



Stability Properties of Chromium in Cr(VI)-Contaminated Soil Stabilized by Calcium Polysulfide (CaS₅)

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ABSTRACT

Calcium polysulfide (CaS₅) is widely used in stabilizing Cr(VI)-contaminated soils. The stability properties of Cr(VI) and Cr are the most important indexes for evaluating the effectiveness of stabilized soil. This study investigated the effect of CaS₅ dosage and curing age on the stability properties of Cr(VI) and Cr in contaminated soils and the relationship between leachability and Cr speciation. Results show that increasing the CaS₅ dosage and curing age could improve the stability properties of Cr in stabilized soil. The leachability and Cr(VI) content in the stabilized soil significantly decreased along with increasing CaS₅ dosage and curing age. The changes in the leachability of the soil were attributed to the changes in the Cr speciation distribution and microstructure of the stabilized soil. The exchangeable fraction was mainly converted into an oxidizable fraction, and a dense structure (ettringite and elemental sulphur) was formed along with increasing CaS₅ dosage and curing age. The exchangeable and reducible fractions depended on Cr leachability, and the Cr in the synthetic precipitation leaching procedures predominantly resulted from the exchangeable and reducible fractions.

INTRODUCTION

As a common contaminant of soils in China (Zhang et al. 2018), chromium [Cr(VI)] is a toxic and carcinogenic material that has been categorized by the US Environmental Protection Agency (US EPA) as a class A human carcinogen (Kazakis et al. 2018). The chemical reduction can rapidly and effectively remove Cr(VI) and has been widely used to stabilize Cr(VI)-contaminated soils (Chrysochoou et al. 2010). Calcium polysulfide (CaS₅) is commonly used for the remediation of Cr(VI)-contaminated soil due to its cost-effectiveness. Reducing Cr(VI) by using CaS₅ can be formulated as (Zhang et al. 2018)



Although many studies have examined CaS₅-stabilized Cr(VI)-contaminated soils, most of these works have focused on Cr(VI) leachability and content (Wazne et al. 2007, Chrysochoou et al. 2010, Zhang et al. 2018). However, leaching tests, including toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedures (SPLP), and semi-dynamic leaching tests, can only provide a single leaching result at a specific period, and the leachability of Cr in stabilized soil is not a good predictor of the effectiveness of stabilized reductants

(Seaman et al. 1999, Tinjum et al. 2008). Previous studies show that the toxicity and mobility of heavy metals in soil are not only related to their content but are also greatly determined by the distribution of their speciation (Petrucci et al. 2011). Therefore, the speciation distribution of Cr(VI) is crucial in ensuring the environmental security of stabilized soil. In addition, the leachability content of Cr in stabilized soil remains constant regardless of the environment and service time. Many factors can also affect the stabilization process of Cr(VI)-contaminated soil, among which reductant dosage and curing age are the most important (Tinjum et al. 2008). However, very few studies have methodically investigated the effect of reductant dosage and curing age on the leachability and species distribution of Cr(VI) in contaminated soils stabilized by CaS₅.

Accordingly, this study explores the effect of CaS₅ dosage and curing age on the stability properties of Cr(VI) in CaS₅-stabilized soil. The relationship between the leachability and speciation distribution of the Cr(VI) in CaS₅-stabilized soil is also examined. The findings of this work provide novel insights that can aid in evaluating the environmental security of CaS₅-stabilized soil and in remediating Cr(VI)-contaminated soils by using CaS₅.

MATERIALS AND METHODS

Cr(VI)-Contaminated Soil

Given its representativeness and repeatability, Cr(VI)-contaminated soil was simulated by Chinese clay and $K_2Cr_2O_7$ in this study (Zhang et al. 2019). The Cr(VI) content of the soil was 1000 mg/kg, which is representative of Cr(VI)-contaminated soils in China (Zhang et al. 2009, Wang et al. 2014). The contaminated soil was mixed evenly and braised for 180 days under standard curing conditions (20°C, 95% humidity) to allow $K_2Cr_2O_7$ and the soil to react adequately and to obtain an ageing contaminated soil.

Stabilization of Cr(VI)-Contaminated Soil by CaS_5

The CaS_5 used in the study was Cascade®, a 29% CaS_5 solution obtained from Lian Yun Gang Industrial Technology Co. Ltd. without further purification. The experimental design is given in Table 1. The Cr(VI)-contaminated soil, CaS_5 and distilled water were homogenized in a mixer. The mixture was withdrawn from sealed plastic bottles after incubating for 3, 7, 15, 28, and 56 days at room temperature (20°C).

