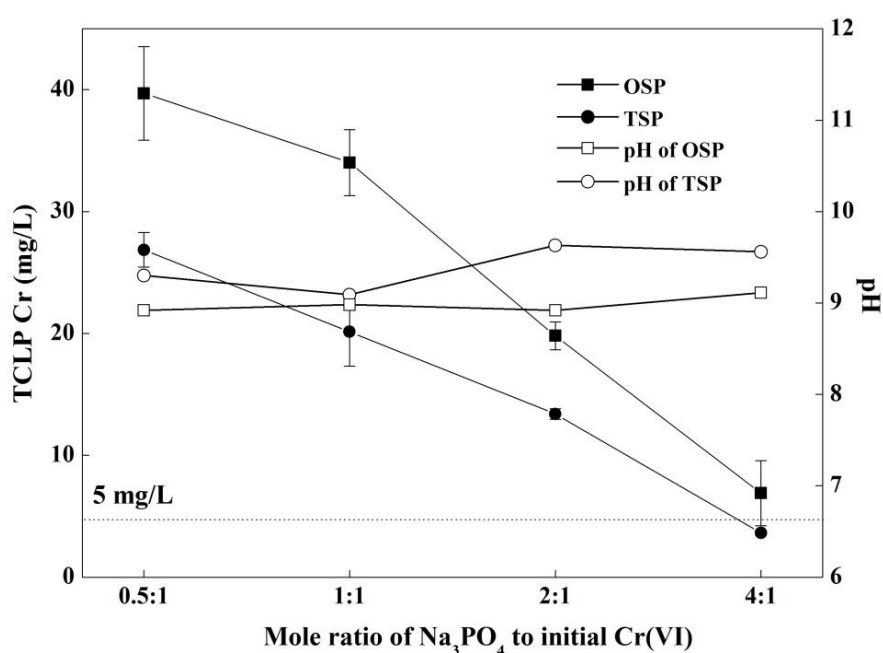
### 3.3. Remediation of COPR by $\text{Na}_2\text{S}_2\text{O}_4$ combined with $\text{Na}_3\text{PO}_4$

To further immobilize Cr(III),  $\text{Na}_3\text{PO}_4$  was introduced in one-step (OSP) and two-step (TSP) process experiments, and the results are shown in Fig. 3. TCLP Cr decreased with increasing  $\text{MR}_{\text{P/Cr}}$  for both OSP and TSP, indicating that  $\text{Na}_3\text{PO}_4$  could immobilize Cr(III). In addition, the TCLP Cr in TSP was lower than that in OSP, which demonstrated that TSP was more effective in immobilizing Cr than OSP. In TSP, when the  $\text{MR}_{\text{P/Cr}}$  was increased to 4:1, the TCLP Cr of COPR decreased to 3.8 mg/L, lower than the EPA regulatory limit (5 mg/L).

Notably, the TCLP Cr of COPR treated through OSP with an  $\text{MR}_{\text{P/Cr}}$  of 0.5:1 and 1:1 (39.7 and 34.0 mg/L) was much higher than COPR treated by  $\text{Na}_2\text{S}_2\text{O}_4$  alone (23.5 mg/L). This indicates that the addition of  $\text{Na}_3\text{PO}_4$  in small amounts may act to impede Cr(VI) reduction by  $\text{Na}_2\text{S}_2\text{O}_4$ . As noted above, the catalytic process via Fe(III) is an important mechanism in the reduction of Cr(VI) to Cr(III) by  $\text{Na}_2\text{S}_2\text{O}_4$ . The addition of  $\text{Na}_3\text{PO}_4$  might hinder this catalytic process through converting available Fe(III) to insoluble and crystalline  $\text{FePO}_4$  (Shen et al., 2001). As shown in Fig. 2,  $\text{Fe}(\text{OH})_3$  increased Cr(VI) removal efficiency by 30.2%, 46.7%, 33.5%, 10.5% and 0.9% for  $\text{SR}_{\text{S/Cr}}$  of 1 $\times$ , 2 $\times$ , 4 $\times$ , 8 $\times$  and 12 $\times$ , respectively, while  $\text{FePO}_4$  only marginally increased Cr(VI) removal efficiency, by 2.6%, 3.7%, 5.1%, 3.8% and -0.1% for each corresponding  $\text{SR}_{\text{S/Cr}}$ , indicating that the catalytic ability of  $\text{FePO}_4$  was negligible and much poorer than  $\text{Fe}(\text{OH})_3$ .  $\text{FePO}_4$  is not an available Fe(III) species due to its high stability and insolubility (Nyavor and Egiebor, 1995). After the introduction of  $\text{Na}_3\text{PO}_4$ ,  $\text{PO}_4^{3-}$  can react with Fe(III) to form insoluble  $\text{FePO}_4$ , which decreases the amount of available Fe(III) and subsequently decreases the reduction efficiency for Cr(VI). However, in the TSP,  $\text{Na}_3\text{PO}_4$  was added after the reduction of Cr(VI) by  $\text{Na}_2\text{S}_2\text{O}_4$  had

