

Article

Leachability and Stability of Hexavalent-Chromium-Contaminated Soil Stabilized by Ferrous Sulfate and Calcium Polysulfide

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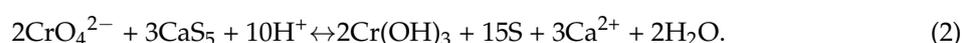
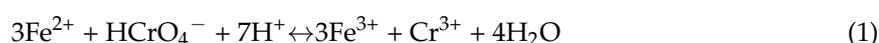


Abstract: Ferrous sulfate (FeSO₄) and calcium polysulfide (CaS₅) stabilization are practical approaches to stabilizing hexavalent chromium (Cr(VI))-contaminated soil. The leachability and stability of Cr(VI) and Cr are important factors affecting the effectiveness of stabilized Cr(VI)-contaminated soil. This study compared the leachability and stability of Cr(VI) and Cr in Cr(VI)-contaminated soil stabilized by using FeSO₄ and CaS₅. The contaminated soil was characterized before and after stabilization, and the effectiveness of FeSO₄ and CaS₅ stabilization was assessed using leaching, bioaccessibility, alkaline digestion, sequential extraction, and X-ray diffraction tests. Results showed that FeSO₄ and CaS₅ significantly reduced the leachability and Cr(VI) content in the contaminated soil. The acid-buffering capacity and stability (leachability, bioaccessibility, speciation distribution, and mineral composition) of the Cr(VI)/Cr and Cr(VI) content of CaS₅ were better than those of FeSO₄. This study demonstrated that CaS₅ had a better effect than FeSO₄ on the stabilization of Cr(VI) in Cr(VI)-contaminated soil. The CaS₅ significantly enhanced the stabilization and immobilization of Cr(VI) and reduced its leachability and toxicity.

Keywords: hexavalent chromium; contaminated soil; leachability; stability; speciation

1. Introduction

Soil contamination by chromium (Cr) is a serious problem in China [1–3]. Cr is released into the soil by various industries, including the wood preservation, leather tanning, chromate manufacturing, and electroplating industries [4]. Cr in soil occurs primarily in its Cr(III) and Cr(VI) redox states; Cr(III) is a nutrient for plant growth, whereas Cr(VI) is a dangerous species and human carcinogen [5]. Chemical reduction removes Cr(VI) rapidly and effectively based on the use of reducing agents, such as ferrous sulfate, calcium polysulfide, or sodium bisulfate, followed by precipitation as Cr(OH)₃ [6]. Calcium polysulfide (CaS₅) and ferrous sulfate (FeSO₄) are promising reagents that have been used at many Cr-contaminated sites and for chromite ore-processing residue (COPR). The reduction of Cr(VI) with FeSO₄ and CaS₅ (denoted by its average chemical formula, CaS₅) can be written as follows [6,7]:



Many studies have been performed on Cr(VI)-contaminated soils stabilized by FeSO₄ and CaS₅. However, most of them focused on the leachability and content of Cr(VI) and Cr. Palma et al. [8]

applied FeSO_4 to reduce Cr(VI) at a contaminated industrial soil site in Italy and found that FeSO_4 successfully lowers the amount of Cr(VI) in the soil. An alkaline digestion test showed that Cr(VI) is almost completely reduced when the Fe(II)/Cr(VI) molar ratio is 30. John et al. [9] reported the use of FeSO_4 to treat Cr(VI)-contaminated soil through a column treatment. The Cr(VI) concentrations in the leachate after a toxicity characteristic leaching procedure test (TCLP) range between 0.59 and 0.7 mg/L. Buerge et al. [10] found that FeSO_4 is a useful treatment reagent in the in-situ remediation of Cr(VI)-contaminated soils in Switzerland. Chrysochoou et al. [11] performed a column treatment of Cr(VI)-contaminated soil treated with CaS_5 and found that up to 99% Cr(VI) was reduced with an injection of CaS_5 at 12 times the stoichiometric requirement. Wazne et al. [12] reported that 62% of Cr(VI) is reduced in COPR with CaS_5 addition at twice the stoichiometric ratio. Chrysochoou et al. [13] applied CaS_5 in batch studies of highly contaminated soil from a Cr plating facility in Putnam. Redox potential results showed that CaS_5 maintains a highly reducing environment for a prolonged period of time and that the alkaline digestion and synthetic precipitation leaching procedure concentrations are lower than Environmental Protection Agency (EPA) regulatory levels.