Test Methods

The Cr(VI) contents of the soil and filtrate were measured by following the US EPA methods 3060A and 7196A, respectively, whereas the leachability of Cr(VI) and Cr was measured by following the US EPA method 1312. The sequential extraction procedure followed the method recommended by Rauret et al. (1999). Agilent 7700 inductively coupled plasma mass spectrometry was used to determine the metal concentrations in the leachate.

Table 1: Experimental design for the study.

Test No.	CaS_5 /Cr(VI) molar ration	Curing age
1	0	7 d
2	1	7 d
3	2	7 d
4	3	7 d
5	5	7 d
6	3	0 d
7	3	3 d
8	3	7 d
9	3	28 d
10	3	56 d

RESULTS AND DISCUSSION

Leachability of Cr(VI) and Cr in Soil Before and After Stabilization

In view of the leaching environment to be encountered when the stabilized soils are reused, an SPLP test was conducted to simulate the scenario of leaching associated with acid rain. Fig. 1 shows the leaching characteristics of the stabilized soil under different conditions. Fig. 1(a) reveals that both Cr(VI) and Cr concentrations decrease along with an increasing CaS_5 /Cr(VI) molar ratio. For untreated soil, the Cr(VI) and Cr leaching concentrations were approximately 32.6 mg/L and 35.8 mg/L, respectively, which exceeded China's regulatory limits for hazardous wastes (China GB/T5085.3-2007). For CaS_5 stabilized contaminated soil, when the CaS_5 /Cr(VI) molar ratio increased from 1 to 5, the Cr(VI) and Cr leaching concentrations decreased from 8.2 mg/L and 17.6 mg/L to 0.14 mg/L and 4.08 mg/L, respectively.

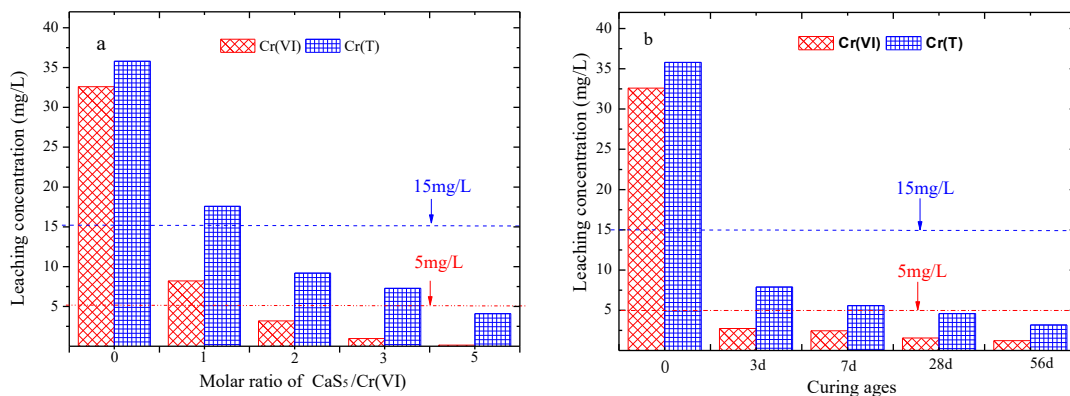


Fig. 1: Cr(VI) and Cr concentration of SPLP leachate under different conditions, (a) different CaS_5 and Cr(VI) molar ratio, (b) different curing ages.

In addition, when the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio exceeded 2, the Cr(VI) and Cr leaching concentrations complied with the regulatory limits of China and the US EPA (Moon 2008). The reduction in Cr(VI) concentration could be ascribed to the fact that Cr(VI) was reduced to Cr(III) and subsequently formed Cr(OH)_3 and ettringite precipitation or Cr(III) was bound to sulphides and adsorbed sulphur surface, thereby hindering Cr from migrating through the soil (Chrysochoou et al. 2010).

The variations in the Cr(VI) and Cr concentrations of the stabilized soil under different curing ages are shown in Fig. 1 (b). The leaching concentrations of Cr(VI) and Cr in the leachate decreased along with an extended curing age. When the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio was 3, the Cr(VI) and Cr concentrations complied with the regulatory limits of China and US EPA with a curing age of longer than 3 d. The decrease in Cr(VI) and Cr concentrations may be attributed to the ageing process, more and more Cr(VI) solubilization, reduction and the following Cr(OH)_3 and ettringite precipitation or adsorbed sulphur surface, making it harder for Cr to migrate through the soil, increasing the effectiveness of stabilized (Chrysochoou et al. 2010). As a result, the leaching concentrations of Cr(VI) and Cr decreased along with an extended curing age.

