

Stabilization of hexavalent chromium with pretreatment and high temperature sintering in highly contaminated soil

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HIGHLIGHTS

- Separate reduction and sintering cannot be effective for Cr stabilization.
- Combined treatment of reduction and sintering is effective for Cr stabilization.
- Almost all the Cr in the reduced soil is residual form after sintering at 1000°C.

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ABSTRACT

This study explored the effectiveness and mechanisms of high temperature sintering following pre-reduction with ferric sulfate (FeSO_4), sodium sulfide (Na_2S), or citric acid ($\text{C}_6\text{H}_8\text{O}_7$) in stabilizing hexavalent chromium (Cr(VI)) in highly contaminated soil. The soil samples had an initial total Cr leaching of 1768.83 mg/L, and Cr(VI) leaching of 1745.13 mg/L. When FeSO_4 or $\text{C}_6\text{H}_8\text{O}_7$ reduction was followed by sintering at 1000°C, the Cr leaching was reduced enough to meet the Safety Landfill Standards regarding general industrial solid waste. This combined treatment greatly improved the stabilization efficiency of chromium because the reduction of Cr(VI) into Cr(III) decreased the mobility of chromium and made it more easily encapsulated in minerals during sintering. SEM, XRD, TG-DSC, and speciation analysis indicated that when the sintering temperature reached 1000°C, almost all the chromium in soils that had the pre-reduction treatment was transformed into the residual form. At 1000°C, the soil melted and promoted the mineralization of Cr and the formation of new Cr-containing compounds, which significantly decreased subsequent leaching of chromium from the soil. However, without reduction treatment, chromium continued to leach from the soil even after being sintered at 1000°C, possibly because the soil did not fully fuse and because Cr(VI) does not bind with soil as easily as Cr(III) .

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1 Introduction

Chromium (Cr) is one of the most abundant heavy metal pollutants in soil and, due to its high toxicity and carcinogenicity at particular certain oxidation states, has been listed in the Chinese National Hazardous Waste Directory (Coetzee et al., 2018). According to the national

soil pollution investigation bulletin in 2014, Cr-contaminated soil was generally concentrated around industrial waste sites. The majority of chromium slag was released from the 1960s to the 2000s by early chromate production plants, which lacked sufficient environmental protection regulations. According to the Comprehensive Treatment Plan of Chromium Residue Pollution, more than 6 million tons of chromium slag had been produced by 2007. By the end of 2012, the majority of the chromium slag in China had been safely disposed of, but leaching had polluted the soil during the long-term storage of the chromium residue,

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and this polluted soil remains a significant problem requiring remediation by China's environmental protection agency.

Chromium primarily exists as trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)), and the redox transformations between the two can occur given particular conditions in the natural environment. Cr(VI) can be reduced to Cr(III) by ferrous materials (or Fe), dissolved sulfide, and organic compounds, meanwhile, the Cr(III) may be oxidized by manganese dioxide (MnO_2) and dissolved oxygen, but at a slow speed. The transformation between Cr(III) and Cr(VI) in soil is influenced by pH, Eh, organic matter, and clay minerals (Zhao et al., 2019). The main form of chromium in soil is Cr(III), most of which is immobilized through adsorption by colloidal substances, being enclosed in iron oxide and forming the Fe(III)-Cr(III)-hydroxide compound. This immobilized Cr(III) is more difficult to move than Cr(VI), making it more stable and less of an environmental danger (KožUš et al., 2000). Chromium residue usually leaches high concentrations of Cr(VI) into surrounding substrates like soils, making it necessary to reduce the Cr(VI) to Cr(III) so that the contaminated soil can be safely disposal of.

It is hard to return soils heavily contaminated with Cr(VI) to their original functions, such as agriculture (Ertani et al., 2017). When considering both economics and safety, the best remediation strategy for highly Cr-contaminated soil is stabilization/solidification, followed by disposal in landfills (Kumpiene et al., 2008). Stabilization reduces the mobility and toxicity of chromium, and the solidification process can further reduce its mobility by encapsulating it within materials with low permeabilities (Grasso, 1993; Shen et al., 2018). Cement solidification and thermal treatment are two common solidification/stabilization methods commonly applied to chromium contaminated soil and solid waste (Bakhshi et al., 2019). Previous research has found that thermal treatment of Cr-contaminated solid waste in a reduced state is better than the cement solidification (Wei, 2012), this was because cement solidification increases the total volume of the treated soil, necessitating additional landfill space (Hu et al., 2013). Among the available treatments for highly contaminated soil, landfills have been widely utilized due to their low costs. However, landfills require large areas of land, which are then made unsuitable for other human activities. For this reason, the development of more environmentally friendly treatments would clearly be preferred, and has been the subject of extensive research (Liu et al., 2009). Cr-contaminated soil, if its toxicity is sufficiently reduced, could be a useful resource in applications such as building foundations or as wetland backfill in urban environments (Chrysochoou et al., 2010; Elzinga and Cirimo, 2010; Meegoda and Kamolpornwijit, 2011).

