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The enhancement effect of pre-reduction using zero-valent iron on the solidification of chromite ore processing residue by blast furnace slag and calcium hydroxide

Jinchunzi Li, Zhonglin Chen, Jimin Shen *, Binyuan Wang, Leitao Fan

State Key Laboratory of Urban Water Resource and Environment, School of Municipal & Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

HIGHLIGHTS

- Blast furnace slag-based S/S is used for the solidification of COPR.
- Zero-valent iron is used to enhance the solidification performance of COPR.
- The performance of S/S treatment was superior to that of solidification alone.
- The leaching test is used to evaluate the Cr release from the treated samples.
- All of the S/S treated specimens were suitable for utilization at certain levels.

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ABSTRACT

A bench scale study was performed to assess the effectiveness of the solidification of chromite ore processing residue (COPR) by blast furnace slag and calcium hydroxide, and investigate the enhancement effect of pre-reduction using zero-valent iron (ZVI) on the solidification treatment. The degree of Cr immobilization was evaluated using the Toxicity Characteristic Leaching Procedure (TCLP) as well as the solid waste-extraction procedure for leaching toxicity–sulfuric acid & nitric acid method (Chinese standard HJ/T299-2007). Strength tests and semi-dynamic leaching tests were implemented to investigate the potential for reusing the final treatment product as a readily available construction material. The experimental results showed that the performance of pre-reduction/solidification (S/S) was superior to that of solidification alone. After pre-reduction, all of the S/S treated COPR samples met the TCLP limit for total Cr (5 mg L^{-1}), whereas the samples with a COPR content below 40% met the pollution control limit of bricks and building block products (Chinese standard HJ/T 301-2007) produced with COPR for total Cr (0.3 mg L^{-1}). At the same time, all of the S/S treated specimens tested were suitable for utilization at certain levels.

1. Introduction

Chromite ore processing residue (COPR) is the waste product generated during the isolation of chromium from chromite ore using a high-lime processing (Moon et al., 2009). The major concern of COPR is the presence of hexavalent Cr, which is a strong carcinogen and mutagen that may account for up to 35% or more of the total residual Cr in COPR. The rest of the residual Cr in COPR is Cr(III), which is lower toxicity and solubility than Cr(VI) because it is a micronutrient (Elzinga and Cirmo, 2010). In China, untreated COPR is disposed in open-air in most cases, and in some case, the deposited site is close to water sources or densely populated areas. The migratory Cr(VI) contaminates soil and surface water as well as groundwater, and the contamination process is accelerated by local precipitation (Li and Kai, 2012).

Several remediation technologies have already been applied in the treatment of Cr(VI) in COPR (Rodríguez-Piñero et al., 1998; Wang et al., 2007; Velasco et al., 2012). One promising technology is the stabilization/solidification (S/S) (Dermatas and Meng, 2003; Dalmacija et al., 2011) of solid wastes by mixing the waste with a binder to reduce the leachability of the contaminants and to convert the hazardous waste into an environmentally acceptable form of waste for land disposal or as recyclable construction material. Cement-based, cement/fly ash-based and lime/fly ash-based S/S technologies are the generic S/S processes, and solidification of Cr

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* Corresponding author. Tel.: +86 18645003297; fax: +86 451 86283028.
E-mail address: shenjimin@hit.edu.cn (J. Shen).

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in cementitious matrices has been studied by many researchers (Dechesne and Laforest, 2004; Yu et al., 2005; Zhang et al., 2009; Bulut et al., 2009; Shi and Kan, 2009). However, it has been reported that some metals such as chromium (VI), arsenic (III) and mercury are not suitable for use with this type of binding material since they do not form highly insoluble hydroxides (Mulligan et al., 2001). In addition, another report (Batchelor, 2006) demonstrated that cements generally provide a moderately oxidizing environment, which is adverse to the reduction of Cr(VI)–Cr(III), but the addition of blast furnace slag can produce reducing conditions by releasing sulfide and other reduced sulfur compounds. Blast furnace slag is a by-product of the manufacture of pig iron from iron ore, limestone and coke. It has been used as a secondary cementing material for more than 100 years (Bellmann and Stark, 2009). For above reason, slag is considered to be used for the solidification of COPR as an alternative material for cement.

The major toxic component of COPR is hexavalent Cr(VI), which is difficult to stabilize due to its mobility. It is a common method to pretreat Cr(VI)-bearing wastes to reduce Cr(VI)–Cr(III) (Rodríguez-Piñero et al., 1998). The most commonly used reducing agents are reduced iron and reduced sulfur compounds (Li, 2003; Erdema and Tumen, 2004; Graham et al., 2006; Ludwig et al., 2007; Wazne et al., 2007; Cheng et al., 2009). In recent years, there has been growing concern with the use of ZVI for the stabilization of Cr(VI) in water and soil (Cissoko et al., 2009; Mitra et al., 2011; Singh et al., 2012). ZVI is a very promising reactive medium because it is low-cost, easy to obtain, and effective (Junyapoon and Weerapong, 2006), while the reduction capacity of the micro-scale iron is severely limited in an alkaline environment (Cao and Zhang, 2006), and Cr(VI) was reduced more efficiently in an acid medium by ZVI (Junyapoon and Weenrapong, 2006; Gheju and Iovi, 2006; Fiúza et al., 2010). However, due to the high acid neutralization capacity (ANC), using acid to neutralize COPR or to maximize Cr(VI) in solution requires a large amount of acid, and the mobilization of the Cr(VI) may not be wholly completed (Tinjum et al., 2008). Considering the above reasons, in this study, pre-reduction was accomplished by three steps: first water was used to extract the Cr(VI) from COPR; second after solid–liquid separation, the supernatant pH was adjusted to be extremely acidic and ZVI was added into the supernatant to reduce the extracted Cr(VI); finally the residue was added into the reduced supernatant, and Fe(II) as the reaction product in the supernatant was used to reduce the Cr(VI) in the residue.