Although these applications indicated that FeSO_4 and CaS_5 are effective reductants, insufficient information is available about the difference between the FeSO_4 and CaS_5 remediation of Cr(VI) in contaminated soil. Moreover, most works only used the TCLP or alkaline digestion test, and systematic investigations about the remediation capacities of FeSO_4 and CaS_5 on Cr(VI), based on the bioaccessibility and speciation of Cr, are lacking. The toxicity and mobility of heavy metals in soil are not only related to their total content but are also determined to a greater degree by the distribution of their speciation [14]. Zimmerman et al. [15] demonstrated that the availability and extraction effectiveness of heavy metals in soil decrease in the order of acid soluble forms > reducible forms > oxidizable forms > residual forms.

This study compared the leachability and stability of Cr(VI)-contaminated soils stabilized by FeSO_4 and CaS_5 . Toxicity characteristic leaching procedure (TCLP), simplified bioaccessibility extraction test (SBET), alkaline digestion, sequential extraction, and X-ray diffraction (XRD) tests were performed on Cr(VI)-contaminated soils. This study can serve as a basis for designing the remediation of Cr(VI)-contaminated soils by using FeSO_4 and CaS_5 .

2. Materials and Methods

2.1. Cr(VI) Contaminated Soil Preparation

The raw soil was collected from a subway excavation site in Wuhan City (China). The soil was dried, ground, and then sieved through a 2-mm screen. The detailed description of the physical characterization of the raw soil and Cr(VI)-contaminated soil are presented in Table 1, which was obtained according to the "Standard for soil test method" of China. The Light Proctor compaction method was used for the compaction test [16,17]. Cr(VI)-contaminated soils were obtained by adding $\text{K}_2\text{Cr}_2\text{O}_7$ solution until the Cr(VI) content in the soil reached 1000 mg/kg, which represents a universal content for Cr(VI)-contaminated soil in China [18–22]. Deionized water was then added to the contaminated soil until the water content reached 19.5% (optimum moisture content). The contaminated soil was mixed evenly and braised for 180 days under standard curing conditions (20 ± 2 °C, 95% humidity) to allow $\text{K}_2\text{Cr}_2\text{O}_7$ and the soil to react adequately. After homogenization, the contaminated soil was air dried and pulverized to achieve the required particle size (<2 mm). The entire quantity of soil was made to pass through the sieve to avoid any fractionation [23].

All reagents in this study were supplied from Sinopharm Chemical Reagent Co., Ltd. (Ningbo, China) and used as American Chemical Society-certified reagents without any further purification.

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
	C.E.C (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
	Brunauer-Emmett-Teller 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 O	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 ₂ O ₃	—	0.11

2.2. Stabilized of Cr(VI) Contaminated Soil

Representative 500 g of air-dried Cr(VI)-contaminated soil were introduced into a 10 L SPAR type mixer. FeSO₄ and CaS₅ were added to the Cr-contaminated soil as reductant to a dry soil ratio of 1%, 3%, and 5%. The experimental design is presented in Table 2. The soil was homogenized for 10 min prior to the addition of distilled water. It was ensured that the ratio of addition of water to the reductant and dry soil was 1:2. The mixture was withdrawn from the sealed plastic bottles after being incubated for 7 d at room temperature (20 ± 1 °C). All the samples were prepared in triplicate. The reported stability results are the averages of three replicates.

Table 2. Experimental design for the stability study.