The reduction of Cr(VI) into Cr(III) is the most favorable strategy for the effective treatment of heavily

Cr(VI)-contaminated soil for two reasons: first, Cr(III) in soil is available for adsorption by colloidal substances, and may be enclosed in iron oxide or as a Fe(III)-Cr(III)-hydroxide compound; second, as such, Cr(III) is almost non-toxic (KožUš et al., 2000; Jurate et al., 2008). The chemical reduction of Cr(VI) to Cr(III) for in situ and ex-situ remediation can be achieved using Fe(II), zero-valent iron (ZVI), sulfite, sulfide, pyrite, and other organic compounds (Qian et al., 2008; Kanchinadham et al., 2015; Wei et al., 2016; Eyvazi et al., 2019; Jiang et al., 2019; Pan and Giammar, 2020). However, further stabilization/solidification is still necessary because reduction treatment alone does not sufficiently restrict Cr from leaching into surrounding substrates when the soil Cr(VI) content is exceedingly high.

Herein, this study aimed to establish a treatment process for the stabilization of Cr(VI) in soil by reducing it to Cr(III) with FeSO_4 , Na_2S , or $\text{C}_6\text{H}_8\text{O}_7$, before subjecting it to a high-temperature sintering process. Leaching experiments and sequential extraction experiments were conducted to quantify the effectiveness of Cr stabilization in soil and evaluated according to landfill safety standards. In addition, a series of batch experiments were conducted to investigate the effects of sintering temperature on Cr leaching and the Cr fraction of pre-reduction contaminated soil. The mechanisms of chromium stabilization were further explored using X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis–differential scanning calorimetry (TG-DSC).

2 Materials and methods

2.1 Materials

The Cr-contaminated soil used in this study was collected from a defunct chemical plant in Sichuan province, China ($105^\circ 19' \text{E}$ – $105^\circ 33' \text{E}$, $28^\circ 52' \text{N}$ – $28^\circ 04' \text{N}$) that primarily produced foundry coating and potassium dichromate. The soil sample collection area was in the Sichuan basin, an area with purple soil rich in silica and minerals, according to China's soil classification survey (Soil Science Database, Nanjing Institute of Soil Research, Chinese Academy of Sciences). The plant was built in 1978, and operated until 1998 when it was closed to stop further production of hazardous waste.

Ferrous sulfate (FeSO_4), sodium sulfide (Na_2S), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), and the other reagents used in experiments were all analytical grade. All solutions were prepared in deionized water.

2.2 Characterization and measurements

An XRF (X-ray fluorescence spectrometer, XRF1800,

SHIMADZU, Japan) was used to analyze the chemical elements of the soil samples. X-ray diffraction analysis (XRD, Empyrean, Holland), operating at 40 kV and 100 mA from 10° – 80° 2θ , was conducted to determine soil mineralogy. Scanning electron microscopy (SEM, JEOL JSM-7500F, Japan) was conducted to investigate the morphology of soil samples.

Experiments following the toxicity characteristic leaching procedure (TCLP) were conducted to evaluate the safety of contaminated soils after stabilization (Zhang et al., 2012). The chromium leaching solutions were collected using an acetic acid buffer solution (HJ/T 300-2007, Chinese National Standards). In the TCLP experiments, when the pH of a sample was less than 5.00, the pH of the extraction agent used was 4.93 ± 0.05 , and when the pH of a sample was greater than 5.00, the pH of the extraction agent used was 2.64 ± 0.05 . Leaching Cr(VI) concentrations were measured spectrophotometrically using diphenyl hydrazine as the chromogenic reagent (GB/T7467-1987, Chinese National Standards). Total Cr concentrations leached were measured using a standard test method (ICP-2000, GB/T7466-1987, Chinese National Standards).

