

Effect of Ferrous Sulfate Dosage and Soil Particle Size on Leachability and Species Distribution of Chromium in Hexavalent Chromium-Contaminated Soil Stabilized by Ferrous Sulfate

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Ferrous sulfate (FeSO₄) is widely used to effectively stabilize bexavalent chromium (Cr(VI))-contaminated soil. The leaching behavior, Cr(VI) content, and chromium speciation distribution in the stabilized soil are the most important indexes for determining the effectiveness of reduction treatment. Numerous factors, such as reductant dosage and soil particle size, affect the stabilization process; these factors are relatively important. This study investigated the influence of FeSO₄ dosage and soil particle size on leachability and speciation distribution of chromium in contaminated soil. Results showed that the increase in FeSO₄ significantly reduced the leachability and Cr(VI) content in the soil given the increased reducible species that stem from an acid soluble fraction of chromium. The small particle size of the soil that contains a large surface area facilitated the reaction between Cr(VI) and FeSO₄, thereby resulting in low leachability and high reducible species of Cr(VI) in the stabilized soil. The leached Cr(VI) concentration was exponentially correlated to Cr(VI) content in the stabilized soil, and the leachability of Cr from the stabilized soil was linearly correlated to the exchangeable phase of Cr. In addition, the leached Cr(VI) concentration from the stabilized soil conform to the US Environmental Protection Agency and China regulatory limits; meanwhile, considerable Cr(VI) remained in a few stabilized soil and exceeded the environmental quality standards for soil in China. These results illustrated the importance of a comprehensive assessment of Cr(VI)-contaminated soil, which is treated by reductants for enabling flexible future land use. © 2018 American Institute of Chemical Engineers Environ Prog, 00: 000-000, 2018

Keywords: hexavalent contaminated soil, ferrous sulphate, leachability, chromium speciation

INTRODUCTION

Soil contamination by chromium is becoming a major environmental concern in China [1-3], and Chinese officials have classified chromium as the first major heavy metal that should be managed and controlled [4]. Chromium in soil occurs primarily in Cr(III) and Cr(VI) redox states. Cr(VI) species are more soluble and toxic than the relatively immobile Cr(III). Cr(VI) is 100 times more toxic than Cr(III) and has been added to the Class A Human Carcinogens list by the US Environmental Protection Agency (US EPA) [5]. Therefore, researchers worldwide have exerted considerable efforts to remove Cr(VI) from soil [6,7]. Chemical reduction can remove Cr(VI) effectively by using ferrous sulfate (FeSO₄), calcium polysulfide (CaS₅), or organic compounds [8,9]. FeSO₄ is commonly used for remediation of Cr(VI)-contaminated soil and chromite ore-processing residue (COPR) because this compound is relatively inexpensive and highly effective. The reduction of Cr(VI) and Fe(II) is based on the following reaction [10]:

$$3Fe^{2+} + CrO_4^{2-} + 8H_2O \rightarrow 4Fe_{0.75}Cr_{0.25}(OH)_3 + 4H^+.$$
 (1)

Palma et al. [11] applied FeSO₄ to remediate Cr(VI)-contaminated industrial soil in Italy and found that FeSO₄ completely reduced Cr(VI) when the molar ratio of Fe(II)/Cr(VI) is higher than 30. John et al. [12] utilized FeSO₄ to treat Cr(VI)contaminated soil with column techniques in South Carolina; the Cr(VI) concentrations in leachate after a toxicity characteristic leaching procedure (TCLP) test range between 0.59 and 0.7 mg/L. Li et al. [13] used FeSO₄ to treat Cr(VI)-contaminated soil in Chongqing and concluded that FeSO₄ is a valuable treatment technology for in situ remediation of Cr(VI)-contaminated soil. Jagupilla et al. [14] and Wazne et al. [15] conducted the field application of FeSO₄ to reduce Cr(VI) and COPR in Jersey City.

According to previous studies reported in the literature, leachability and Cr(VI) content in a stabilized soil are widely

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Table 1. Physicochemical and mechanical properties of raw soil and chromium-contaminated soil.

