Combined Treatment of Cr(VI)-Contaminated Soils by Reduction, Adsorption, and Solidification

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Abstract: Remediation of Cr(VI)-contaminated soil usually includes reducing Cr(VI) to Cr(III) with subsequent solidification. In this paper, a treatment technique that combines reduction, adsorption, and solidification was proposed. By introducing an adsorbent into the reduction process, the remediation effectiveness was improved and the amount of reducing and solidified agent was decreased. Synthetic precipitation leaching procedure (SPLP), unconfined compressive strength (UCS) test, and scanning electron microscope (SEM) analysis were carried out to evaluate the remediation effect under different agent combinations and different agent-adding procedures. The results of SPLP showed that the reduction/adsorption/solidification treatment significantly reduced the leachability of Cr. UCS increased with increasing dosage of cement and CaS₅, and decreased with an increasing dosage of vermiculite. The best agent dosage was CaS₅ of 2 times molar stoichiometric ratio of Cr(VI), 15% of vermiculite, and 20% of cement. Orthogonal test showed that for soil with low Cr(VI) content, CaS₅ dosage was the most important factor that affected the leachability of Cr. Cement and vermiculite have greater impact in limiting the leachability of Cr when Cr(VI) content in soil increased.

Keywords: Cr(VI)-contaminated soil; combined treatment; leached concentration; reduction/adsorption/solidification; agent-adding procedure

1. Introduction

Industrial and agricultural activities such as metallurgy, mining, electroplating, tanning, dumping of waste, and fertilizer application have caused serious concerns about chromium (Cr) contamination. Although Cr can exist in several oxidation states, the most prevalent natural forms are Cr(III) and Cr(VI) [1]. In the pedosphere, Cr(III) is nearly immobile with relatively low toxicity. However, Cr(VI) is highly soluble, mobile, and toxic over a wide pH range [2]. Cr(VI) can accumulate in plants and animals, ultimately result in severe damage to human health through accumulation by the food chain, and it is classed as a class-1 carcinogen [3]. Extensive studies have been conducted about remediation of Cr(VI)-contaminated soil. However, complex geochemical properties of Cr(VI) still have not been fully elucidated.

Solidification method refers to the use of solidified agent (e.g., cement) to physically encapsulation of the contaminants within the treated contaminated soil [4]. However, Cr(VI) mainly exists in the form of anionic groups, which is difficult to be adsorbed and solidified. As a result, solidification of Cr(VI)-contaminated soil solely with cement can barely achieve sufficient results [5–7]. The cement-based solidification/stabilization (S/S) technique has been extensively applied for treatment of contaminated soils containing heavy metals [8–12]. Stabilization refers to the reduction of mobility of the contaminants by converting the contaminants into more chemically stable forms. Therefore, the most common approach for treating the Cr(VI)-contaminated soil is reducing Cr(VI) to Cr(III) by using electron donors and subsequently immobilize Cr(III) with cement. A lot of reductants,
such as CaS$_5$, FeSO$_4$, Fe$^0$, and FeS$_2$(am), have been used to treat Cr(VI)-contaminated soils [13–16]. Although reduction-solidification treatment of Cr(VI)-contaminated soil can generate better results than single solidification, problems such as excessive use of reducing agent or solidified agent in the treatment still exist. For example, Bulut et al. [17] treated ferrochrome dust with 5 stoichiometric amounts of FeSO$_4$ and 30% cement and found that the leached concentration could not meet the requirement for landfill. In order to obtain a satisfied remediation efficiency, Li et al. [16] treated Cr(VI)-contaminated soil with Cr(VI) content of 250 mg/kg using 4 molar ratio of FeS$_2$(am). For a field treatment case with Cr(VI) content of only 12.5 mg/kg, Lu et al. [18] achieved the criteria of remediation by adding 6% FeSO$_4$ and 3% Na$_2$S$_2$O$_4$. Chen et al. [19] found that the immobilization of Cr could be significantly improved by adding metakaolin-based geopolymer to FeSO$_4$ treated soil. However, excessive iron-based reducing agents may result in soil acidification, and excessive solidified agents will reduce the efficiency of landfilling due to the increased volume of the waste. Therefore, a highly efficient remediation technique that requires less dosage of reducing and solidified agents is urgently needed.