The total Cr in soil was detected by ICP-9000 after a total digestion of the soil sample (HJ 491-2009, Chinese National Standards). After the 0.5 g soil sample was completely digested, the full amount was transferred to a 50 mL volumetric flask and 5 mL aqueous ammonium chloride solution was added. After cooling, the sample volume was adjusted to the 50 mL with the addition of deionized water, shaken well, and the total chromium content was measured using the ICP-9000.

The BCR (the European Community Bureau of Reference) sequential extraction method was used to classify and quantify the individual Cr fractions (Kartal et al., 2006). The sequential extraction steps were as follows:

(1) First, acid soluble chromium was extracted. At room temperature, 1 g soil sample was placed in a 100 mL polypropylene centrifuge tube and 40 mL of 0.11 mol/L acetic acid was added. The mixture was kept in suspension for 16 h by shaking at room temperature (200 r/min). Then the supernatant was separated and collected after centrifugation (8000 r/min, 10 min). Then, to clean the residue, 20.00 mL high purity water was added, and the mixture was oscillated for 20 min before being centrifuged, and the supernatant was discarded.

(2) Second, reducible chromium was extracted. Taking the acid soluble chromium residue from the previous step, 40.00 mL of 0.50 mol/L hydroxylamine hydrochloride was added and the mixture was oscillated for 16 h before being centrifuged. The supernatant was collected and cleaned with deionized water as in the first step.

(3) Third, oxidizable chromium was extracted. Using the

residue from the second step, 10 mL H_2O_2 was slowly added with the residue and then covered by a watch-glass, the watch-glass was occasionally shaken, and the residue was allowed to dissolve at room temperature for 1 h. After dissolving, the watch-glass was removed and heated in a water bath to $85^{\circ}C$ for 1 h, allowing the solution to dry. To this, 10 mL H_2O_2 was again added and the process above was repeated. After cooling, 50 mL of 1 mol/L NH_4OAc extract was added, and the oxidizable chromium fraction residue was collected following the same methods as the first step.

(4) Fourth, the residue form was extracted. The residue from the third step was carefully transferred to a 50 mL polytetrafluoroethylene vessel for digestion by nitric acid, hydrofluoric acid, and perchloric acid in triacid. After the digestion liquid was cooled, it was transferred to a 25 mL volumetric bottle, which was shaken and measured after the volume was constant.

After each extraction, the suspensions were centrifuged at 4000 r/min for 20 min. The supernatants of the solutions were then collected to determine the Cr concentrations.

2.3 Batch experiments on the reduction of Cr(VI) in soil

A series of batch experiments were conducted to investigate the optimum dosages of $FeSO_4$, Na_2S , and $C_6H_8O_7$ for Cr(VI) reduction. The prospective reducing agents were added into a 250 mL wide-mouth plastic bottles along with 50 g Cr-contaminated soil, after filtration through a 60 mm mesh, deionized water was added to obtain a final moisture content of 30%. The mixtures were stirred thoroughly, and then kept static. The temperature during the process was maintained at $23 \pm 2^{\circ}C$. After 7 days, a quantity of the soil sample was taken out to test the pH, and after air-drying, measure total Cr leaching, Cr(VI) leaching, and Cr species composition.

All the samples were processed in triplicate alongside a quality control sample.

2.4 Sintering experiments for chromium stabilization

The effect of sintering on chromium stabilization was investigated using a muffle furnace. Samples of unaltered Cr-contaminated soil and the soils reduced by optimal dosages of $FeSO_4$, Na_2S , and $C_6H_8O_7$ were sintered at temperatures of 600, 800, and $1000^{\circ}C$ for 30 min. Before sintering, the soil samples (sieved through a 60 mm mesh, air-dried) were made into a disc shape after mixing with deionized water, and then dehydrated in the oven at $105^{\circ}C$ for 8 h. After air cooling, samples were taken from the muffle furnace for analysis of total Cr, Cr(VI) leaching, Cr species composition, and to explore the stabilization mechanisms via XRD, SEM, and TG-DSC.