	Items	Raw soil	Chromium-contaminated soil
Physicochemical properties	Water content (%)	20.78	
	pH	8.53	7.76
	Specific gravity	2.72	2.79
	Liquid limit (%)	41.63	40.18
	Plastic limit (%)		
		21.84	21.33
	Mn (mg/kg)	798.36	797.48
	MnO_2 (mg/kg)	652.68	653.74
	CEC (meq/100 g)	9.12	9.87
Mechanical properties	Optimum moisture content (%)	19.53	18.95
	Maximum dry density (g/cm ³)	1.72	1.73
	BET specific surface area (m^2/g)	30.74	29.62
Grain size distribution (%)	Clay content (<0.005 mm)	4.62	3.23
	Silt content (0.005–0.075 mm)	74.29	71.76
	Sand content (0.075-2 mm)	21.09	25.01
Chemical composition (%)	Al ₂ O ₃	22.12	21.67
	SiO ₂	64.2	64.37
	K ₂ Õ	2.78	2.85
	CaO	1.43	1.42
	TiO ₂	0.84	0.86
	MnO	0.12	0.13
	Fe ₂ O ₃	8.51	8.59
	Cr_2O_3		0.11

used to evaluate the effectiveness of reductants on the stabilized Cr(VI)-contaminated soil [11-15] and are also the important indexes in considering the reuse of the stabilized soil. However, no peer-reviewed literature that methodically investigated the relationship between leachability and Cr(VI) content in the stabilized soil is found. In addition, minimal information on the chromium speciation distribution of the stabilized soil is available. In most cases, the leachability of Cr(VI) in the stabilized soil is an unfavorable indicator for predicting the effectiveness of stabilized reductants [12,13]. The toxicity and mobility of heavy metals in the soil are related to the total concentration and distribution of speciations of these heavy metals [16]. The availability and extraction efficiency of metals in soil follow this order: acid soluble forms > reducible forms > oxidizable forms > residual forms [17]. Thus, the relationship between leachability and Cr(VI) content and chromium speciation analysis can provide a realistic evaluation of the effectiveness of reductant-stabilized Cr(VI)-contaminated soil.

Numerous factors affect the stabilization process of Cr(VI)-contaminated soil; among these factors, reductant dosage and soil particle size are relatively important [11,14,15]. However, few studies that methodically investigated the effect of reductant dosage and soil particle size on the leachability and species distribution of chromium in the FeSO₄-stabilized Cr(VI)-contaminated soil are reported.

This study investigated the relationship between leachability and Cr(VI) content and chromium speciation of the FeSO₄-stabilized Cr(VI)-contaminated soil. The influence and mechanism of the FeSO₄ dosage and particle sizes of contaminated soil on the remediation efficiency are investigated. This study can provide a new insight on evaluating a stabilized Cr(VI)-contaminated soil and is relatively valuable for facilitating the remediation design of the FeSO₄-stabilized Cr(VI)-contaminated soil.

MATERIALS AND METHODS

Cr(VI)-Contaminated Soil

The chromium-free soil sample was collected from a subway excavation site in Wuhan City (China). The detailed description of the physical characterization of the soil, which was obtained in accordance with the "Standard for soil test method" in China, is presented in Table 1. A light Proctor compaction method was used for a compaction test [18,19]. The clay was dried, grounded, and sieved through a 2 mm screen. The Cr(VI)-contaminated soil was obtained by adding K₂Cr₂O₇ solution until the Cr(VI) concentration in the soil has reached 1000 mg/kg, which represents a universal concentration for the Cr(VI)-contaminated soil in China [20-24]. Deionized water was then added to the contaminated soil until the water content reached 19.5% (optimum moisture content). The contaminated soil was mixed consistently and braised for 180 days under standard curing conditions (20°C, 95% humidity) to allow K₂Cr₂O₇ and clay to react adequately and obtain an aging contaminated soil. The contaminated soil was air-dried and pulverized after homogenization to achieve the required particle sizes (<2, <0.5, and <0.15 mm) using particular sieves (China standard #10, #35, and #100 meshes). The entire quantity of soil was passed through the sieve to avoid any fractionation [14].

All reagents in this study were obtained from Sinopharm Chemical Reagent Co., Ltd. and were used as ACS-certified reagents without any purification.

Stabilization of Cr(VI)-Contaminated Soil Using FeSO₄

FeSO₄ was added to the Cr(VI)-contaminated soil at Fe(II) to Cr(VI) molar ratios of 0, 3, 5, 10, and 20. The experimental design is presented in Table 2. The mixture of these materials was performed in a 10 L SPAR-type mixer. The soil was homogenized for 15 min prior to adding distilled water. The addition ratio of water to FeSO₄ was ensured, and dry soil was 1:2. The mixture was removed from the sealed plastic bottles after incubation for 7 days at room temperature (20°C). All samples were prepared in triplicates. The reported results were the averages of the three replicates.