Theoretically, Cr(III) is more readily adsorbed and the addition of an adsorbent should improve the effectiveness of the S/S technology and reduce the amount of reducing agent and solidified agent used in the treatment process. Amongst other things, Vermiculite is a natural clay mineral with a 2:1 phyllosilicate structure that can be used as an adsorbent. When silicon is replaced by aluminum, a negative charge appears which is usually counterbalanced by magnesium cation. The magnesium cation is easily exchanged with other cations, such that vermiculite exhibits high adsorption capacity and has great potential in treatment of heavy metals [20]. For example, vermiculite has been used to treat Cr(VI) and Cr(III) in waste water. Moreover, the adsorption of vermiculite to Cr(III) was more effective than Cr(VI) [21]. However, the application of vermiculite in soil remediation is still limited. Malandrino et al. [22] found through vermiculite significantly reduced the uptake of Cr by plant and confirmed the possibility of using vermiculite in amendment treatment of Cr-contaminated soils based on pot experiments. In addition, the utilization rate of adsorption sites on vermiculite directly affects the adsorption capacity, which limits the application of vermiculite in treatment of Cr(VI)-contaminated soil [23,24]. From this point of view, the combination of vermiculite and reducing agent likely will increase the adsorption of Cr. Although the reduction/adsorption/solidification treatment can be considered as a promising remediation method of Cr(VI)-contaminated soil, experimental investigations of the treatment mechanisms are still missing.

In this study, a novel treatment technique for Cr(VI)-contaminated soil that combined reduction, adsorption, and solidification was proposed. The concept of this technique included reducing Cr(VI) to Cr(III) by reducing agent, further adsorbing of Cr(III) by vermiculite, and finally solidifying the contaminated soil by cement. Synthetic precipitation leaching procedure (SPLP), unconfined compressive strength (UCS) tests, and scanning electron microscope (SEM) analysis were carried out to evaluate the remediation effect. The best agent combination and agent-adding procedure were investigated. In order to study the impact of agent dosages on the remediation efficiency, orthogonal experiments were performed using soil samples with different Cr(VI) content.

2. Materials and Methods

2.1. Contaminated Soil

The soil used in this study was collected from a construction site in Pudong District, Shanghai, China. The soil contained 62% silt, 33% clay, and 5% sand particles. The liquid limit and plastic limit of the soil was 38.1% and 24.3%, respectively. The specific gravity of the soil was 2.71. The soil pH ranged from 6.5 to 7.5. The background total Cr and other metal contents in the soil were measured by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Model Prodigy, Leeman), as shown in Table 1. The original soil was free from Cr(VI). Thus, two batches of Cr(VI)-contaminated soil samples (soil No.1 and No.2) were prepared by mixing K$_2$Cr$_2$O$_7$ solution into the soil and leaving
it sealed for 15d. The total Cr content of soil No.1 was 1200 mg/kg, with the final Cr(VI) content as 823 ± 20 mg/kg after reacting with the soil. The total Cr content of soil No.2 was 3000 mg/kg, with a final Cr(VI) content of 2400 ± 20 mg/kg. The decrease in Cr(VI) concentrations in soils No.1 and No.2, probably because of the presence of Fe^{2+} or small amounts of dissolved organic matter in the soil, which could reduce Cr(VI) to Cr(III). The studied Cr(VI) content accorded with the common content range of Cr(VI)-contaminated soil in China [25,26]. Soil No.1 was used to investigate the best agent combination and agent-adding procedure. Both soil No.1 and No.2 were used in the orthogonal experiment.

### Table 1. Metal element content of original soil.

| Metal Ion | Al  | Mg  | Fe  | Mn  | K   | Ca  | Zn  | Cr  | Pb  | Cd  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content (mg/g) | 11.07 | 7.36 | 18.05 | 0.47 | 21.20 | 5.43 | 0.06 | 0.08 | 0.04 | 0.03 |

2.2. Specimen Preparation

The reducing agent was diluted with deionized water, then evenly mixed with the Cr(VI)-contaminated soil for 72 h to reach a complete reduction. The vermiculite was sieved through a 2-mm sieve and evenly mixed with the reduced soil. Then, ordinary Portland cement and tap water was added into the soil in a mud mixer with the final water content of 40 wt. %. Finally, the mixture was poured into the cylindrical perspex molds (diameter of 5 cm and height of 10 cm) to form solidified specimens. The specimens were removed from the molds after being allowed to set for 24 h, and then they were conditioned at 20 °C and 95% relative humidity for 28 days. The specimens were used for subsequent SPLP and UCS tests. Afterwards, the morphological structure was analyzed by scanning electron microscope (SEM, JSM-7500F, Tokyo, Japan). All measurements in this study were performed in triplicates.