3 Results and discussion

3.1 Physical and chemical properties of Cr-contaminated soil

XRF spectrometric analysis revealed relatively high levels of SiO_2 , Al_2O_3 , and Fe_2O_3 in the Cr-contaminated soil, making up 66.17 wt.%, 13.76 wt.% and 5.23 wt.%, respectively (Table 1). XRD analysis of the Cr-contaminated soil, shown in Fig. 1(a), revealed that it was primarily composed of SiO_2 and $\text{Na}(\text{Si}_3\text{Al})\text{O}_8$, which was consistent with the XRF analysis. The soil collection area was located within the surveyed area that had purple soil, and XRF and XRD analysis revealed characteristics consistent with a purple soil rich in SiO_2 , $\text{Na}(\text{Si}_3\text{Al})\text{O}_8$, and other minerals, and also revealed high contents of Al and Fe. SEM analysis demonstrated that the soil surface was moderately dense and compact with a porous structure, shown in Fig. 1(b).

The Cr-contaminated soil had a pH value of 8.04, and an organic matter content of 0.93%. At this pH, the majority of the hexavalent chromium exists in the CrO_4^{2-} form, which is highly mobile and toxic.

Table 1 The main chemical composition of Cr-contaminated soil

Elements	Contents (wt.%)
SiO_2	66.17±0.41
Al_2O_3	13.76±0.19
Fe_2O_3	5.23±0.11
K_2O	3.47±0.09
MgO	2.49±0.08
Na_2O	2.28±0.08
CaO	1.50±0.06
Ti_2O	1.18±0.05

Leaching tests revealed high levels of Cr pollution, with 1768.83 ± 57.24 mg/kg of total Cr and 1745.13 ± 27.93 mg/kg of Cr(VI) leached from the soil in the tests. Cr(VI) made up more than 98% of the total Cr leached. The total Cr content in the soil, measured after total digestion, was 2215.32 ± 41.53 mg/kg. The sequential extraction (BCR) of Cr-contaminated soil was used to determine the composition of chromium species, and it showed that the acid dissolved chromium, reducible form of Cr, oxidizable form of Cr, and residual chromium were present at 1444.3 ± 11.49 mg/kg (64.85%), 277.93 ± 2.75 mg/kg (12.48%), 364.82 ± 23 mg/kg (16.74%), and 129.84 ± 5.83 mg/kg (5.83%), respectively. This result suggested that the chromium in the soil was highly mobile and presented a high environmental risk.

3.2 Reduction reaction of Cr(VI) in soil by FeSO_4 , Na_2S , and $\text{C}_6\text{H}_8\text{O}_7$

As shown in Figs. 2(a)–2(c), significant Cr(VI) reductions were observed. After reacting with FeSO_4 (1.5%), Na_2S (0.4%), and $\text{C}_6\text{H}_8\text{O}_7$ (2.0%), the total Cr leaching decreased from 1768.83 mg/L (without reduction) to 67.79, 410.87, and 1362.79 mg/L, respectively, and Cr(VI) leaching decreased from 1745.13 mg/L (without reduction) to 17.65, 25.50, and 14.29 mg/L. However, the amounts of total Cr and Cr(VI) leached from the soil after reduction by the three agents still exceeded the standards of safety for landfills (< 10 mg/L for leached total Cr and < 1.5 mg/L for leached Cr(VI)).

The environmental risk of chromium in soil is not only determined by the total Cr and Cr(VI) leached, but also by the chromium speciation (Rinehart et al., 1997; Khan et al., 2010). Speciation analysis of the chromium in the contaminated soil (Figs. 2(d)–2(f)) showed that reductions by FeSO_4 and Na_2S transformed the chromium in the soil