Test Methods

The soil cation exchange capacity (CEC) and MnO_2 content were determined using standard methods [25], Soil acid digestion was performed to determine the Mn content in

soil, according to EPA Method 3050B [26]. Nitrogen adsorption-desorption measurements was determined by a surface area analyzer (Nova 1000e series, USA). The chemical composition of the samples was measured by X-ray fluorescence (XRF) scan. The size distribution of the waste particles was measured using a Malvern MS3000 laser diffraction particle size analyzer. The Cr (VI) content of the soil was measured using the USEPAUS EPA Method 3060A, (alkaline digestion method) [27]. The Cr (VI) content in the filtrate was measured using the US EPA Method 7196A, (colorimetric analyses) [28]. The TCLP test of Cr was conducted based on the US EPA Method 1311 [29]. The leachability of SO_4^{2-} was conducted based on the China Environmental Regulation HJ 557-2009 [30] and HJ 84-2016 (ion chromatography) [31]. The sequential extraction procedure was conducted in accordance with the method recommended by Rauret et al. [32]. The sequential extraction procedure consisted of four steps, that is, exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residue fraction (F4). Table 3 summarizes the detailed testing procedures, and one replicate sample was used in BCR test. Agilent 7700 inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the metal concentrations in the leachate.

RESULTS AND DISCUSSION

Cr(VI) Content in Soil before and after FeSO₄ Stabilization

The Cr(VI) contents of the contaminated soil with different molar ratios of Fe(II)/Cr(VI) are illustrated in Figure 1. For the untreated soil, the Cr(VI) content was ~971.3 mg/kg. The Cr(VI) content was significantly reduced after FeSO₄ stabilization with the increase in Fe(II)/Cr(VI) molar ratio. In addition, the Cr(VI) content in the contaminated soil was below the threshold allowed by the China Environmental Regulation for industrial reuse (<30 mg/kg) when the Fe(II)/ Cr(VI) molar ratio was 10, and the threshold of civil reuse (<5 mg/kg) was achieved when the Fe(II)/Cr(VI) molar ratio was 20 [33]. The decreased Cr(VI) content of the soil was attributed to the reduction of Cr(VI) by Fe(II) with FeSO₄ addition. The results also indicated a relatively low efficiency

Table 2. Experimental design for the treatment of Cr contaminated soil by $FeSO_4$.

Experimental series	Particle size (mm)	Fe(II)/Cr(VI) molar rate
Effect of FeSO ₄ dosage	<2	0 3
		5 10
	-0.15	20
Effect of particle size	<0.15 <0.5 <2	3

Table 3.	The	sequential	extraction	procedure.
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of FeSO₄ in terms of the theoretical molar ratio. Palma et al. [11] and Bartlett et al. [34] found that FeSO₄ is oxidized by manganese oxide in the soil. The soil used in this study contained a high concentration of manganese oxide, and partial FeSO₄ was consumed by manganese oxide. Therefore, the effect of manganese oxide on FeSO₄ should be completely considered when stabilizing the Cr(VI)-contaminated soil by using FeSO₄. A scientific measure (such as increased FeSO₄ dosage or preliminary separation) could be adopted to ensure the effectiveness of FeSO₄ treatment when the contaminated soil contains a high concentration of manganese oxide.

The effect of particle size on the Cr(VI) content of the contaminated soil is depicted in Figure 2. The results showed that the particle size of the contaminated soil reduction enhanced the stabilization efficiency. The Cr(VI) content decreases with the decrease in particle size. For illustration, the Cr(VI) content decreased from 134.3 to 63.9 mg/kg when the particle size decreased from 2 to 0.15 mm. This finding was due to reducing particle size exposes many surface areas, thereby resulting in the release of considerable Cr(VI) and made Cr available to react with Fe(II) [14,35]. In addition, the small particle size reduced the reaction time between Cr(VI) and Fe(II), thus minimizing the FeSO₄ consumption caused by manganese oxide [11].

Leachability of Cr(VI) and Cr in Soil before and after Stabilization

Figure 3 demonstrates the variations in the leached Cr concentration with different molar ratios of Fe(II)/Cr(VI). The Cr concentration decreases with the increase in Fe(II)/ Cr(VI) molar ratio. For the untreated soil, the Cr(VI) and total Cr leaching concentrations were \sim 38.8 and 40.4 mg/L, respectively; these amounts exceeded the China standards for hazardous waste regulatory limit [36]. For the FeSO₄-stabilized Cr(VI)-contaminated soil, the Cr(VI) and total Cr leaching concentrations were ~4.68 and 8.9 mg/L, respectively, when the molar ratio of Fe(II)/Cr(VI) was 3; these amounts were in accordance with the US EPA and China regulatory limits [35,36]. The total Cr leaching concentration was ~ 0.76 mg/L when the molar ratio of Fe(II)/Cr(VI) was increased to 20, and Cr(VI) was lower than the detection limits (0.04 mg/L) [28]. In comparing Figures 1 and 3, considerable Cr(VI) remained in the stabilized soil, although the Cr(VI) and total Cr leaching concentrations of the stabilized soil were negligible. The Cr(VI) content part residue of the stabilized soil exceeded the environmental quality standards of soil in China. The TCLP test underestimated the Cr(VI) content residue in the stabilized soil. The leaching method could not reliably predict the remaining Cr(VI) in the stabilized soil without using the alkaline digestion test. The TCLP test results showed that Cr(VI) is lower than the detection limits. However, the Cr(VI) content residue in the stabilized soil was significant.