Test No.	Reductant	Dosage (%)
1	FeSO ₄	0
2	FeSO ₄	1
3	FeSO ₄	3
4	FeSO ₄	5
5	CaS ₅	0
6	CaS ₅	1
7	CaS ₅	3
8	CaS ₅	5

3. Test Methods

The soil cation exchange capacity (CEC) and MnO₂ content were determined using standard methods [24]. Soil acid digestion was performed to determine the Cr and Mn content in soil according to EPA Method 3050B [25]. Nitrogen adsorption-desorption measurements were determined by a surface area analyzer (Nova 1000e, Quantachrome Instruments, USA). The chemical composition of the samples was measured by an X-ray fluorescence (XRF) scan. The size distribution of the waste particles was measured using a Malvern MS3000 laser diffraction particle size analyzer. pH values for all soil were measured as per ASTM D4972-01 [26]. The toxicity characteristic leaching procedure (TCLP) of Cr was conducted as per USEPA Method 1311 [27]. The bioaccessibility test was performed according to the U.S. EPA (2007) protocol [28] and the British Geological Survey [29]. The Cr(VI) content of contaminated soil was measured using the USEPA Method 3060A alkaline digestion method [30].

The Cr(VI) concentration in the filtrate was measured using U.S. EPA Method 7196A colorimetric analyses [31]. The modified European Community Bureau of Reference (BCR) sequential extraction procedure was conducted as per the method recommended by Rauret et al. [32]. The sequential extraction procedure consisted of four steps, which corresponded to the exchangeable, reducible, oxidizable, and residue fractions.

4. Results and Discussion

4.1. pH of Stabilized Soils

Figure 1 shows the pH of the stabilized soils with different FeSO_4 and CaS_5 dosages. The results indicated that CaS_5 addition can increase the pH of the stabilized soil, which was contrary to the effect of FeSO_4 addition. For illustration, the pH of the FeSO_4 stabilized soil decreased from 7.86 to 2.62 when the reductant dosage increased from 0% to 5%. However, the pH of the CaS_5 stabilized soil increased from 7.86 to 9.57. The changes in the FeSO_4 and CaS_5 treated soil were attributed to the different stabilization mechanisms in the Cr(VI)-contaminated soils. For the FeSO_4 stabilized soil, Cr(VI) was reduced by Fe(II) and formed Fe(III) hydroxide precipitation and released a considerably greater amount of H^+ [33]. The alkalinity of the CaS_5 stabilized soils can be attributed to the fact that CaS_5 is an alkaline material [13]. This result indicates that CaS_5 was more advantageous than FeSO_4 in which stabilized soil pH can reach values of 9.57 or higher, which increases the acid-buffering capacity.

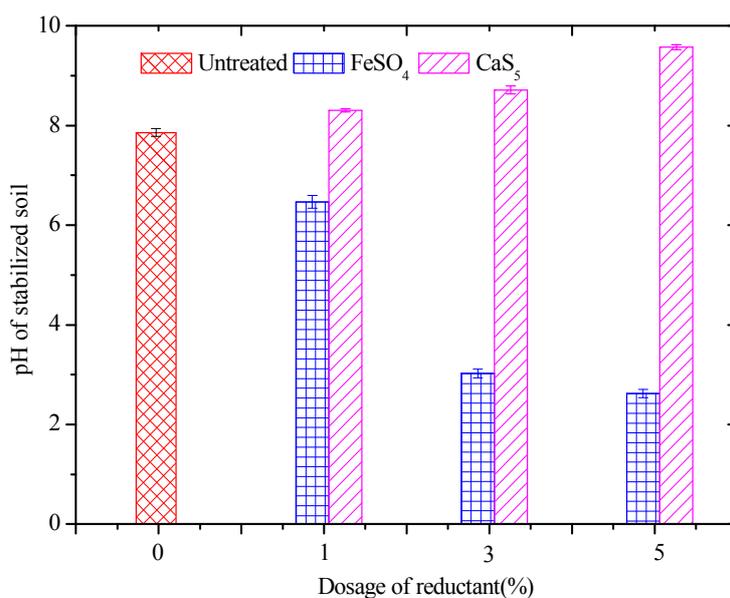


Figure 1. Effect of reductant types and dosage on the pH of stabilized soils.