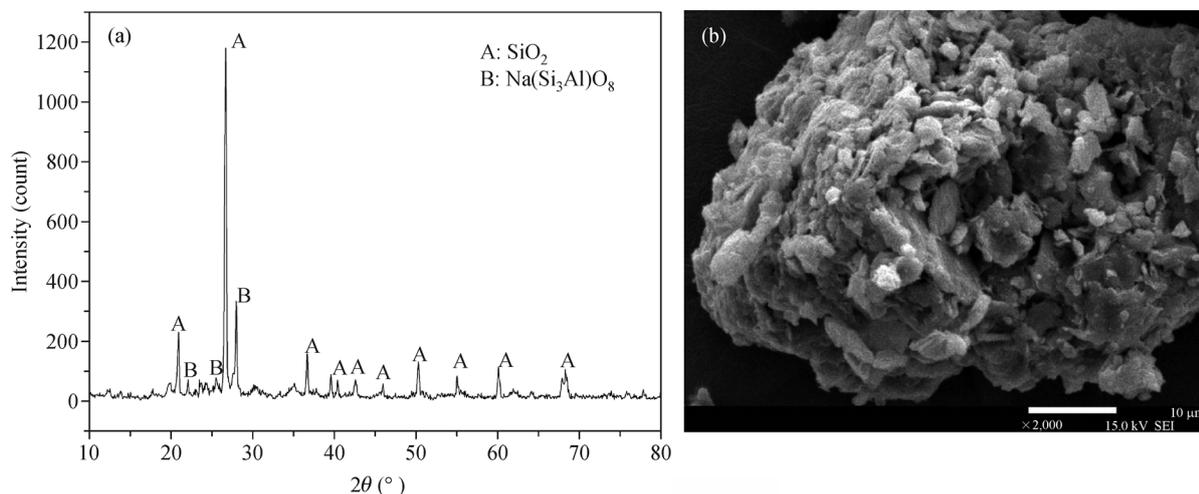


Fig. 1 Characterization of Cr-contaminated soil (a. X-ray diffraction pattern, b. SEM image).

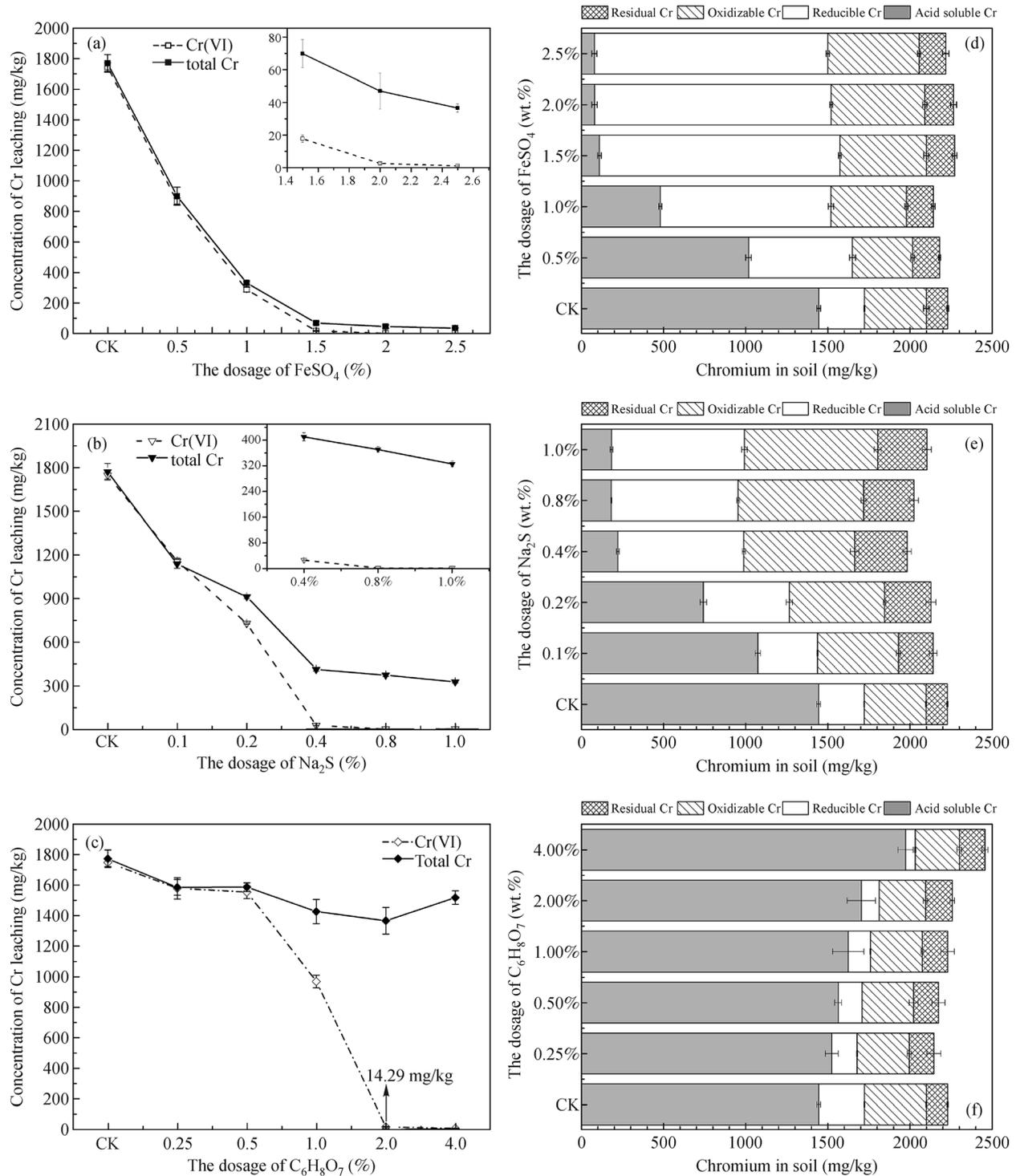
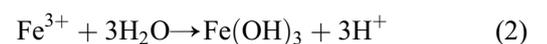
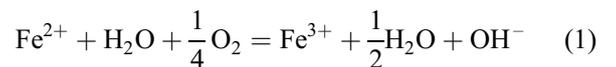