Figure 4 displays the variations in the leached Cr concentration with the particle size, which had different effects on the untreated and stabilized soils. For the untreated soil, the

Step	Extraction procedures	Chemical phases
1	Extracted by 0.11 mol/L HOAc at a liquid-to-solid (L/S) ratio of 40	Exchangeable
2	Extracted by 0.5 mol/L NH ₂ OH-HCl (adjusted to $pH = 1.5$ with HNO ₃) at a liquid-to-solid (L/S) ratio of 40	Reducible
3	Extracted by 8.8 mol/l H_2O_2 at a liquid-to-solid (L/S) ratio of 10, and then for extracted by 1 mol/l NH ₄ OAc (adjusted to pH = 2.0 with HNO ₃) at a liquid-to-solid (L/S) ratio of 50	Oxidizable
4	HNO_3 -HF-HClO ₄ digestion	Residual

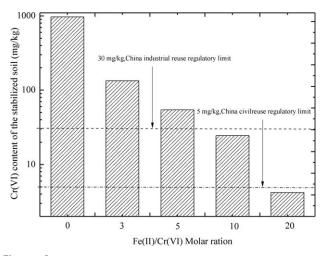


Figure 1. Effect of $FeSO_4$ dosage on Cr (VI) content in the contaminated soils.

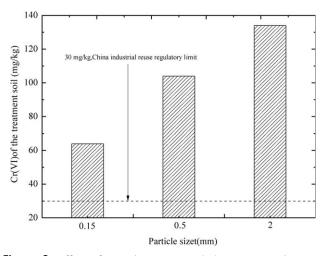


Figure 2. Effect of particle size on Cr(VI) content in the contaminated soils.

Cr(VI) and total Cr leaching concentrations decrease with the increase in particle size, whereas these amounts increased in the stabilized soil. The Cr(VI) and total Cr concentrations of the untreated soil were decreased from 42.8 and 48.5 to 38.8 and 40.4 mg/L, correspondingly, when the particle size increased from 0.15 to 2 mm. The Cr(VI) and total Cr concentrations of the stabilized soil were changed from 2.8 and 3.2 to 4.7 and 8.9 mg/L, respectively. This trend for the untreated soil was due to the reduction of particle size improve many contact areas with extraction fluid, thus resulting in the release of considerable Cr(VI) and Cr(VI). This result agreed with the results of Jagupilla et al. [14] and Moon et al. [35]. For the FeSO₄-stabilized soil, particle size reduction promoted the reaction between Fe(II) and Cr(VI), Cr(VI) was reduced to Cr(III), and Cr(III)-Fe(III) hydroxide precipitation was formed (Cr(OH)₃ and Cr_xFe_{1-x}(OH)₃) [37].

Leachability of SO_4^{2-} in Soil before and after Stabilization

Figure 5 demonstrates the variations in the leached SO_4^{2-} concentration with different molar ratios of Fe(II)/Cr(VI). The SO_4^{2-} concentration increases with the increase in Fe(II)/Cr(VI) molar ratio. For the untreated soil, the SO_4^{2-} leaching

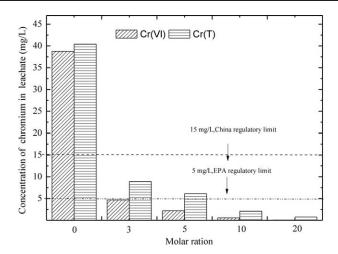


Figure 3. Effect of $FeSO_4$ dosage on leached Cr concentration in leachate.

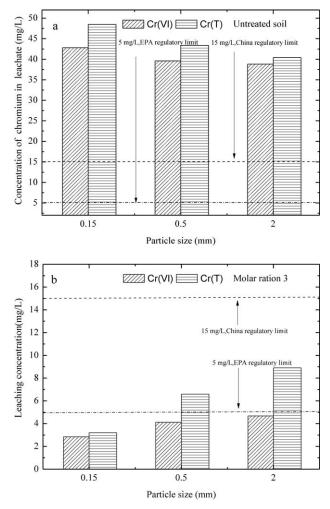


Figure 4. Effect of particle size on leached Cr concentration in leachate.

concentrations was 7.68 mg/L. The SO_4^{2-} leaching concentrations was increased from 43.28 to 216.45 mg/L, when the molar ratio of Fe(II)/Cr(VI) was increased from 3 to 10, these amounts were in accordance with the China Environmental

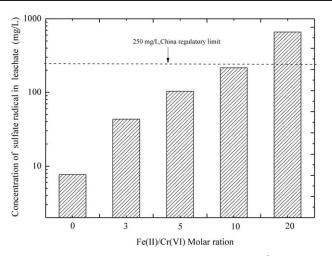


Figure 5. Effect of $FeSO_4$ dosage on leached SO_4^{2-} concentration in leachate.