2.3. Experimental Scheme

Soil No.1 was used to investigate the effectiveness of the proposed treatment technique, with the experiment program shown in Table 2. The relative amount of cement was 20 wt. % in the solid components, which is an appropriate dosage ratio for S/S treatment [4,27,28]. Dosage of FeSO_4 or CaS_5 was 2 times of the molar stoichiometry ratio of Cr(VI), which was lower than the regular amount reported in the literature. In addition, 10 wt. % of vermiculite was used in this study. Specimen No.1 was set to be the control with no agent added. For specimens No.2–5, only one type of agent was added to each specimen to study the individual effect of reduction, adsorption, or solidification. For specimens No.6–8, two types of agents were added to each specimen. For specimens No.9–10, the effect of combined treatment was investigated by adding the reducing, adsorbent and solidified agent one by one at three times. Specimens No.11–14 were used to investigate the agent-adding procedure. The three types of agents were added in two times, i.e., adding reducing agent and adsorbent at a time and subsequently adding cement (Specimens No.11–12) or adding reducing agent first, then adding adsorbent and cement together (Specimens No.13–14).

### Table 2. Experimental program for the combined remediation.

| Specimen No. | Agent Combination | Reducing Agent | Adsorbent | Solidified Agent |
|--------------|-------------------|----------------|-----------|-----------------|
| 1            | /                 | /              | /         | /               |
| 2            | C                 | /              | /         | Cement          |
| 3            | Fe                | FeSO_4         | /         | /               |
| 4            | Ca                | CaS_5          | /         | /               |
| 5            | V                 | /              | Vermiculite | /               |
Table 2. Cont.

|   | V-C | Fe-C | FeSO$_4$ | Vermiculite | Cement |
|---|-----|------|----------|-------------|--------|
| 6 |     |      | /        | /           | Cement |
| 7 | Fe-C| FeSO$_4$ | /        | /           | Cement |
| 8 | Ca-C| CaS$_5$ | /        | /           | Cement |
| 9 | Fe-V-C| FeSO$_4$ | Vermiculite | Cement |
| 10 | Ca-V-C| CaS$_5$ | Vermiculite | Cement |
| 11 | Fe-V-C| FeSO$_4$ + Vermiculite | Cement |
| 12 | Ca-V-C| CaS$_5$ + Vermiculite | Cement |
| 13 | Fe-VC| FeSO$_4$ | Vermiculite + Cement |
| 14 | Ca-VC| CaS$_5$ | Vermiculite + Cement |

C, Fe, Ca, and V denote cement, FeSO$_4$, CaS$_5$, and vermiculite, respectively.

Orthogonal tests were performed to study the effect of the dosage ratios on the treatment. Soil No.1 and No.2 were treated under the combination of CaS$_5$, vermiculite, and cement. The adopted dosages corresponding to different levels are shown in Table 3.

Table 3. Orthogonal experiment levels and dosage ratios.

| Level | CaS$_5$ (Times) | Vermiculite (%) | Cement (%) |
|-------|-----------------|-----------------|------------|
| 1     | 1               | 5               | 10         |
| 2     | 1.5             | 10              | 15         |
| 3     | 2               | 15              | 20         |

2.4. Leaching and UCS Test

SPLP Method 1312 simulates the worst-case scenario applied to the solidified waste by acid rain [29]. In the acid environment, heavy metals become more vulnerable to leaching. Sulfuric/nitric acid (6:4 g/g) solution at pH of 4.20 was used as the extraction fluid; 50 g of crushed specimens passed 9.5 mm sieve were placed in polyethylene bottles with 1 L of extraction fluid in order to achieve a mass ratio of leachant to solid of 20:1. The bottles were then agitated at 30 rpm for 18 h. After filtered through a 0.45 µm pore size membrane filter, the total Cr concentration was measured by ICP-AES, and Cr(VI) was measured by UV-Vis spectrophotometer (4802UV/VIS).

The compressive strength obtained by UCS was used to evaluate the treatment effect. The UCS values of the specimens were determined according to ASTM D4219-08. A stress controlled loading speed setting of 0.05 kN/s was applied for the compression testing.