Fig. 2 The effect of adding amount of FeSO₄, Na₂S, C₆H₈O₇ on the concentrations of Cr(VI) and total Cr leaching (a, b, c), and chromium speciation in soil (d, e, f).

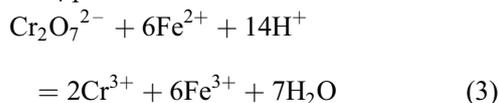
to more stable forms, while the addition of C₆H₈O₇ transformed most of the chromium to an acid-soluble form.

The pH value of the original soil was 8.04, but with the addition of FeSO₄, the pH gradually decreased to 3.70 (shown in Fig. 3(a)). This resulted from the ferrous ions reacting with naturally occurring compounds as follows:



As seen in Eqs. (1) and (2), with the addition of ferrous

ions, the concentration of H^+ will increase in the soil environment, which will acidify the soil and further promote the reaction between Fe^{2+} and $Cr(VI)$. This can be observed in Fig. 2(a), when the Cr -contaminated soil was dosed with 1.5% $FeSO_4$, the $Cr(VI)$ was reduced to $Cr(III)$, except for the $Cr(VI)$ that was preserved in minerals. In the pH range of 2–6, $Cr(VI)$ can remain in the dichromate form ($Cr_2O_7^{2-}$) and $Cr(III)$ will be in the Cr^{3+} form (Rai et al., 1989). The reaction by which $Cr(VI)$ was removed by $FeSO_4$ proceeded as follows:



After reduction by $FeSO_4$, in soil at $pH < 4$, Cr exists mainly as Cr^{3+} , which can be incorporated into iron(III) oxyhydroxides or adsorbed (on the inner sphere) into a Cr -complex, resulting in the transition of Cr species from acid soluble to a reducible form (Fig. 2(d)) (Covelo et al., 2007; Hsu et al., 2015).

In the process of the reduction reaction between $Cr(VI)$ and Na_2S at a dosage of 0.4%, the soil pH increased from 8.05 to 9.85 (Fig. 3(b)). Under this pH, $Cr(III)$ in soil exists

as $Cr(OH)_3$, which increases the content of reducible Cr (Moon et al., 2009), which was consistent with the observed trends in this study (Fig. 2(e)).

Citric acid ($C_6H_8O_7$) contains three carboxyl hydroxyl groups, which make it an optimal reductant. Consistent with the discovery by Grasso (1993), the low pH from the addition of $C_6H_8O_7$ (shown in Fig. 3(c)) not only increased the rate of $Cr(VI)$ reduction by organic acids, but also enhanced the release of $Fe(II)$ from the soil minerals, which further promoted $Cr(VI)$ reduction. The amount of leached $Cr(VI)$ decreased by 99.81%, but the amount of total Cr leached only decreased by 22.96% with a $C_6H_8O_7$ dosage of 2.0%, this meant that most of the $Cr(III)$ still existed in its soluble form after reduction by citric acid. Reduction of $Cr(VI)$ by an organic acid can produce a soluble $Cr(III)$ -organic acid complex, which can improve the mobility of $Cr(III)$ in soil compared to free $Cr(III)$. Free $Cr(III)$ generally binds strongly to soils, while $Cr(III)$ -organic acid complexes interact very little with soil, if at all. The adsorption capacity of $Cr(III)$ -organic acid complexes is decreased with increases of organic matter content in soil (Cao et al., 2011; Taghipour and Jalali, 2016). Previous research has shown that when citric acid is