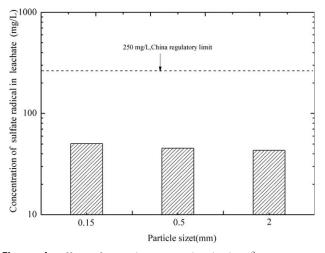


Figure 6. Effect of particle size on leached SO_4^{2-} concentration in leachate.

quality standards for surface water of civil use [38]. The SO_4^{2-} leaching concentration was ~659.43 mg/L, when the molar ratio of Fe(II)/Cr(VI) was increased to 20, and this amount was exceeded the China Environmental quality standards for surface water of civil use [38]. Therefore, the SO_4^{2-} leaching concentration was need fully completely considered when stabilized of the Cr(VI)-contaminated soil by FeSO₄.

Figure 6 demonstrates the variations in the leached SO_4^{2-} concentration with different particle size. The SO_4^{2-} concentration decreases with the increase in particle size. The SO_4^{2-} leaching concentrations was increased from 50.42 to 43.28 mg/L, when the particle size was increased from 0.15 to 2 mm, these amounts were in accordance with the China Environmental quality standards for surface water of civil use [38]. In comparing Figures 5 and 6, though increasing the FeSO₄ dosage could significantly decreased the leachability of Cr(VI), the leached SO_4^{2-} concentration was need fully completely considered. When Fe(II)/Cr(VI) was larger than 20, the leached SO_4^{2-} concentration exceeded the China Environmental quality standards for surface water of civil use. Therefore, comprehensive measures (such as increased FeSO₄ dosage and reduced particle size) could be adopted to ensure the environmental security characteristics of the

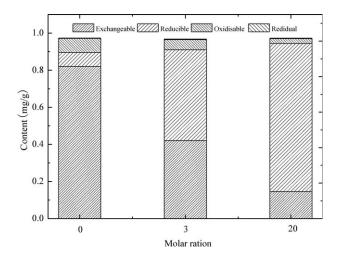


Figure 7. Effect of $FeSO_4$ dosage on chromium speciation distribution in the treated soil.

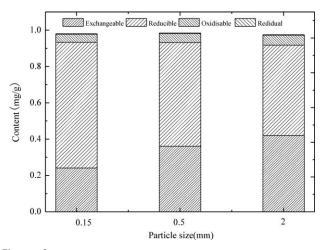


Figure 8. Effect of particle size on chromium speciation distribution in the treated soil.

stabilized soil when the contaminated soil contains a high concentration of Cr(VI).

Species Distribution of Cr(VI) in Soil before and after Stabilization

The result of the sequential extraction procedure is exhibited in Figure 7. For the untreated soil, Cr was mainly distributed in the F1 content (0.82 mg/g), F2 content (0.075 mg/g), and F3 content (0.074 mg/g). However, the F4 content (0.0026 mg/g) was negligible compared with their noticeable fraction. Cr was mobile and toxic for the untreated contaminated soil. For the stabilized soil, the F1 fraction was mainly converted to the F2 fraction, which was increased to 0.78 mg/g when the Fe(II)/Cr(VI) molar ratio was increased from 3 to 20. The changes in Cr speciation was attributed to Cr(VI) solubilization, reduction, and formation of Cr(III)-Fe(III) hydroxide precipitation (Cr(OH)₃ and Cr_xFe_{1-x}(OH)₃) [37]. Figure 7 also displays a slight decrease in the F3 content adding FeSO₄. The decrease in the F3 content can also be attributed to the acidic conditions established by using FeSO₄. These acidic conditions caused Cr-organic complex solubilization [37]. This result agreed well with the research result of Palma et al. [11].

The effect of particle size on Cr speciation in soil is illustrated in Figure 8. The particle size reduction promoted the conversion of the F1 fraction to the F2 fraction, and the F2 content increased from 0.49 to 0.68 mg/g when the particle size was decreased from 2 to 0.15 mm. This trend was attributed to the decrease in particle size, thereby allowing Cr(VI) to be available for reduction and then Cr(III)–Fe(III) hydroxide precipitation. The Cr(III)–Fe(III) hydroxide precipitation caused the increase in the F2 fraction content [37].