effectively completed. Hence the addition of  $\text{Na}_3\text{PO}_4$  did not impede the reduction of Cr(VI) by  $\text{Na}_2\text{S}_2\text{O}_4$  in the TSP. In contrast, the addition of  $\text{Na}_3\text{PO}_4$  hindered the Cr(VI) reduction in the OSP, owing to the competitive reaction of  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Na}_3\text{PO}_4$  with available Fe(III). As a consequence, the two-step process was significantly more efficient in reducing Cr(VI) in high-Fe COPR than the one-step process.

Therefore, the optimal remediation technique can be summarised as follows: firstly, add  $\text{Na}_2\text{S}_2\text{O}_4$  with  $\text{SR}_{\text{S/Cr}}$  of  $12\times$  in COPRs to reduce Cr(VI) for 15 days; secondly, add  $\text{Na}_3\text{PO}_4$  to the treated COPRs with a  $\text{MR}_{\text{P/Cr}}$  of 4:1 for another 15 days to immobilize Cr(III). To further investigate mechanisms involved in the remediation of Cr(VI) in COPRs by combined  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Na}_3\text{PO}_4$  addition, COPRs with different treatments were further analyzed by sequential extraction studies, XRD, and XPS.



**Fig. 3.** TCLP Cr and pH of COPR samples treated in OSP and TSP experiments after 30-day treatment period. OSP: one-step procedure; TSP: two-step procedure.

### 3.4. Sequential extraction studies

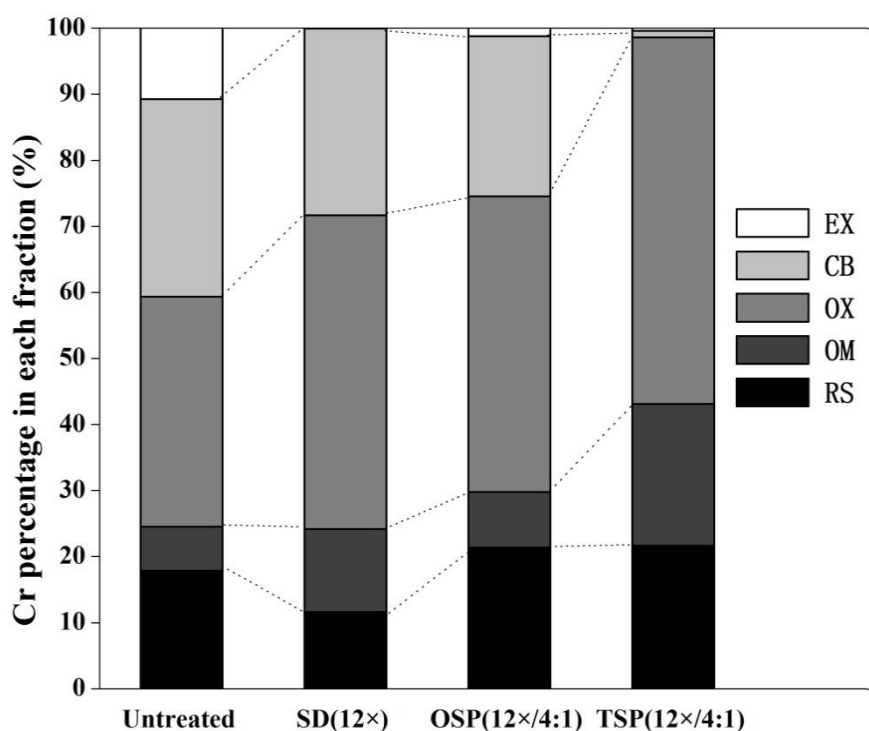
The sequential extraction procedure developed by Tessier et al. (Tessier et al., 1979)