Cr(VI) Content in Soil Before and After CaS_5 Stabilization

Cr(VI) content is often measured to guarantee the environmental security of stabilized soils being reused as construction materials. The China Environmental Regulation recommends minimum Cr(VI) contents of 30 mg/kg and 5 mg/kg for industrial and civil reuse, respectively (China GB15618-2008). The Cr(VI) content in the soil before and after the stabilization of CaS_5 is shown in Fig 2. As shown in Fig. 2(a), the Cr(VI) content in soil decreased along with

an increasing $\text{CaS}_5/\text{Cr(VI)}$ molar ratio, thereby suggesting that the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio significantly influences the effectiveness of the stabilized treatment. In addition, when the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio was 5, the Cr(VI) content of the contaminated soil was below the threshold specified by the China Environmental Regulation for industrial reuse (<30 mg/kg) (China GB15618-2008). Although the Cr(VI) and Cr leaching concentrations of the stabilized soil were negligible compared with those shown in Fig. 1, a considerable amount of Cr(VI) was still detected in the stabilized soil. Part residue Cr(VI) content of stabilized soil exceeded Environmental quality standards soil of China. The SPLP test underestimated the residue Cr(VI) content in the stabilized soil, and the leaching method could not reliably predict the remaining Cr(VI) content in the stabilized soil without performing an alkaline digestion test.

Fig. 2 (b) shows the variations in the Cr(VI) content in the soil as a function of curing age. As expected, the Cr(VI) content decreased along with an extended curing age, thereby suggesting that CaS_5 has good stability and long residence time in the soil. In addition, when the curing age was 3 d, the Cr(VI) content in the contaminated soil was below the threshold set by the China Environmental Regulation for industrial reuse (<30 mg/kg) yet satisfied the threshold for civil reuse (<5 mg/kg) when the curing age was extended to 56 d (China GB15618-2008) probably due to the fact that as the curing age increased from 3 d to 56 d, most of the reactions between Cr(VI) and CaS_5 were gradually completed, which could explain why the redox potential increased along with curing period.

Species Distribution of Cr(VI) in Soil Before and After Stabilization

The species distribution of Cr(VI) in the soil as a function of different $\text{CaS}_5/\text{Cr(VI)}$ molar ratios and curing ages is shown

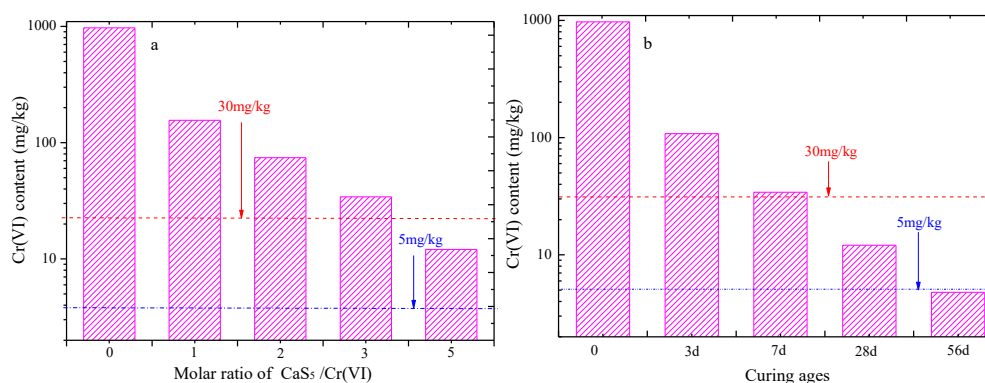


Fig. 2: Cr(VI) content in soil under different conditions, (a) different $\text{CaS}_5/\text{Cr(VI)}$ molar ratio, (b) different curing ages.