Relationship between the Cr(VI) Content in Soil and the Leachability of Cr(VI)

The relationship between the Cr(VI) content of the stabilized soil ($S_{Cr(VD)}$) and the Cr(VI) concentration of the TCLP leachate ($T_{Cr(VI)}$) is depicted in Figure 9. In this figure, the leachability of Cr(VI) in the stabilized soil were all in accordance with the US Environmental Protection Agency (EPA) regulatory limit. However, the experimental data of FeSO₄ dosage were all less than that of particle size. This condition indicated that increased FeSO₄ dosage could reduce leachability significantly compared with reduced particle size. This

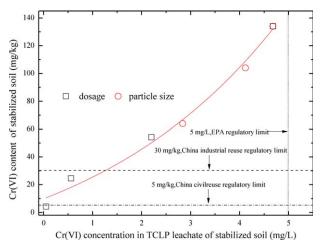


Figure 9. Relationship between Cr(VI) content in soil and leached Cr(VI) concentration by TCLP. [Color figure can be viewed at **wileyonlinelibrary.com**]

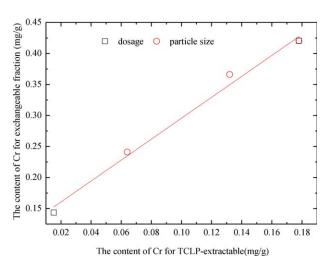


Figure 10. Relationship between exchangeable Cr content in soil and leached Cr(VI) concentration by TCLP. [Color figure can be viewed at **wileyonlinelibrary.com**]

might be due to increased FeSO4 dosage improved the chemical stability of Cr in stabilized soil (Figures 7 and 8). Increased FeSO₄ dosage was an effective method to improve the environmental security characteristics of stabilized soil. In addition, Figure 9 also showed that the considerable Cr(VI) remained in the stabilized soil, although the Cr(VI) leaching concentration of the stabilized soil was in accordance with the US EPA and China regulatory limits. The Cr(VI) content part residue of the stabilized soil exceeded the environmental quality standards for soil in China, and the TCLP test underestimated the Cr(VI) content residue in the stabilized soil. In addition, the results showed that an exponential function relationship was found between the $S_{Cr(VI)}$ and the $T_{Cr(VI)}$, where $S_{Cr(VI)} = 3.64e^{T_{Cr(VI)}/-3.28} - 23.2$. The exponentially fitted formula can predict the Cr(VI) content in soil by the TCLP test in the remediation of Cr(VI)-contaminated soil. This study would be relatively valuable for facilitating the design or modification of remediation parameters for Cr(VI)contaminated soil by using FeSO₄.

Relationship between the Exchangeable Phase and Leachability of Cr

The relationship between the Cr content in an exchangeable fraction of the BCR test (B_{Cr}) and Cr concentration of the TCLP leachate (T_{Cr}) is demonstrated in Figure 10. T_{Cr} increased linearly with $B_{Cr\!\!\!,}$ where $B_{Cr}\!=\!1.7T_{Cr}\!+\!0.13.$ This finding can be due to the liquid-solid ratio (the volume of extraction fluid to the weight of solid phase) and the acidity of the extraction fluid were higher in the sequential extraction test than in the TCLP test. Therefore, the Cr in the $T_{\mbox{Cr(VI)}}$ was predominantly obtained from exchangeable fraction (F1). The F1 content of Cr depended on the Cr leachability in the TCLP test. This condition also indicated that the F1 content of Cr depended on the safety of the stabilized soil. The linearly fitted formula can predict the F1 content of Cr in the stabilized soil. The F1 content reduction of Cr was an effective measure for improving the remediation effectiveness in the contaminated soil.

CONCLUSIONS

This study investigated the relationship between the leachability and Cr(VI) content and chromium speciation of Cr(VI)-contaminated soil stabilized by using FeSO₄. The influence and mechanism of the FeSO₄ dosage and particle sizes of the contaminated soil on remediation efficiency were investigated. The effectiveness of FeSO₄ stabilization was assessed using TCLP, alkaline digestion, and sequential extractions. The following conclusions can be drawn based on this study:

- 1. FeSO₄ significantly reduced the leachability and Cr(VI) content in the stabilized soil. The leachability of Cr(VI) and total Cr concentration of the stabilized soil were lower than the China standards for hazardous waste regulatory limit and the US EPA regulation when the Fe(II)/Cr(VI) molar ratio was 3. Furthermore, the Cr(VI) content in the soil was lower than the threshold of the environmental quality standards of soil in China for industrial reuse [Cr(VI) < 30 mg/kg] when the Fe(II)/Cr(VI) molar ratio was 20.
- 2. Soil particle size reduction improved the effectiveness of the stabilized soil. The leachability and Cr(VI) content in the stabilized soil were reduced with the decrease in soil particle size because the small soil particle size contained considerable surface areas that facilitated the reaction between Cr(VI) and FeSO₄.
- 3. The change in the leachability of soil was attributed to the change in the Cr speciation distribution on the basis of the sequential extraction test, and the exchangeable

fraction was mainly converted to a reducible fraction after $\ensuremath{\text{FeSO}_4}$ stabilization.