4.2. Redox Potential of Stabilized Soils

The redox potentials of the stabilized soils are presented in Figure 2. The results indicated that addition of FeSO_4 and CaS_5 could decrease the redox potential of stabilized soil. This phenomenon can be attributed to the fact that Cr(VI) was reduced with increasing FeSO_4 and CaS_5 dosages. Figure 2 also shows that the redox potential of the FeSO_4 -stabilized soil was higher than that of the CaS_5 -stabilized soil with the same reductant dosage. When the reductant dosage increased from 0% to 5%, the redox potential in the FeSO_4 -stabilized soil was decreased from 530.5 mv to -96.3 mv. For the CaS_5 -stabilized soil, the redox potential was decreased from 530.5 mv to -390.6 mv. Compared with FeSO_4 -stabilized soil, CaS_5 could maintain a reducing environment in the stabilized soil.

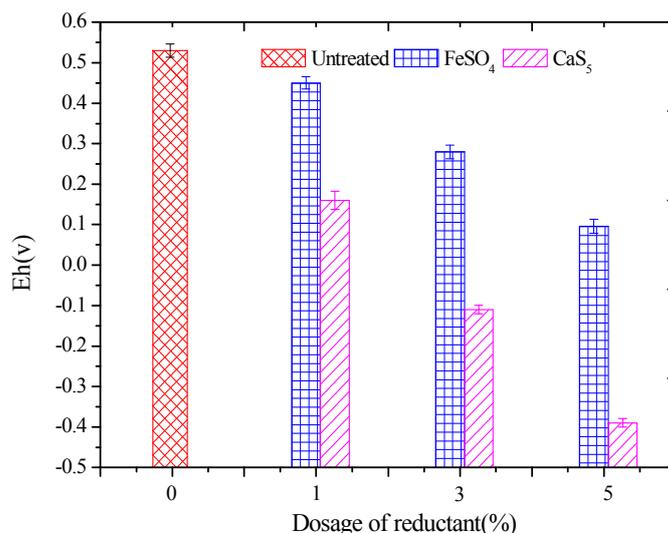


Figure 2. Effect of reductant types and dosage on the redox potential of stabilized soils.

4.3. Leachability of Cr/Cr(VI) from Contaminated Soil in TCLP Leaching

Figure 3 shows the Cr(VI) and Cr concentrations of the TCLP leachate. The Cr(VI) and Cr concentrations decreased with the increase of reductant addition. For the untreated soil, the Cr(VI) and total Cr leaching concentrations were approximately 38.8 mg/L and 40.4 mg/L, respectively, which exceeds the regulatory limit in the standards for hazardous wastes in China [34]. For the FeSO₄-stabilized soil, the leached Cr(VI) and Cr concentrations decreased from 6.4 mg/L and 12.6 mg/L to 0.62 mg/L and 2.6 mg/L, respectively, when the reductant dosage was increased from 1% to 5%. For the CaS₅-stabilized soil, the leached Cr(VI) and Cr concentrations decreased from 4.6 mg/L and 7.4 mg/L to 0.05 mg/L and 0.86 mg/L, respectively. In addition, with the same reductant dosage, the leached Cr(VI) and Cr concentrations of the CaS₅-stabilized soils decreased more noticeably relative to those of the FeSO₄-stabilized soils. These results clearly demonstrate the lower leachability of Cr in the CaS₅-stabilized soil than in the FeSO₄-stabilized soil under acidic solution conditions. This result agrees with most previous research results [10,13].