in Fig. 3. Fig. 3(a) shows that for the untreated soil, Cr was mainly distributed in exchangeable (0.79 mg/g) and reducible fractions (0.13 mg/g), thereby indicating that Cr was highly mobile and toxic in the untreated contaminated soil. After CaS_5 was stabilized, the species distribution of Cr(VI) in the soil was significantly changed. Specifically, as the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio and curing ages increased, the oxidizable content of Cr in the stabilized soil significantly increased. As shown in Fig. 3(a), the exchangeable fraction was mainly converted into an oxidizable fraction. Meanwhile, as the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio of the stabilized soil increased from 0 to 5, the oxidizable content of Cr increased from 0.076 mg/g to 0.88 mg/g. In addition, a higher $\text{CaS}_5/\text{Cr(VI)}$ molar ratio benefitted the conversion of reducible fraction into an oxidizable fraction and decreased the reducible content of Cr from 0.15 mg/g to 0.021 mg/g. As shown in Fig. 3 (b), the oxidizable content of Cr increased from 0.076 mg/g to 0.68 mg/g, thereby demonstrating that the CaS_5 could significantly improve the chemical stability of Cr. $\text{CaS}_5/\text{Cr(VI)}$ molar ratio and curing age were identified as crucial factors that control the species distribution of Cr.

Species Distribution of Cr(VI) in Soil Before and After SPLP Extraction

The species distribution of Cr(VI) in the soil before and after SPLP extraction is shown in Fig. 4. After the SPLP extraction, the species distribution of Cr(VI) in the soil was significantly changed. The content of exchangeable and reducible fractions in all soils decreased, while the oxidizable and residual fractions were nearly unchanged. Fig. 4(a) shows that as the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio of the stabilized soil increases from 0 to 5, the exchangeable content decreases from 0.79, 0.13, and 0.03 mg/g to 0.18, 0.06, and 0.010 mg/g, respectively, whereas the reducible content decreases from 0.13, 0.24, and 0.08 mg/g to 0.06, 0.16, and 0.02 mg/g, respectively. Meanwhile, Fig. 4 (b) shows that the exchangeable content decreases from 0.79, 0.13, and 0.02 mg/g to 0.18, 0.06, and 0.008 mg/g, respectively, whereas the reducible content decreases from 0.13, 0.24, and 0.14 mg/g to 0.06, 0.16, and 0.09 mg/g, respectively, as the curing age extends from 0 d to 56 d. These results clearly demonstrate that the exchangeable and reducible content of Cr depended on the Cr leachability in the SPLP test and on the safety of the stabilized soil.

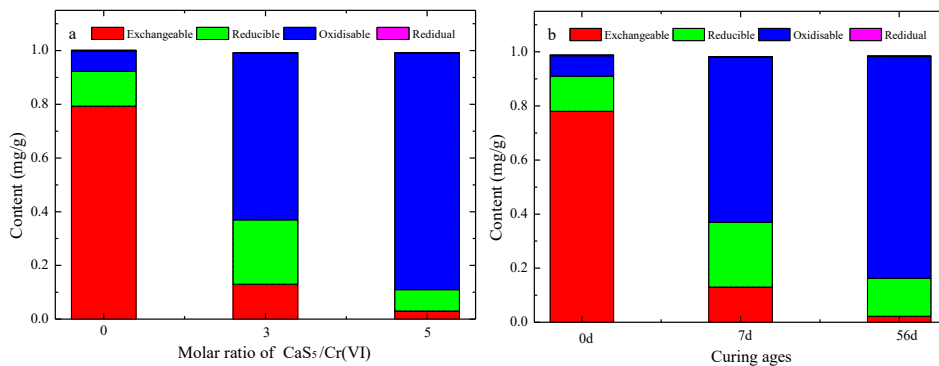


Fig. 3: Species distribution of Cr in soil under different conditions: (a) different $\text{CaS}_5/\text{Cr(VI)}$ molar ratio; (b) different curing ages.