3. Results and Discussions

3.1. Leached Concentration from SPLP Test

The variations of leached concentrations of the total Cr and Cr(VI) after treatment were summarized in Figure 1. The leached concentrations of total Cr and Cr(VI) of the untreated soil (Specimen No.1) were 69.82 mg/L and 30.93 mg/L, respectively, which significantly exceeded the limit of 5 mg/L for landfill disposal [29]. The individual treatment by vermiculite (denoted as V in Figure 1) only slightly reduced the leached concentrations, indicating that vermiculite was not effective for Cr(VI) adsorption. When treated by cement (C), the leached concentrations were 17.18 and 7.42 mg/L for total Cr and Cr(VI), respectively. For the individual use of FeSO$_4$ (Fe) or CaS$_5$ (Ca), the leached concentrations were significantly reduced, but still could not meet the limit of 5 mg/L.

Under the combined treatment of FeSO$_4$ and cement (Fe-C), or CaS$_5$ and cement (Ca-C), the leached concentration further decreased, with the 5-mg/L limit being met for the Ca-C case. As Cr(VI) was reduced to Cr(III), precipitation and encapsulation became easier. Note that the adopted molar ratio of 2 for FeSO$_4$/Cr(VI) in this study was less than the stoichiometric value, with the reaction presented as follows: $3\text{Fe(II)} + \text{Cr(VI)} \rightarrow 3\text{Fe(III)} + \text{Cr(III)}$ [19]. For CaS$_5$, the molar ratio was consistent in accordance with the reaction: $3\text{CaS}_5 + 2\text{Cr(VI)} \rightarrow 2\text{Cr(III)} + 15\text{S} + 3\text{Ca}^{2+}$ [30]. The reduction efficiency (at
the same dosage ratio) of CaS$_5$ was higher than that of FeSO$_4$, so the remediation effect of the Ca-C case was better. For the combination of vermiculite and cement (V-C), the leached concentrations were close to the individual C case, indicating that the treatment by vermiculite was ineffective without Cr(VI) reduction.

3.2. UCS of Solidified Specimens

The 28-day UCS values of the specimens treated with Fe-C and Ca-C were 1.63 and 1.75 MPa, respectively, which were higher than the value of the C case (Figure 2). The enhancement could be attributed to the fact that reducing Cr(VI) to Cr(III) produced either Cr(OH)$_3$ or Fe-Cr coprecipitation. Furthermore, Ca$^{2+}$ produced during the reaction of CaS$_5$ and Cr(VI) resulted in larger production of calcium-silicate-hydrate (CSH), therefore a higher strength. The introduced SO$_4^{2-}$ during the Fe-C treatment can somewhat alter the hardening process of cement due to the interaction with hydrating paste [32]. The values of UCS of the Fe-V-C and Ca-V-C cases showed that the presence of vermiculite slightly reduced the strength, partly because the strong water-adsorption of vermiculite hindered the cement hydration as well as the soft texture of vermiculite [32]. However, the UCS values (1.34 MPa for Fe-V-C and 1.38 MPa for Ca-V-C) were still higher than that of the C case. The strength extensively exceeded the minimum limit of landfill disposal of 0.35 MPa in the United State [33] and United Kingdom [34], so UCS was not a dominating factor for application of the combined treatment technique.

Under the Ca-V-C and Fe-V-C combinations, high treatment efficiencies were achieved. Comparing to the untreated case, the leached Cr(VI) concentration decreased by 99.7% under the Ca-V-C combination. Total Cr and Cr(VI) concentrations were 0.53 and 0.09 mg/L, respectively, which met the specified Water Standard Level IV in China, i.e., Cr(VI) ≤ 0.1 mg/L (GB/T 14848-2017). Compared with the case of Fe-C and Ca-C, the leached Cr was reduced significantly due to adsorption of Cr(III) on vermiculite. Treatment efficiency of Ca-V-C was a slightly higher than that of Ca-V-C. In addition, CaS$_5$ was more environment friendly than other reducing agents [28,31], such that Ca-V-C was concluded to be the optimum agent combination for treatment of Cr(VI)-contaminated soil. When the leached concentration is factor of interest, the combined treatment technique has promising potentials in applications such as in-situ remediation and waste resource utilization.

![Figure 1. Leached concentration of total Cr and Cr(VI) after treatment.](image-url)
As shown in Figure 3, when adding reducing agent and vermiculite simultaneously (FeV-C), it is necessary to optimize the amount of agent and mixing duration. This indicated that vermiculite was almost completely ineffective under this circumstance. The main reason may lie in the encapsulation of vermiculite by the cement hydration product, which prevented the direct contact between vermiculite and Cr and thus limited adsorption. Also for this reason, the effect of adding the three types of agent at the same time was not tested.