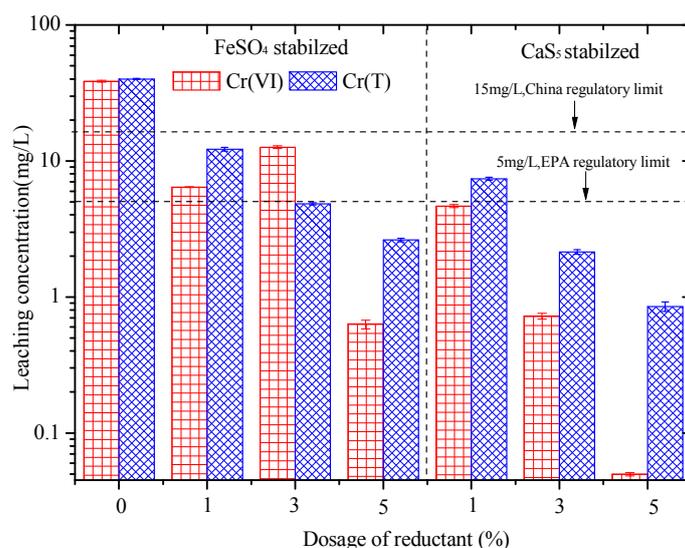


Figure 3. Effect of reductant types and dosage on Cr/Cr(VI) concentration in the toxicity characteristic leaching procedure (TCLP) leachate. EPA, Environmental Protection Agency.

4.4. Bioaccessibility of Cr/Cr(VI) from Contaminated Soil

As shown in Figure 4, the leached Cr(VI) and Cr concentrations in the SBET test were higher than those from the TCLP leaching method. In addition, the Cr(VI) concentrations decreased with the increase in FeSO₄ and CaS₅ dosage. The leached Cr(VI) of the CaS₅-stabilized soils decreased more noticeably relative to that of the FeSO₄-stabilized soils. For the FeSO₄-stabilized soils, the Cr concentrations changed slightly (9.8–10.1 mg/L) regardless of the FeSO₄ dosage, suggesting that the bioaccessibility risk of Cr was not reduced. The increased availability of Cr in the FeSO₄-stabilized soils can be explained by the pH-dependent characteristics of Cr for the pH of the leachant used in the SBET test, which was 1.5. The leached Cr concentration of the CaS₅-stabilized soil decreased from 5.4 mg/L to 0.9 mg/L when the CaS₅ dosage was increased from 1% to 5%. This phenomenon indicated that CaS₅ could notably reduce the bioaccessibility risk compared to FeSO₄-stabilized soil.

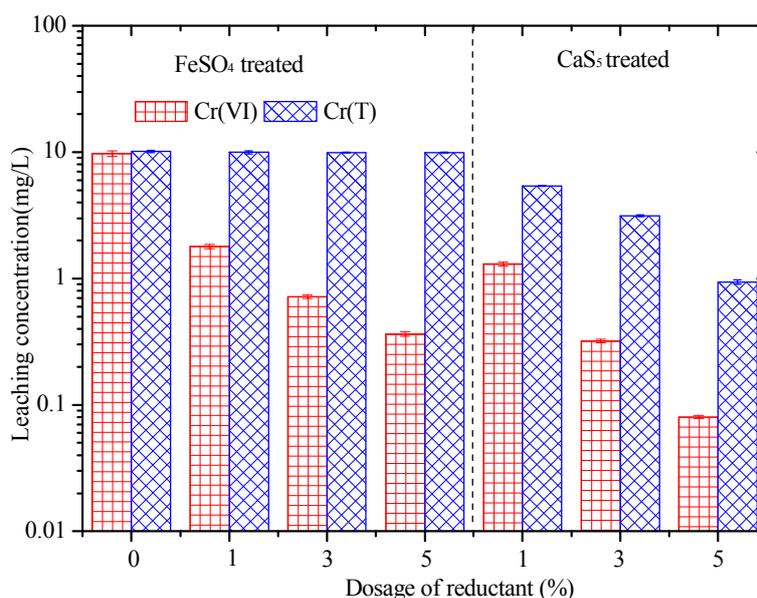


Figure 4. Effect of reductant types and dosage on Cr/Cr(VI) concentration in the simplified bioaccessibility extraction test (SBET) leachate.