was performed to identify the relative availability of Cr in COPRs. The total content of Cr was separated into five (operationally defined) fractions by this method: exchangeable (EX); bound to carbonates (CB); Fe-Mn oxide bound (OX); organic matter bound (OM) and residual (RS). The relative availability and toxicity follows the following order: EX > CB > OX > OM > RS. Among these, EX and CB are considered readily bioavailable (Wang et al., 2014a).

Figure 4 shows the changes in the fractions of the five Cr species in the untreated and treated COPRs. The primary Cr species in the untreated COPR (Untreated) were split between EX (10.7%), CB (29.9%), OX (34.9%), OM (6.6%), and RS (17.9%). The bioavailable Cr fractions (EX and CB) accounted for 40.6% of the total Cr species. In COPR treated by  $\text{Na}_2\text{S}_2\text{O}_4$  alone with a  $\text{SR}_{\text{S/Cr}}$  of  $12\times$  (SD( $12\times$ )), the EX fraction was almost completely converted to other fractions while the CB fraction remained unchanged, which demonstrated that the reduction of Cr(VI) to Cr(III) by  $\text{Na}_2\text{S}_2\text{O}_4$  led to an apparent decrease in the bioavailability of Cr. Moreover, a substantial increase in the OX fraction in SD( $12\times$ ) was found, which might be largely attributed to the precipitation of  $\text{Cr}(\text{OH})_3$  during the  $\text{Na}_2\text{S}_2\text{O}_4$  treatment (Li et al., 2008; Manning et al., 2007). Compared with the Untreated sample, the Cr content of the RS fraction in SD( $12\times$ ) however decreased from 17.9% to 11.6%, indicating that the addition of  $\text{Na}_2\text{S}_2\text{O}_4$  may destroy or degrade some Fe(III)-containing minerals, according to Eq.2 (Istok et al., 1999; Su and Ludwig, 2005). In parallel, the content of the OM fraction increased from 6.6% to 12.6%, implying that the Cr(III) in the destroyed minerals was oxidized by  $\text{H}_2\text{O}_2$  (one of the extractants for the OM fraction) to Cr(VI) (Kimbrough et al., 1999) and extracted with the OM fraction. In COPR treated through the one-step procedure with a  $\text{SR}_{\text{S/Cr}}$  of  $12\times$  and a  $\text{MR}_{\text{P/Cr}}$  of 4:1 (OSP( $12\times/4:1$ )), an obvious increase in the RS fraction occurred compared with Untreated and SD( $12\times$ ), which indicated that the addition of  $\text{Na}_3\text{PO}_4$  effectively immobilized Cr(III). In COPR treated through