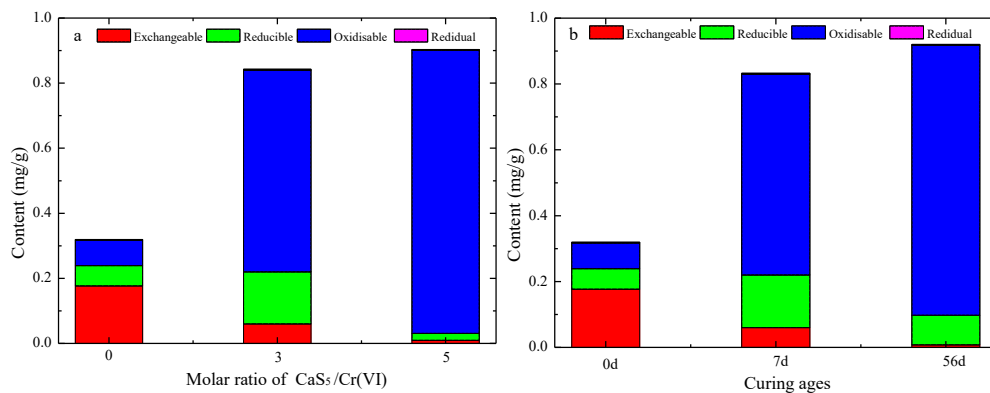
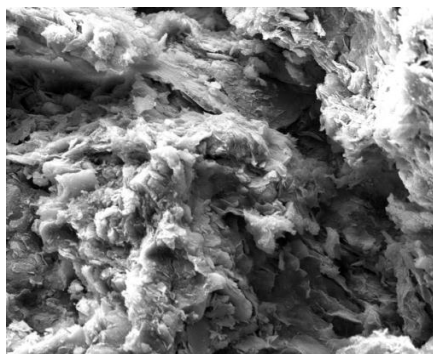


Fig. 4: Species distribution of Cr in soil after SPLP extraction (a) different $\text{CaS}_5/\text{Cr(VI)}$ molar ratio, (b) different curing ages.



(a) untreated contaminated soil.

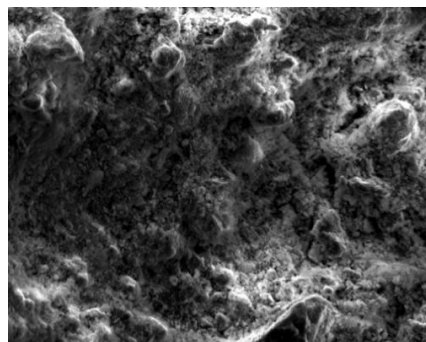
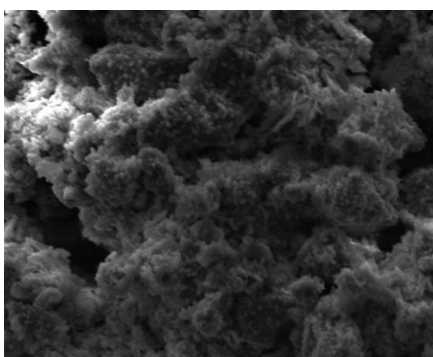
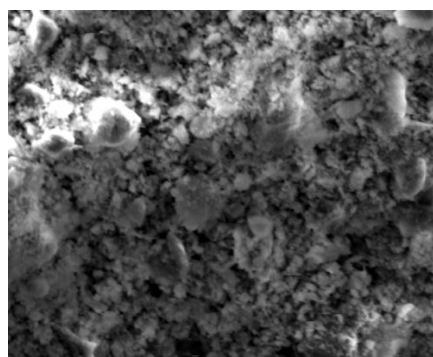
(b) $\text{CaS}_5/\text{Cr(VI)}$ molar ratio was 5 and Curing age was 7 d.(c) $\text{CaS}_5/\text{Cr(VI)}$ molar ratio was 3 and Curing age was 7 d.(d) $\text{CaS}_5/\text{Cr(VI)}$ molar ratio was 3 and Curing age was 56 d.

Fig. 5: SEM images of the stabilized soil under different conditions.

SEM Analysis

The typical SEM images of the stabilized soil under different conditions are shown in Fig. 5. The untreated contaminated soil (Fig. 5a) showed a large aggregate structure with a large void space between aggregations. When the $\text{CaS}_5/\text{Cr(VI)}$ molar ratio was 3 (Fig. 5 c), a low amount of ettringite and elemental sulphur was observed on the surface of the soil particles. By contrast, the SEM image of the soil with a $\text{CaS}_5/\text{Cr(VI)}$ molar ratio of 5 showed a large amount of ettringite and elemental sulphur covering the surface of soil particles and forming a dense structure in the stabilized soil (Fig. 5 b). When the curing age was extended from 7 d to 56 d (Fig. 5 c and d), the void volume was decreased, and the soil particles showed a dense structure, thereby suggesting that increasing the CaS_5 dosage and curing age would significantly change the microstructure of the soil and the stability properties of Cr. Zhou et al. (2017) and Chrysochoou et al. (2010) found that the Cr(III) uptake in ettringite hinders the release of Cr(III) from the soils during the leaching test.