The objectives of this study are to investigate the performance of the developed method for the treatment of COPR and to evaluate the potential to reuse the final treatment product as a readily available construction material.

2. Materials and methods

2.1. Materials and chemicals

COPR samples were collected from a ferroalloy work sample. Slag from the process of smelting ore was used, along with calcium hydroxide, as the main binder. The chemical composition of COPR and slag were analyzed by an X-ray fluorescence spectrometer (AXIOS-PW4400, PANalytical Co., Holland), and the metal contents are shown in Table 1. The total Cr in the COPR was 27.2 g kg^{-1}. The Cr(VI) content, which was determined using the alkaline digestion method, was 9.35 g kg^{-1}, which was approximately 34% of the total chromium. The calcium and magnesium content was 203 and 119.6 g kg^{-1}, respectively. The high calcium concentration and a high pH of 12.7 were the results of the high-lime processing of chromite ore for chromate production. Mineral phase COPR was characterized by X-ray diffraction (XRD) with a diffractometer (Empyrean, PANalytical Co., Holland). The commercial iron powder used in this study was purchased from Tianjin Bodi chemical Inc., China. The specific surface area of the iron powder, which was measured by a Brunauer–Emmett–Teller (BET) surface area analyzer (ASAP2020, Micromeritics Co., USA), was 2.06 m^2 g^{-1}.

2.2. Preparation of solidification samples

A certain amount of COPR (20–45% by total weight of COPR, slag and calcium hydroxide) was weighed and mixed with slag and calcium hydroxide at a certain ratio (weight ratio of slag and calcium hydroxide is 4:1), and then, deionized water was added and the resulting mixture, which had a water/solid (total COPR, slag and calcium hydroxide weight) ratio of approximately 0.5, was agitated in a mixer. Rectangular molds (4 cm $*$ 4 cm $*$ 16 cm) made of stainless steel were filled with the obtained mixture and were compacted. During setting, the specimens were placed in a moisture controlled chamber (95% relative humidity (RH)) for 28 days. After 28 days, the specimens were tested for their compressive strength. Afterwards, the specimens were crushed and sieved to less than 9.5 mm and then extracted using leaching tests (TCLP and HJ/T299-2007). Monolith leaching (a semi-dynamic leaching test) was implemented at the same time.

2.3. Preparation of pre-reduction/solidification samples

Reduction is regarded as a specific stabilization technology; therefore, the samples made in this part were named S/S samples. The method for obtaining S/S samples was established and includes the following steps: a certain amount of water is added into the COPR (20–45% by total COPR, slag and calcium hydroxide weight) to extract the Cr(VI) from the COPR, mixed for 30 min using glass rod and standing for 20 min; after solid–liquid separation, (1 + 1) H_2SO_4 (1.4–2.9 MH^+ kg^{-1} COPR) is added into the Cr(VI)-bearing supernatant to adjust the pH to be extremely acidic (the ratio of the total water and (1 + 1) H_2SO_4 volume and the total COPR, slag and calcium hydroxide weight is 0.5); then, iron powder (15–40 g kg^{-1} COPR) is added to the supernatant to reduce the extracted Cr(VI)–Cr(III), and mixed using glass rod and reacted for 30 min. Then, the COPR residue is added to the supernatant, and mixed using glass rod and reacted for 30 min, the Fe(II), as the reaction product in the supernatant, and residual ZVI are used to reduce the Cr(VI) in the residue. Finally, the slag and calcium hydroxide is added to the reduced COPR, and the resulting mixture is agitated in a mixer. The following process is the same as Section 2.2.

To determine the concentration of Cr(VI) in the reduced COPR, a certain amount of the reduced COPR (10 g) is diluted to 100 mL, and the liquid is separated from the solid by filtration through a 0.45 μm glass fiber filter. The content of Cr(VI) in the liquid is measured by a spectrophotometric method.

Table 1
The metal contents and pH of COPR and slag (g kg^{-1}).

	Ca	Mg	Fe	Al	Na	Mn	K	Si	S	Cr	Cr(VI)	pH
COPR	203	120	72.4	32.8	16.6	2.20	0.34	34.2	1.48	27.2	9.35	12.7
Slag	304	33.2	6.33	63.1	2.70	3.66	4.28	160	7.38	–	–	9.6