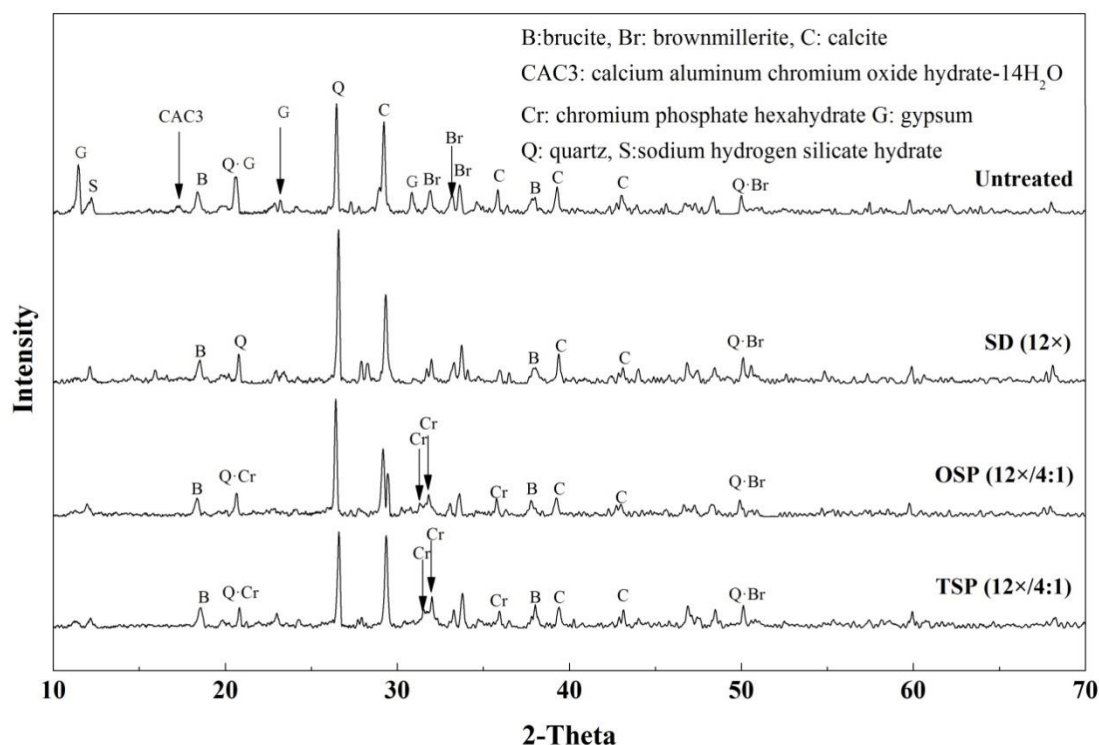
the two-step procedure with a  $SR_{S/Cr}$  of  $12\times$  and a  $MR_{P/Cr}$  of 4:1 (TSP( $12\times/4:1$ )), the content of the RS fraction was similar to OSP( $12\times/4:1$ ), and higher than in the Untreated sample. The EX and CB fractions in TSP( $12\times/4:1$ ) had almost totally converted to OX, OM and RS, indicating that the immobilization of bioavailable fractions of Cr by the TSP was much more efficient than when using the OSP, which agreed well with our conclusions in section 3.3. Clearly, TSP( $12\times/4:1$ ) was the optimal procedure in remediation of Cr(VI) in high-Fe COPR.



**Fig. 4.** Cr speciation for the treated and untreated COPR samples after 30-day treatment period. Untreated: the untreated COPR; SD( $12\times$ ): COPR treated by  $Na_2S_2O_4$  alone with a  $SR_{S/Cr}$  of  $12\times$ ; OSP( $12\times/4:1$ ): COPR treated through the one-step procedure with a  $SR_{S/Cr}$  of  $12\times$  and a  $MR_{P/Cr}$  of 4:1; TSP( $12\times/4:1$ ): COPR treated through the two-step procedure with the same  $Na_2S_2O_4$  and  $Na_3PO_4$  dosages as OSP( $12\times/4:1$ ).