4.5. Cr(VI) Content in Soils before and after Stabilization

The Cr(VI) contents of the stabilized soils are shown in Figure 5. For the untreated soil, the Cr(VI) content was approximately 971.3 mg/kg. After FeSO₄ and CaS₅ stabilization, the Cr(VI) content in the stabilized soils was reduced significantly with the increase of reductant dosage. This phenomenon can be attributed to the fact that Cr(VI) was reduced as the FeSO₄ and CaS₅ dosage increased. Figure 5 also shows that the Cr(VI) content of the FeSO₄-stabilized soil was higher than that of the CaS₅-stabilized soil with the same reductant dosage. When the reductant dosage increased from 1% to 3%, the Cr(VI) content in the FeSO₄-stabilized soil was decreased from 168 mg/kg to 58 mg/kg, whereas that in the CaS₅-stabilized soil was decreased from 94 mg/kg to 22 mg/kg. The Cr(VI) content in the CaS₅-stabilized soil with 3% dosage was below the threshold allowed by China's Environmental Regulations for industrial reuse (<30 mg/kg) [35]. Similarly, the Cr(VI) content in the FeSO₄-stabilized soil with 5% dosage was 21 mg/kg higher than that in the CaS₅-stabilized soil (4.2 mg/kg). The Cr(VI) content in the CaS₅-stabilized soil with 5% dosage was below the threshold of civil reuse (<5 mg/kg) [35]. CaS₅ presented a better effect than FeSO₄ in the stabilization of Cr(VI).

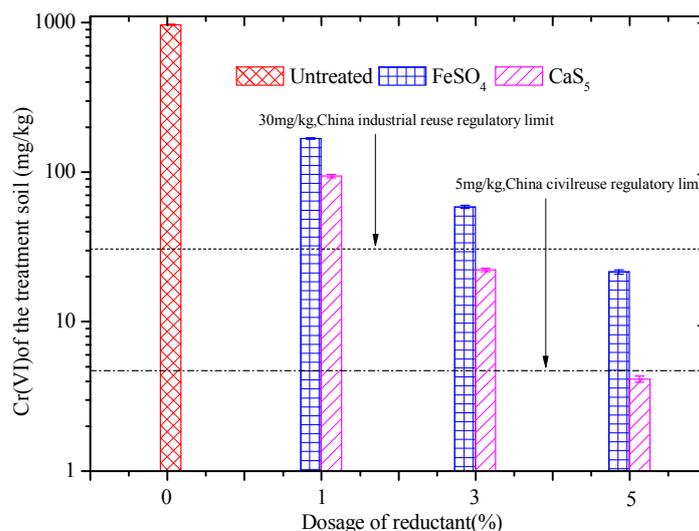


Figure 5. Effect of reductant types and dosage on Cr(VI) content of stabilized soils.

4.6. Species Distribution of Cr in Soils before and after Stabilization

Figure 6 shows the changes in the Cr speciation distribution of the untreated and stabilized soils. The primary Cr species for the untreated soil were mainly distributed in the exchangeable content (0.82 mg/g), and the reducible, oxidizable, and residual contents were 0.075 mg/g, 0.074 mg/g, and 0.0026 mg/g, respectively. These results indicated that Cr was more mobile and toxic in the untreated contaminated soil. The Cr speciation of stabilized soil was changed significantly. For the FeSO₄-stabilized soil, the exchangeable fraction was mainly converted to reducible fraction, which was increased to 0.76 mg/g, when the FeSO₄ dosage was increased from 0% to 5%. For the CaS₅-treated soil, the exchangeable fraction was mainly converted to oxidizable fraction. The oxidizable fraction of Cr in the CaS₅-stabilized soil with 3% dosage was 0.40 mg/g higher than that in the FeSO₄-stabilized soil (see Figure 6), Similarly, the oxidizable fraction of Cr in the CaS₅-stabilized soil with 5% dosage was 0.61 mg/g higher than that in the FeSO₄-stabilized soil. These results clearly demonstrate the better chemical stability of Cr in the CaS₅-stabilized soil compared to that in the FeSO₄ stabilized soil. This distinctive alteration in the Cr speciation of the CaS₅-stabilized soil, especially the substantial increase in the oxidizable fraction, accounted for the reduced leachability and bioaccessibility of Cr.