The previous experiments showed adequate treatment effects when the reducing agent, vermiculite and cement were added separately. However, in order to facilitate the practical application, it is necessary to optimize the amount of agent and mixing duration. As shown in Figure 3, when adding reducing agent and vermiculite simultaneously (FeV-C and CaV-C), the leached Cr concentration was similar to that of the cases of adding the three agents separately (Fe-V-C and Ca-V-C). The leached Cr(VI) concentration corresponding to CaV-PO was still lower that 0.10 mg/L, showing an excellent remediation effect. However, when adding vermiculite and cement together (Fe-VC and Ca-VC), the resulting leached Cr concentration was much higher and was similar to that of the case without vermiculite, i.e., the Fe-C and Ca-C cases in Figure 1. This indicated that vermiculite was almost completely ineffective under this circumstance. The main reason may lie in the encapsulation of vermiculite by the cement hydration product, which prevented the direct contact between vermiculite and Cr and thus limited adsorption. Also for this reason, the effect of adding the three types of agent at the same time was not tested.

**Figure 2.** UCS of specimens under different agent combinations.

**Figure 3.** Leached concentrations under different agent-adding procedures.
From the perspective of strength (Figure 4), the agent-adding procedures had only minor influence on UCS, and values of the FeV-C and CaV-C cases were slightly higher than that of the Fe-V-C and Ca-V-C cases, respectively. Therefore, the procedure of adding reducing agent and vermiculite together then following by cement was recommended. This procedure is time-saving and cost-effective, and can facilitate application of the combined treatment.

![Figure 4. UCS under different agent-adding procedures.](image)

### 3.4. Results of SEM Analysis

In order to observe the microscopic morphology of the specimens, specimen No.1, specimen No.2, and specimen No.12 were selected for SEM analysis. As shown in Figure 5a, the Cr-contaminated soil is composed of flaky soil and some soil particles, with dispersed and independent structure and low density. The density of Cr-contaminated soil increased significantly after cement conservation, with the appearance of flaky calcium hydroxide crystals (CAH) and CSH in a fibrous network structure (Figure 5b). Figure 5c shows the SEM image of the Cr-contaminated soil after the combined reduction/adsorption/solidification, specimen 12 is dense and smooth without pores because Ca²⁺ in Ca₅S producing CSH to fill the pores. Based on the analysis of the SEM results, Figure 5d–f shows the mechanism of combined reduction/adsorption/solidification remediation of Cr-contaminated soil, where Cr(VI), which is homogeneously dispersed in the soil, is easily leached out by dissolving in water when the Cr-contaminated soil is untreated (Figure 5d). However, as shown in Figure 5e, with cement as a solidified agent for treatment of Cr-contaminated soil, the Cr-contaminated soil particles are encapsulated in the hydration products of the cement (e.g., CSH, CAH), preventing Cr(VI) from coming into contact with water and greatly reducing the leaching concentration of Cr(VI), thus acting as a solidified agent for Cr(VI). In particular, when a combined reduction/adsorption/solidification remediation method is used to treat Cr-contaminated soil (in Figure 5f), Ca₅S and vermiculite are added to the Cr-contaminated soil, Ca₅S will first reduce the Cr(VI) in the contaminated soil to Cr(III), which is more easily adsorbed on the vermiculite surface under electrostatic action. Finally, both the free Cr(III) and the Cr(III) adsorbed on the surface of vermiculite were encapsulated by the hydration products of the cement, resulting in a total Cr leaching concentration of 0.54 mg/L for sample 12, which was 99.23% lower than that of specimen 1.
Contaminated soil particles are encapsulated in the hydration products of the cement (e.g., CSH, CAH), preventing Cr(VI) from coming into contact with water and greatly reducing the leaching concentration of Cr(VI), thus acting as a solidified agent for Cr(VI). In particular, when a combined reduction/adsorption/solidification remediation method is used to treat Cr-contaminated soil (in Figure 5f), CaS\textsubscript{5} and vermiculite are added to the Cr-contaminated soil, CaS\textsubscript{5} will first reduce the Cr(VI) in the contaminated soil to Cr(Ⅲ), which is more easily adsorbed on the vermiculite surface under electrostatic action. Finally, both the free Cr(Ⅲ) and the Cr(Ⅲ) adsorbed on the surface of vermiculite were encapsulated by the hydration products of the cement, resulting in a total Cr leaching concentration of 0.54 mg/L for sample 12, which was 99.23% lower than that of specimen 1.