4. The leachability of Cr(VI) in the stabilized soil was linearly correlated to the exchangeable phase of Cr. In addition, the leached Cr(VI) concentration in the stabilized soil conformed to the US EPA and China regulatory limits, although considerable Cr(VI) remained in a few stabilized soil and exceeded the environmental quality standards for soil in China. These results illustrated the importance of a comprehensive assessment of the Cr(VI)-contaminated soil that is treated by reductants for enabling a flexible future land use.

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LITERATURE CITED

- CMEP, 2014. Bulletin on national survey of soil contamination. People's Republic of China: Ministry of Environmental Protection. Reference No. 000014672/2014-00351, April 2014.
- Yin, W., Li, Y., Wu, J., Chen, G., Jiang, G., Li, P., Gu, J., Liang, H., & Liu, C. (2017). Enhanced Cr (VI) removal from groundwater by Fe⁰-H₂O system with bio-amended iron corrosion, Journal of Hazardous Materials, 332, 42–50.
- Gao, Y., & Xia, J. (2011). Chromium contamination accident in China: viewing environment policy of China, 8605–8606.
- Huang, S.H., Bing, P.E.N.G., Yang, Z.H., Chai, L.Y., Xu, Y.Z., & Su, C.Q. (2009). Spatial distribution of chromium in soil contaminated by chromium-containing slag, Transactions of Nonferrous Metals Society of China, 19, 756– 764.
- Dhal, B., Thatoi, H.N., Das, N.N., & Pandey, B.D. (2013). Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: a review, Journal of Hazardous Materials, 250–251, 272–291.
- Němeček, J., Lhotský, O., & Cajthaml, T. (2014). Nanoscale zero-valent iron application for in situ reduction of hexavalent chromium and its effects on indigenous microorganism populations, Science of the Total Environment, 485–486, 739–747.
- Liao, Y., Min, X., Yang, Z., Chai, L., Zhang, S., & Wang, Y. (2014). Physicochemical and biological quality of soil in hexavalent chromium-contaminated soils as affected by chemical and microbial remediation, Environmental Science and Pollution Research, 21, 379–388.
- Lyu, H., Zhao, H., Tang, J., Gong, Y., Huang, Y., Wu, Q., & Gao, B. (2018). Immobilization of hexavalent chromium in contaminated soils using biochar supported nanoscale iron sulfide composite, Chemosphere, 194, 360–369.
- 9. Dahlawi, S.M., & Siddiqui, S. (2017). Calcium polysulphide, its applications and emerging risk of environmental pollution—a review article, Environmental Science and Pollution Research, 24, 92–102.
- Diao, Z.-H., Xu, X.-R., Jiang, D., Liu, J.-J., Kong, L.-J., Li, G., Zuo, L.-Z., & Wu, Q.-H. (2017). Simultaneous photocatalytic Cr (VI) reduction and ciprofloxacin oxidation over TiO₂/Fe⁰ composite under aerobic conditions: Performance, durability, pathway and mechanism, Chemical Engineering Journal, 315, 167–176.