Relationship Between Species Distribution and Leachability of Cr

The relationship between Cr species distribution and

leachability is given in Table 2. The content of exchangeable and reducible fractions in all soils was decreased, whereas the oxidizable and residual fractions were nearly unchanged. In other words, the Cr in the SPLP leachate predominantly resulted from the exchangeable and reducible fractions, and the Cr content depended on the Cr leachability recorded in the SPLP test and on the environmental security characteristics of the stabilized soil. As for CaS_5 -stabilized Cr(IV)-contaminated soils, the leachability content of Cr remained constant regardless of the environment and service time.

Table 2 shows that the Cr content in the SPLP leachate is approximately equal to the decrements in the exchangeable and reducible fractions of the soil after the SPLP extraction. These results indicate that the content of exchangeable and reducible fractions can be used to evaluate the potential leachability of Cr.

CONCLUSIONS

This study explores the speciation and leachability of Cr(IV)-contaminated soils stabilized by CaS_5 . A series of SPLPs, alkaline digestions, sequential extractions, and SEM tests were performed on Cr(VI)-contaminated soil. The effect of CaS_5 dosage and curing age on Cr(VI) speciation and

Table 2: Relationship between Cr species distribution and leachability of Cr in soil.

Soil types	Test indexes	Species distribution of Cr (mg/g)			
		Exchangeable	Reducible	Oxidizable	Residual
Untreated soil	Before SPLP extraction	0.793	0.13	0.076	0.0026
	After SPLP extraction	0.177	0.062	0.078	0.0023
	Variation	0.616	0.068	-0.002	0.0003
	Cr content in SPLP leachate	0.716	0.716	0.716	0.716
	Percentage	86.03%	9.50%	-0.27%	0.042%
CaS ₅ /Cr(VI) molar ratio was 3	Before SPLP extraction	0.13	0.24	0.62	0.00255
	After SPLP extraction	0.06	0.16	0.62	0.00255
	Variation	0.07	0.08	0	0
	Cr content in SPLP leachate	0.146	0.146	0.146	0.146
	Percentage	47.94%	54.79%	0	0
CaS ₅ /Cr(VI) molar ratio was 5	Before SPLP extraction	0.03	0.08	0.86	0.00253
	After SPLP extraction	0.0098	0.021	0.87	0.00253
	Variation	0.02	0.059	-0.01	0
	Cr content in SPLP leachate	0.082	0.082	0.082	0.082
	Percentage	24.40%	71.95%	-12.2%	0
Curing age was 7d	Before SPLP extraction	0.13	0.24	0.62	0.00255
	After SPLP extraction	0.06	0.16	0.62	0.00255
	Variation	0.07	0.08	0	0
	Cr content in SPLP leachate	0.146	0.146	0.146	0.146
	Percentage	47.94%	54.79%	0	0
Curing age was 56d	Before SPLP extraction	0.022	0.141	0.82	0.00256
	After SPLP extraction	0.0078	0.09	0.81	0.00256
	Variation	0.0142	0.051	0	0
	Cr content in SPLP leachate	0.064	0.064	0.064	0.064
	Percentage	22.19%	79.69%	0	0

leachability were evaluated, and the relationship between Cr(VI) leachability and speciation was investigated. The following conclusions can be drawn from the results:

1. Increasing the CaS₅ dosage and curing age can improve the stability of Cr in stabilized soil. The Cr(VI) leachability and content in stabilized soil significantly decreased along with increasing CaS₅ dosage and curing age. The leachability and Cr content of the stabilized soil was lower than the regulatory limits imposed by China and the US EPA when the CaS₅/Cr(VI) molar ratio was 3. Meanwhile, when the CaS₅/Cr(VI) molar ratio was 5, the Cr(VI) content in the soil met the environmental quality standards of China for industrial reuse (Cr(VI) < 30 mg/kg).
2. The change in the leachability of soil was attributed to the changes in Cr speciation distribution. According to the results of the sequential extraction test, the exchangeable fraction was mainly converted into oxidizable fraction

as the CaS₅ was stabilized. The exchangeable and reducible fractions depended on Cr leachability, and the Cr in the SPLP leachate predominantly resulted from these fractions. The content of exchangeable and reducible fractions can be used to evaluate the potential leachability of Cr.

3. Along with increasing CaS₅ dosage and curing age, the microstructure of the stabilized soil was changed along with the stability properties of the soil. The SEM images showed that the stabilized soil had a large amount of ettringite, and elemental sulphur covered the surface of the soil particles and formed a dense structure in the stabilized soil.

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