Figure 5. SEM images of (a) specimen No.1, (b) specimen No.2 and (c) specimen No.12, and mechanistic diagrams of (d) untreated, (e) cement-solidified remediation, and (f) combined reduction/adsorption/solidification remediation of Cr-contaminated soil.

3.5. Results of the Orthogonal Experiments

Soil No.1 and No.2 were treated by the combined remediation technique under different agent dosages. The orthogonal experiments included 9 batches and the corresponding SPLP and UCS results were shown in Table 4.

Table 4. Results of the orthogonal experiments.

| Test No. | CaS\textsubscript{5} (Molar Times) | Vermiculite (%) | Cement (%) | Soil No.1 | Soil No.2 | Soil No.1 | Soil No.2 |
|----------|----------------------------------|----------------|------------|-----------|-----------|-----------|-----------|
| 1        | 1 (1)                            | 1 (5)          | 1 (10)     | 6.31      | 10.46     | 0.73      | 0.67      |
| 2        | 1 (1)                            | 2 (10)         | 2 (15)     | 3.43      | 6.58      | 0.88      | 0.80      |
| 3        | 1 (1)                            | 3 (15)         | 3 (20)     | 2.31      | 2.78      | 1.19      | 1.08      |
| 4        | 2 (1.5)                          | 1 (5)          | 2 (15)     | 2.02      | 5.55      | 1.05      | 0.96      |
| 5        | 2 (1.5)                          | 2 (10)         | 3 (20)     | 1.48      | 2.17      | 1.32      | 1.21      |
| 6        | 2 (1.5)                          | 3 (15)         | 1 (10)     | 1.95      | 4.79      | 0.60      | 0.56      |
| 7        | 3 (2)                            | 1 (5)          | 3 (20)     | 1.12      | 3.64      | 1.43      | 1.27      |
| 8        | 3 (2)                            | 2 (10)         | 1 (10)     | 1.41      | 4.46      | 0.73      | 0.71      |
| 9        | 3 (2)                            | 3 (15)         | 2 (15)     | 0.62      | 1.88      | 0.90      | 0.80      |

The result of the range (R) analysis based on the SPLP results were summarized in Table 5. According to the R value, the order of influence was determined. The effect of agent dosage on the leached concentration for soil No.1 was CaS\textsubscript{5} > cement > vermiculite (2.97 > 1.59 > 1.52). Comparing to vermiculite and cement, the dominating effect was the dosage of CaS\textsubscript{5}. For Soil No.2 (with higher Cr content), the order of influence was cement > vermiculite > CaS\textsubscript{5} (3.94 > 3.63 > 3.05), indicating that cement and vermiculite had greater effect than CaS\textsubscript{5}. Therefore, cement and vermiculite played more important roles in treatment when Cr content in soil increased.
The range analysis on UCS results was shown in Table 6. The order of influence of both Soil No.1 and No.2 were cement > vermiculite > CaS5. The $R$ values of cement were much larger than those of vermiculite and CaS5, which is consistent with the fact that cement dosage was the dominated factor for the strength of the solidified soil.

Table 5. Range analysis of SPLP results.

| Parameter | Soil No.1 | Soil No.2 |
|-----------|-----------|-----------|
|           | CaS5 | Vermiculite | Cement | CaS5 | Vermiculite | Cement |
| $K_1$     | 4.02 | 3.15 | 3.22 | 6.38 | 6.55 | 6.57 |
| $K_2$     | 1.82 | 2.11 | 2.02 | 4.17 | 4.40 | 4.67 |
| $K_3$     | 1.05 | 1.63 | 1.64 | 3.33 | 2.92 | 2.63 |
| $R$       | 2.97 | 1.52 | 1.59 | 3.05 | 3.63 | 3.94 |

$K_1$–$K_5$ is effect level, and $R$ is range.

