



## Research article

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



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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 (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) was used to reduce Cr(VI) to Cr(III) in COPR containing high available Fe, and then sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>) 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 Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> effectively reduced Cr(VI) to Cr(III), catalyzed by Fe(III). The subsequent addition of Na<sub>3</sub>PO<sub>4</sub> further immobilized Cr(III) by the formation of crystalline CrPO<sub>4</sub>·6H<sub>2</sub>O. However, addition of Na<sub>3</sub>PO<sub>4</sub> simultaneously with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (via a one-step procedure, OSP) impeded Cr(VI) reduction due to the competitive reaction of Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> 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 (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> at a dosage of 12× the stoichiometric requirement for 15 days, and then Na<sub>3</sub>PO<sub>4</sub> in a molar ratio (i.e. Na<sub>3</sub>PO<sub>4</sub>: 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).

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## 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, 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.,

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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 ( $\text{Na}_2\text{S}_2\text{O}_4$ ), is a widely used industrial chemical. The effective use of  $\text{Na}_2\text{S}_2\text{O}_4$ , 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  $\text{Na}_2\text{S}_2\text{O}_4$  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

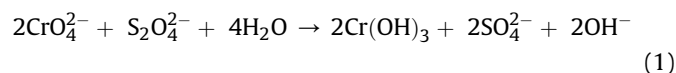
COPR samples used in this study were collected from a COPR disposal site in Yima, Henan province, China (34.796 N, 111.877 E),

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  $\text{Na}_2\text{S}_2\text{O}_4$  dosage of once (1 $\times$ ), twice (2 $\times$ ), four times (4 $\times$ ), eight times (8 $\times$ ), twelve times (12 $\times$ ), sixteen times (16 $\times$ ) and twenty times (20 $\times$ ) 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  $\text{Na}_2\text{S}_2\text{O}_4$  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 $\text{Na}_2\text{S}_2\text{O}_4$ combined with $\text{Na}_3\text{PO}_4$

$\text{Na}_3\text{PO}_4$  was introduced to further immobilize Cr(III) after the reduction of Cr(VI) by  $\text{Na}_2\text{S}_2\text{O}_4$  (via a two – step procedure, TSP). In order to simplify the addition process, the effect of a one-step procedure (whereby  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{Na}_3\text{PO}_4$  were added simultaneously, OSP) was also investigated.

The optimal  $\text{Na}_2\text{S}_2\text{O}_4$  dosage was determined according to the optimal stoichiometric ratio of  $\text{Na}_2\text{S}_2\text{O}_4$  to Cr(VI) (see 2.2.1 above). In the OSP experiments, the solutions with the optimal dosage of  $\text{Na}_2\text{S}_2\text{O}_4$  and the designated dosage of  $\text{Na}_3\text{PO}_4$  were added to COPR at a 1:1 liquid to solid (L:S) ratio, and the molar ratios of  $\text{Na}_3\text{PO}_4$  to the initial Cr(VI) in COPR ( $\text{MR}_{\text{P/Cr}}$ ) 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  $\text{Na}_2\text{S}_2\text{O}_4$  and treated for 15 days; afterwards, the designated dosage of  $\text{Na}_3\text{PO}_4$  ( $\text{MR}_{\text{P/Cr}}$  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

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