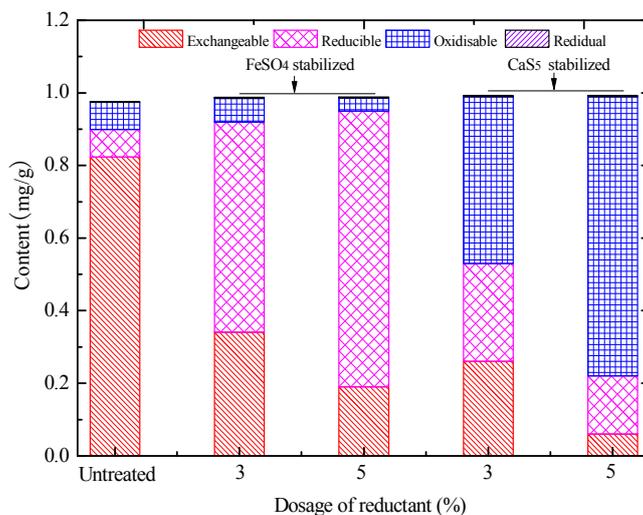


Figure 6. Effect of reductant types and dosage on Cr speciation distribution.

4.7. Probable Immobilization Mechanism of Cr

The XRD results of the Cr(VI)-contaminated soil, FeSO₄-stabilized soil, and CaS₅-stabilized soil are shown in Figure 7. In Cr(VI)-contaminated soil, illite, quartz, albite, and calcite were identified as the major phases. In the FeSO₄-stabilized soil, ferric hydroxide (Fe(OH)₃) and chromium hydroxide (Cr(OH)₃) were identified. For the CaS₅-stabilized soil, sulfur (S) and ettringite (Ca₆Al₂(OH)₁₂(SO₄)₃·26H₂O) were identified. The differences in the leachability, bioaccessibility, and speciation distribution of Cr in the FeSO₄- and CaS₅-stabilized soils can be attributed to (1) the different hydration products in the FeSO₄- and CaS₅-stabilized soils, and (2) the different pH conditions and Eh in the FeSO₄- and CaS₅-stabilized soils. Kostarelos et al. [36] suggested that Cr(VI) was reduced to Cr(III) by FeSO₄ and formed Cr(III)-Fe(III) hydroxide precipitation (Cr(OH)₃ and Cr_xFe_{1-x}(OH)₃). Wang et al. [37] found that Cr(OH)₃ and Cr_xFe_{1-x}(OH)₃ were disintegrated and desorbed Cr(III) under strong acid conditions. Therefore, the Cr(OH)₃ and Cr_xFe_{1-x}(OH)₃ were disintegrated and desorbed Cr(III) in the SBET test. For the CaS₅-stabilized soil, the elemental sulfur precipitated and ettringite formed by the reaction of CaS₅ with Cr(VI) [10]. Sulfur and ettringite were the key compounds responsible for Cr(III) immobilization [38]. Zhou et al. [38] suggested that the ettringite increases Cr(III) uptake into the matrix, making it difficult for Cr(III) to be released from the soils during the leaching test. Chrysochoou et al. [10] and Graham et al. [39] found that Cr(III) was bound to sulfides or adsorbed. Jacobs et al. [40] found that the leachability of Cr(III) was strongly dependent on solution pH, soil pH, and redox potential. The Cr solubility increased at low pH values, specifically at pH values below 6, because amorphous Cr(OH)₃ dissolves to form the soluble chromium hydroxide cations Cr(OH)₃, Cr(OH)₂⁺, and Cr(OH)²⁺. The lowest leachability of Cr was observed between pH 6 and 11. Insoluble and amorphous Cr(OH)₃ forms were observed at a pH of approximately 8.0 and under reducing (-Eh) conditions. Compared with TCLP, the SBET method uses extreme conditions, a more aggressive extracting agent (pH 1.5), and a higher liquid-to-soil ratio (100:1) to simulate the gastrointestinal environment [41,42].