- Di Palma, L., Gueye, M.T., & Petrucci, E. (2015). Hexavalent chromium reduction in contaminated soil: a comparison between ferrous sulphate and nanoscale zero-valent iron, Journal of Hazardous Materials, 281, 70–76.
- Seaman, J., C., Bertsch, P., M., & Schwallie, L. (1999). In situ Cr (VI) reduction within coarse-textured, oxidecoated soil and aquifer systems using Fe (II) solutions, Environmental Science & Technology, 33, 938–944.
- Li, D., Ji, G., Hu, J., Hu, S., & Yuan, X. (2018). Remediation strategy and electrochemistry flushing & reduction technology for real Cr (VI)-contaminated soils. Chemical Engineering Journal, 334, 1281–1288.
- 14. Jagupilla, S.C., Moon, D.H., Wazne, M., Christodoulatos, C., & Kim, M.G. (2009). Effects of particle size and acid addition on the remediation of chromite ore processing residue using ferrous sulfate, Journal of Hazardous Materials, 168, 121–128.
- Wazne, M., Moon, D.H., Jagupilla, S.C., Jagupilla, S.C., Christodoulatos, C., Dermatas, D., & Chrysochoou, M. (2007). Remediation of chromite ore processing residue using ferrous sulfate and calcium polysulfide, Geosciences Journal, 11, 105–110.
- Petrucci, E., Montanaro, D., & Merli, C. (2011). Sequential extraction analysis provides decision-making tools for the use of contaminated sediments, Chemistry and Ecology, 27, 107–118.
- 17. Zimmerman, A.J., & Weindorf, D.C. (2010). Heavy metal and trace metal analysis in soil by sequential extraction: a review of procedures, International Journal of Analytical Chemistry, 2010, 1.
- Li, J.S., Xue, Q., Wang, P., Zhang, T.T., & Zhao, Y. (2016). Comparison of solidification/stabilization of lead contaminated soil between magnesia–phosphate cement and ordinary portland cement under the same dosage, Environmental Progress & Sustainable Energy, 35, 88–94.
- Wang, P., Xue, Q., Li, J.S., & Zhang, T.T. (2016). Effects of pH on leaching behavior of compacted cement solidified/stabilized lead contaminated soil, Environmental Progress & Sustainable Energy, 35, 149–155.
- 20. Zhang, D., Kong, H., Wu, D., He, S., Hu, Z., & Hu, X. (2009). Remediation of chromite ore processing residue by pyrolysis process with sewage sludge, Bioresource Technology, 100, 2874–2877.
- Wang, Y., Fang, Z., Liang, B., & Tsang, E.P. (2014). Remediation of hexavalent chromium contaminated soil by stabilized nanoscale zero-valent iron prepared from steel pickling waste liquor, Chemical Engineering Journal, 247, 283–290.
- 22. Wang, Y., Fang, Z., Kang, Y., & Tsang, E.P. (2014). Immobilization and phytotoxicity of chromium in contaminated soil remediated by CMC-stabilized nZVI, Journal of Hazardous Materials, 275, 230–237.
- 23. Du, J., Lu, J., Wu, Q., & Jing, C. (2012). Reduction and immobilization of chromate in chromite ore processing residue with nanoscale zero-valent iron, Journal of Hazardous Materials, 215–216, 152–158.
- 24. Xu, W., Li, X., Zhou, Q., Peng, Z., Liu, G., & Qi, T. (2011). Remediation of chromite ore processing residue by hydrothermal process with starch, Process Safety and Environmental Protection, 89, 179–185.
- 25. Liu, C., & Evett, J. B. (2002). Soil properties, testing, measurement, and evaluation (5th ed.), New York: Prentice-Hall.
- 26. US EPA, Method 3050 B: acid digestion of sediments, sludges and soils, 1996.
- U.S. Environmental Protection Agency, Alkaline digestion for hexavalentchromium, Method 3060A, Washington, DC, 1996.
- U.S. Environmental Protection Agency, Chromium, hexavalent (colorimetric), Method 7196A, Washington, DC, 1992.

- U.S. Environmental Protection Agency, Toxicity Characteristic Leaching Procedure, Method 1311, Washington, DC, 1992.
- 30. HJ 557–2009, Solid waste-Extraction procedure for leaching toxicity horizontal vibration method [S]. Ministry of Environmental Protection of the People's Republic of China, Beijing, China.
- 31. HJ 84–2016, Water Quality-Determination of Inorganic Anions(F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₃²⁻, SO₄²⁻)-Ion Chromatography [S]. Ministry of Environmental Protection of the People's Republic of China, Beijing, China.
- 32. Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., & Quevauviller, P. (1999). Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, Journal of Environmental Monitoring, 1, 57–61.
- 33. GB15618-2008, Environmental quality standards soil [S]. Ministry of Environmental Protection of the People's Republic of China, Beijing, China.

- Bartlett, R., & James, B. (1979). Behavior of chromium in soil: III. Oxidation, Journal of Environmental Quality, 8, 31–35.
- 35. Moon, D.H., Wazne, M., Jagupilla, S.C., Christodoulatos, C., Kim, M.G., & Koutsospyros, A. (2008). Particle size and pH effects on remediation of chromite ore processing residue using calcium polysulfide (CaS₅), Science of the Total Environment, 399, 2–10.
- 36. GB/T5085.3–2007. Identification standards for hazardous wastes—Identification for extraction toxicity, Ministry of Environmental Protection of the People's Republic of China, Beijing, China.
- 37. Wang, X., Zhang, J., Wang, L., Chen, J., Hou, H., Yang, J., & Lu, X. (2017). Long-term stability of FeSO₄ and H₂SO₄ treated chromite ore processing residue (COPR): importance of H⁺ and SO₄²⁻, Journal of Hazardous Materials, 321, 720–727.
- 38. GB3838-2002. Environmental quality standards for surface water [S]. Ministry of Environmental Protection of the People's Republic of China, Beijing, China.