### 3.5. X-ray diffraction analyses

The XRD spectra for the untreated and treated COPRs are shown in Fig. 5. The major phases in the untreated COPR were quartz, calcite, gypsum and brownmillerite (a crystalline oxide of Ca, Fe and Al common in COPR, which acts as a reservoir for Cr(III)). The Cr(VI)-bearing minerals identified were calcium aluminum oxide chromium hydrates (CAC), also known as Cr(VI)-hydrocalumite, with molecular formula  $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CrO}_4 \cdot 14\text{H}_2\text{O}$ . No CAC was found in the treated COPRs, illustrating that Cr(VI) was effectively reduced. No  $\text{Cr}(\text{OH})_3$  phase was identified in SD(12 $\times$ ), indicating that the reduction product of Cr(VI) by  $\text{Na}_2\text{S}_2\text{O}_4$  was amorphous, which agrees well with previous studies (Istok et al., 1999; Namgung et al., 2014; Rai et al., 2002; Su and Ludwig, 2005; Xu et al., 2004). The addition of  $\text{Na}_3\text{PO}_4$ , either through OSP or TSP, resulted in the formation of crystalline chromium phosphate hexahydrate ( $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$ ) which is more stable and insoluble than amorphous  $\text{Cr}(\text{OH})_3$  (Gomm et al., 2007; Mustafa et al., 2005), leading to the lower TCLP Cr than observed for SD(12 $\times$ ). The results of XRD analyses therefore confirmed that the addition of  $\text{Na}_3\text{PO}_4$  immobilized Cr(III) in COPRs through the formation of crystalline  $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$ .

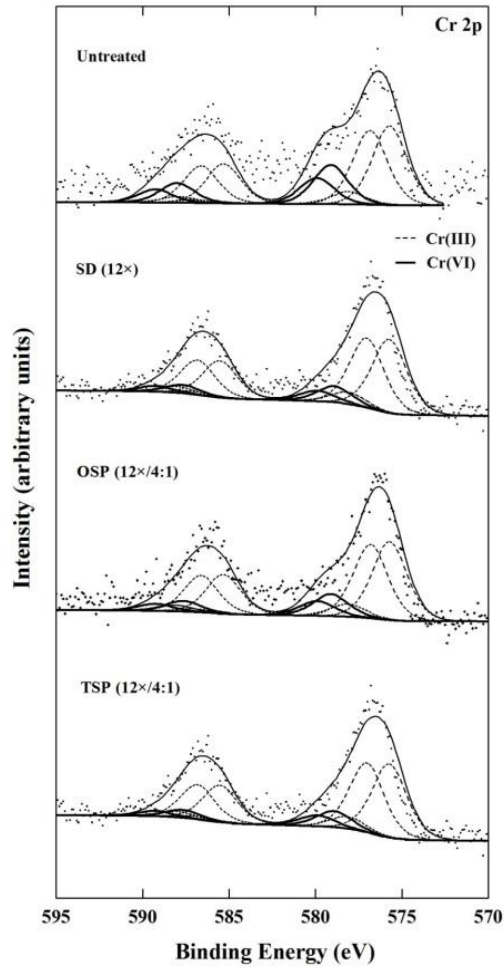


**Fig. 5.** XRD spectra for the treated and untreated COPR samples after 30-day treatment period. Untreated: the untreated COPR; SD(12×): COPR treated by  $\text{Na}_2\text{S}_2\text{O}_4$  alone with a  $\text{SR}_{\text{S/Cr}}$  of 12×; OSP(12×/4:1): COPR treated through the one-step procedure with a  $\text{SR}_{\text{S/Cr}}$  of 12× and a  $\text{MR}_{\text{P/Cr}}$  of 4:1; TSP(12×/4:1): COPR treated through the two-step procedure with the same  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Na}_3\text{PO}_4$  dosages as OSP(12×/4:1).

### 3.6. X-ray Photoelectron Spectroscopy analyses

The XPS Cr 2p spectra for the untreated and treated COPRs are shown in Fig. 6. Semi-quantitative fitting results indicated that the percentage of Cr(VI) in the total Cr was 28.3% for the untreated COPR sample. Because of sample grinding to a fine powder prior to XPS analysis, Cr(VI) present in the interior of COPR particles or agglomerates was exposed and detected by XPS. Thus, the amount of Cr(VI) detected by XPS was much higher than that detected by chemical digestion (17.5%). The proportion of Cr(VI) for SD(12×) decreased to 14.3% after 1-month of treatment,