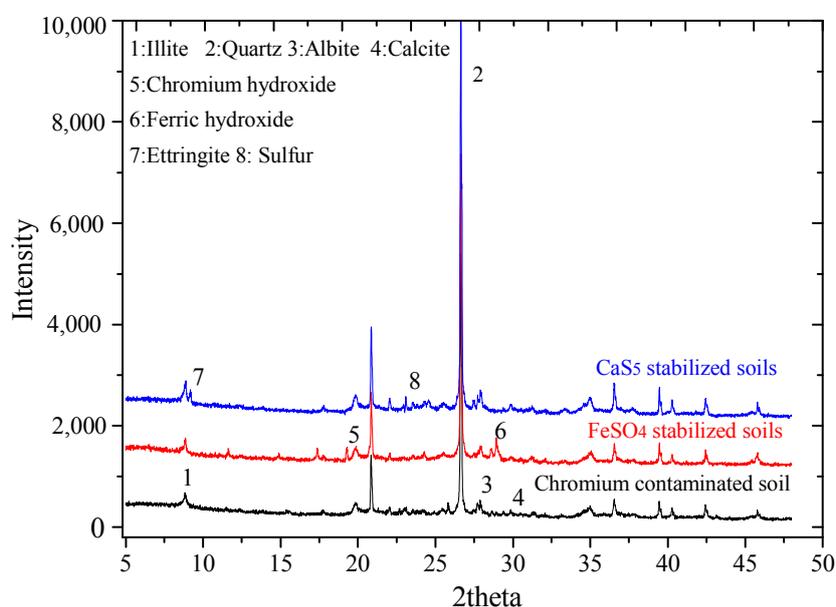


Figure 7. The XRD patterns of the Cr(VI)-contaminated soil, FeSO₄-stabilized soil, and CaS₅-stabilized soil.

4.8. Conclusions

This study compared the leachability and stability of FeSO₄- and CaS₅-stabilized Cr(VI)-contaminated soils. A series of toxicity characteristic leaching procedure (TCLP), simplified bioaccessibility extraction (SBET), alkaline digestion, sequential extraction, and X-ray diffraction

(XRD) tests were performed on Cr(VI)-contaminated soil. The influence of reductant dosage on the leachability and stability was assessed. The following conclusions can be drawn:

1. The pH and redox potential of the CaS₅-stabilized soils were better than those of the FeSO₄-stabilized soils regardless of CaS₅ dosage. The concentrations of Cr(VI) and Cr leached from the stabilized soils with FeSO₄ were larger than those of CaS₅ at the same dosage. The Cr(VI) content in the stabilized soils was decreased with the increase in FeSO₄ and CaS₅ dosages, and that in the CaS₅-stabilized soils decreased more noticeably compared with that in the FeSO₄-stabilized soils at the same dosage. This finding reflected that CaS₅ presented a better effect than FeSO₄ in the stabilization of Cr(VI) and Cr.
2. The leached Cr(VI)/Cr from the SBET leaching test was considerably larger than that from TCLP leaching due to the difference in the stabilization mechanism and the pH of the leaching solutions. The bioaccessibility risk of Cr in the FeSO₄-stabilized soils was higher than that in the CaS₅-stabilized soils due to the difference in stabilization mechanisms of Cr(VI) between FeSO₄ and CaS₅.
3. The differences in the leachability, bioaccessibility, and toxicity of Cr(VI) and Cr in the FeSO₄- and CaS₅-stabilized soils were attributed to the changes in mineral composition. For the FeSO₄-stabilized soil, the Cr(VI) was mainly converted to Cr(OH)₃ and Cr_xFe_{1-x}(OH)₃. For the CaS₅-stabilized soil, the Cr(VI) was reduced to Cr(III) and formed ettringite and sulfur. The Cr(III) was retained in the crystal structures of ettringite and sulfur through anion exchange.

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Conflicts of Interest: The authors declare no conflicts of interest.

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