Table 6. Range analysis of UCS results.

| Parameter | Soil No.1 | Soil No.2 |
|-----------|-----------|-----------|
|           | CaS5 | Vermiculite | Cement | CaS5 | Vermiculite | Cement |
| $K_1$     | 0.93 | 1.07 | 0.69 | 0.85 | 0.97 | 0.65 |
| $K_2$     | 0.99 | 0.98 | 0.94 | 0.91 | 0.91 | 0.85 |
| $K_3$     | 1.02 | 0.90 | 1.31 | 0.93 | 0.81 | 1.19 |
| $R$       | 0.09 | 0.17 | 0.62 | 0.08 | 0.16 | 0.54 |

The trend diagram of effect level ($K$) was used to describe the degree of variation in leached concentration and UCS under different factors (Figure 6). Negative correlations can be found for all three agents (Figure 6a), indicating that the increase of any of the three agents during the combined treatment would result in the reduced leached concentration. Figure 6b showed that the strength of the solidified soil increased with the increasing dosages of cement and CaS5 and decreased with an increasing vermiculite dosage. Furthermore, the UCS values of all samples decreased with increasing Cr(VI) content in contaminated soil, primarily due to the reaction between Ca$^{2+}$ and Cr(VI) help to reduce the cementitious activity [25].

![Figure 6](attachment:figure6.png)

Figure 6. Variation trends with agent dosages. (a) SPLP. (b) UCS.

4. Conclusions

In this study, we propose an integrated reduction/adsorption/solidification treatment technique for Cr(VI)-contaminated soils based on the different adsorption/mobility characteristics of Cr under different states. The combined reduction/adsorption/solidification treatment technology can significantly reduce the amount of reducing agent and solidified agent and has greater economic advantages compared to the conventional solidifica-
tion/stabilization technology. The treatment efficiency was evaluated by SPLP, UCS, and orthogonal tests. The conclusions were summarized as follows:

1. The Ca-V-C combination was optimum for treatment of Cr(VI)-contaminated soil. For the soil with an initial total Cr content of 1200 mg/kg (Cr(VI) content of 823 ± 20 mg/kg), the leached Cr(VI) concentration could be reduced to 0.09 mg/L by the combined treatment with 2 stoichiometric amounts of CaS₅, 15% vermiculite and 20% cement, corresponding to a weight percentage of 75.93% of the treated soil. Meanwhile, the microstructure of the combined reduction/adsorption/solidification remediation of Cr-contaminated soil was analyzed by SEM in agreement with the results of UCS and toxic leaching. From a microscopic point of view, the engineering properties of composite preparations for repairing Cr-contaminated soils were revealed.

2. The leached Cr concentration decreased with the increase of any of the three agents. For soil with a relatively low Cr(VI) content, the influence of CaS₅ dosage on the leached concentration was dominant, whereas for soil with a high Cr(VI) content, the impacts of cement and vermiculite were more significant. The UCS increased with the increasing dosages of cement and CaS₅, whereas it decreased with an increasing vermiculite dosage.

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**Data Availability Statement:** The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

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**References**

1. Zhang, W.; Lin, M. Influence of redox potential on leaching behavior of a solidified chromium contaminated soil. *Sci. Total Environ.* 2020, 733, 139410. [CrossRef] [PubMed]

2. Bakhshi, N.; Sarrafi, A.; Ramezanianpour, A. Immobilization of hexavalent chromium in cement mortar: Leaching properties and microstructures. *Environ. Sci. Pollut. Res.* 2019, 26, 20829–20838. [CrossRef] [PubMed]

3. Lin, X.; Sun, Z.; Zhao, L.; Ma, J.; Li, X.; He, F.; Hou, H. Toxicity of exogenous hexavalent chromium to soil-dwelling springtail Folsomia candida in relation to soil properties and aging time. *Chemosphere* 2019, 224, 734–742. [CrossRef] [PubMed]

4. Zha, F.; Zhu, F.; Kang, B.; Xu, L.; Deng, Y.; Yang, C.; Chu, C. Experimental investigation of cement/soda residue for solidification/stabilization of Cr-contaminated soils. *Adv. Civ. Eng.* 2020, 2020, 8890149. [CrossRef]

5. Park, J.; Kang, W.; Hwang, I. Hexavalent chromium uptake and release in cement pastes. *Environ. Eng. Sci.* 2006, 23, 133–140. [CrossRef]

6. Zha, F.; Liu, J.; Xu, L.; Cui, K. Effect of cyclic drying and wetting on engineering properties of heavy metal contaminated soils solidified/stabilized with fly ash. *J. Cent. South Univ.* 2013, 20, 1947–1952. [CrossRef]

7. Montañés, M.; Sánchez-Tovar, R.; Roux, M. The effectiveness of the stabilization/solidification process on the leachability and toxicity of the tannery sludge chromium. *Environ. Manag.* 2014, 143, 71–79. [CrossRef]
1. Singh, T.; Pant, K. Solidification/stabilization of arsenic containing solid wastes using portland cement, fly ash and polymeric materials. J. Hazard. Mater. 2006, 131, 29–36. [CrossRef]