indicating that reduction of Cr(VI) by  $\text{Na}_2\text{S}_2\text{O}_4$  did occur. Nearly 50% of Cr(VI) remained however after the reductive treatment. This is consistent with results found in previous studies (Chrysochoou et al., 2010; Wazne et al., 2007) on COPR, where the reduction rate of Cr(VI) was only 50 – 60% using  $\text{CaS}_5$ . Most of the remaining Cr(VI) in the  $\text{Na}_2\text{S}_2\text{O}_4$  (SD(12x))-treated sample is not leachable by the TCLP test, and is not readily exchangeable (based on sequential extraction data, above), presumably due to its presence inside larger COPR particles or agglomerates. The proportion of Cr(VI) for SD(12x) was lower than previously reported for 12x sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) on the same treated COPR material (18.0%) (Feng et al. 2015), indicating that the reduction efficiency of  $\text{Na}_2\text{S}_2\text{O}_4$  was higher than  $\text{Na}_2\text{S}_2\text{O}_3$ . Moreover, the percentage of Cr(VI) for OSP(12x/4:1) was 2.8% more than SD(12x), indicating that the addition of  $\text{Na}_3\text{PO}_4$  in OSP inhibited the reduction of Cr(VI) to Cr(III) by  $\text{Na}_2\text{S}_2\text{O}_4$ . The amount of Cr(VI) in TSP(12x/4:1) was similar to that in SD(12x), indicating that the addition of  $\text{Na}_3\text{PO}_4$  in TSP did not contribute to the reduction of Cr(VI). Instead, the enhanced remediation effect observed for TSP can be attributed to the immobilization of Cr(III) by the formation of  $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$ . These results agree well with our conclusions in section 3.3.



**Fig. 6.** Cr 2p spectra of treated and untreated COPRs after 30-day treatment period. Untreated: the untreated COPR; SD(12×): COPR treated by  $\text{Na}_2\text{S}_2\text{O}_4$  alone with a  $\text{SR}_{\text{S/Cr}}$  of 12×; OSP(12×/4:1): COPR treated through the one-step procedure with a  $\text{SR}_{\text{S/Cr}}$  of 12× and a  $\text{MR}_{\text{P/Cr}}$  of 4:1; TSP(12×/4:1): COPR treated through the two-step procedure with the same  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Na}_3\text{PO}_4$  dosages as OSP(12×/4:1). All samples were finely ground prior to analysis.

#### 4. Conclusions

The present study demonstrated, for the first time, that applying  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Na}_3\text{PO}_4$  to treat high-Fe COPR could significantly enhance Cr immobilization. Specifically:

(1)  $\text{Na}_2\text{S}_2\text{O}_4$  alone was effective in reducing Cr(VI) in COPR. When the  $\text{SR}_{\text{S/Cr}}$  was  $12\times$  and the treatment time was 15 days, the decrease in TCLP Cr reached a maximum (approximately 79%) and further increases in dosage of  $\text{Na}_2\text{S}_2\text{O}_4$  and/or treatment time had little effect on the removal of Cr(VI). Nevertheless, the TCLP Cr exceeded the EPA regulatory limit (5 mg/L) by nearly 5 times.

(2) The subsequent addition of  $\text{Na}_3\text{PO}_4$  reduced the TCLP Cr of COPR by immobilizing Cr(III) in a phosphate mineral form, making the Cr(III) in the COPR more stable. The optimal remediation process was a two-step procedure with a  $\text{SR}_{\text{S/Cr}}$  of  $12\times$  and a  $\text{MR}_{\text{P/Cr}}$  of 4:1. The TCLP Cr of the COPR treated by this two-step procedure ( $\text{TSP}(12\times/4:1)$ ) met the EPA regulatory limit.

(3) The results from sequential chemical extractions, XRD and XPS analyses confirmed that the optimal remediation procedure effectively reduced Cr(VI) to Cr(III) and also immobilized the Cr(III) in a more stable, less extractable and less toxic form, crystalline  $\text{CrPO}_4\cdot 6\text{H}_2\text{O}$ .

### **Acknowledgments**

This research was supported by the National Natural Science Foundation of China (No.21077002), Ministry of Environmental Protection (No. 201009006), and National Science and Technology Ministry (2014BAC12B01). Yunyi Li acknowledges support from a China Scholarship Council (CSC) visiting scholarship. We gratefully acknowledge the editor and anonymous reviewers for their valuable help in the review and revision process.

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