2. Li, J.; Wang, L.; Cui, J.; Poon, C.; Beiyuan, J.; Tsang, D.; Li, X. Effects of low-alkalinity binders on stabilization/solidification of geogenic As-containing soils: Spectroscopic investigation and leaching tests. Sci. Total Environ. 2018, 631–632, 1486–1494. [CrossRef]

3. Wang, L.; Chen, L.; Tsang, D.; Li, J.; Yeung, T.; Ding, S.; Poon, C. Green remediation of contaminated sediment by stabilization/solidification with industrial by-products and CO2 utilization. Sci. Total Environ. 2018, 631–632, 1321–1327. [CrossRef]

4. Zhang, W.; Zhao, L.; McCabe, B.; Chen, Y.; Morrison, L. Dredged marine sediments stabilized/solidified with cement and GGBS: Factors affecting mechanical behaviour and leachability. Sci. Total Environ. 2020, 733, 138551. [CrossRef] [PubMed]

5. Feng, Y.; Du, Y.; Zhou, A.; Zhang, M.; Li, J.; Zhou, S.; Xia, W. Geoenvironmental properties of industrially contaminated site soil solidified/stabilized with a sustainable by-product-based binder. Sci. Total Environ. 2021, 765, 142778. [CrossRef] [PubMed]

6. Buerge, I.; Hug, S. Influence of mineral surfaces on chromium(VI) reduction by iron(II). Environ. Sci. Technol. 1999, 33, 4285–4291. [CrossRef]

7. Wazne, M.; Jagupilla, S.; Moon, D.; Jagupilla, S.; Christodoulatos, C.; Kim, M. Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR). J. Hazard. Mater. 2007, 143, 620–628. [CrossRef]

8. Sun, Y.; Song, Y.; Qiao, J.; Pan, B.; Zhang, W.; Guan, X. Enhanced chromium(VI) removal by zero-valent iron in the presence of anions and a weak magnetic field: Batch and column tests. Chem. Eng. J. 2018, 354, 445–453. [CrossRef]

9. Li, Y.; Tian, X.; Liang, J.; Chen, X.; Ye, J.; Liu, Y.; Liu, Y.; Wei, Y. Remediation of hexavalent chromium in contaminated soil using amorphous iron pyrite: Effect on leachability, bioaccessibility, phytotoxicity and long-term stability. Environ. Pollut. 2020, 264, 114804. [CrossRef]

10. Bulut, U.; Ozverdi, A.; Erdem, M. Leaching behavior of pollutants in ferrochrome arc furnace dust and its stabilization/solidification using ferrous sulphate and Portland cement. J. Hazard. Mater. 2009, 162, 893–898. [CrossRef]

11. Lu, S.; Wu, L.; Chen, Z.; Li, T.; Shen, C.; Xuan, L.; Xu, L. Remediation of contaminated soil and groundwater using chemical reduction and solidification/stabilization method: A case study. Environ. Sci. Pollut. R. 2021, 28, 12766–12779. [CrossRef]

12. Chen, J.; Wang, Y.; Zhou, S.; Lei, X. Reduction/immobilization processes of hexavalent chromium using metakaolin-based geopolym. J. Environ. Eng. 2017, 5, 373–380. [CrossRef]

13. Badawy, N.; El-Bayaa, A.; Alkhalik, E. Vermiculite as an exchanger for copper(II) and Cr(III) ions, kinetic studies. Ionics 2010, 16, 733–739. [CrossRef]

14. Zhang, W.; Zhao, L.; McCabe, B.; Chen, Y.; Morrison, L. Dredged marine sediments stabilized/solidified with cement and GGBS: Factors affecting mechanical behaviour and leachability. Sci. Total Environ. 2020, 733, 138551. [CrossRef] [PubMed]

15. Feng, Y.; Du, Y.; Zhou, A.; Zhang, M.; Li, J.; Zhou, S.; Xia, W. Geoenvironmental properties of industrially contaminated site soil solidified/stabilized with a sustainable by-product-based binder. Sci. Total Environ. 2021, 765, 142778. [CrossRef] [PubMed]

16. Buerge, I.; Hug, S. Influence of mineral surfaces on chromium(VI) reduction by iron(II). Environ. Sci. Technol. 1999, 33, 4285–4291. [CrossRef]