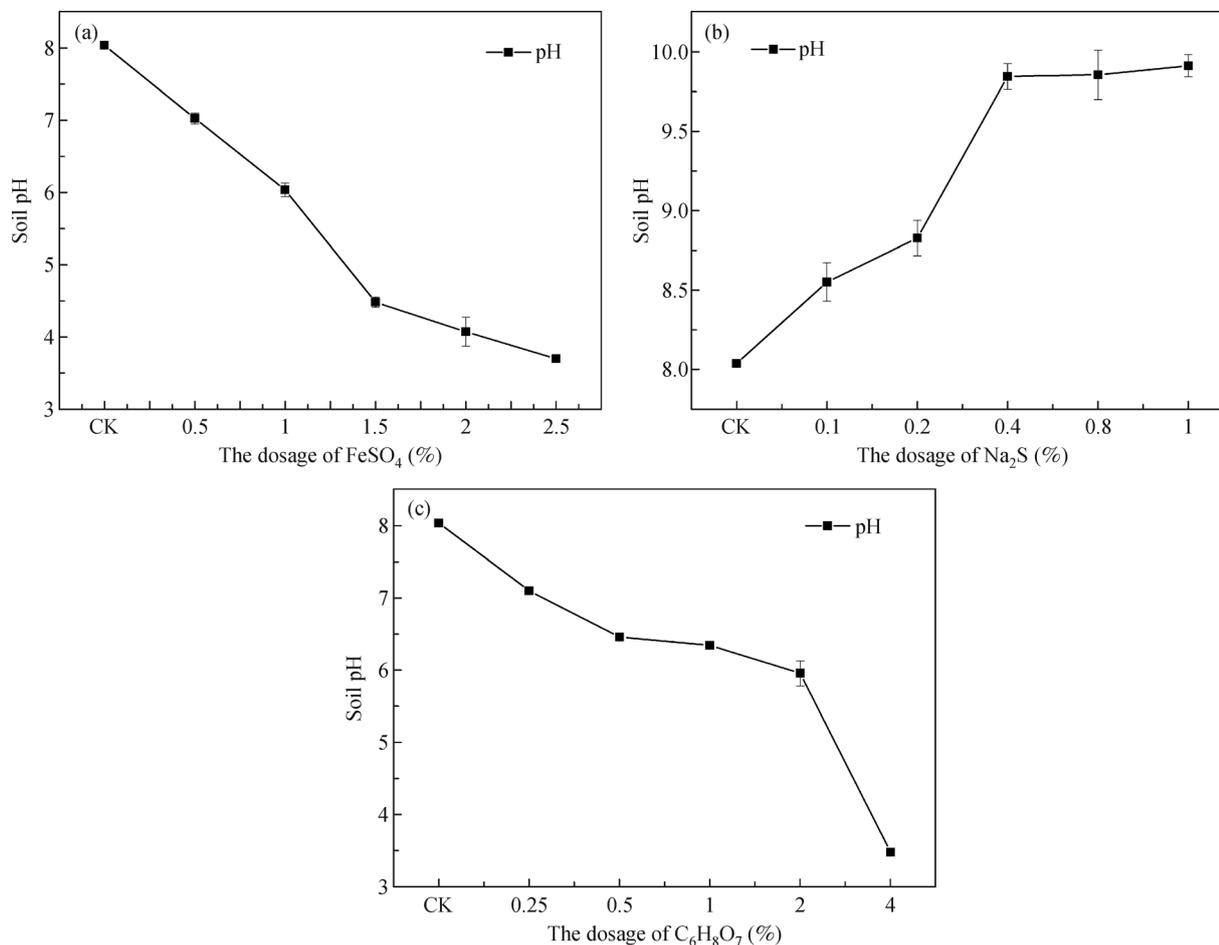


Fig. 3 The effects of adding amount of $FeSO_4$ (a), Na_2S (b), $C_6H_8O_7$ (c) on soil pH.

added to Cr(VI)-containing soil, the Cr combined with Fe-Mn and organic matter can be transferred to the solution, producing complexes with high solubilities (Lan et al., 2008). Indeed, after reduction by $C_6H_8O_7$, we observed that most of the Cr(III) in the soil, which was originally a small proportion of the reducible Cr and oxidizable Cr, had transformed into acid-soluble forms.

In conclusion, the reduction experiments showed that the amounts of total Cr and Cr(VI) leached after reduction with $FeSO_4$, Na_2S , and $C_6H_8O_7$ were still higher than the concentrations considered safe for landfills. All three reducing agents were able to effectively reduce the Cr(VI) in the soil, greatly reducing the leaching of Cr(VI). However, most of the reduced Cr(VI) in the soil still existed in an unstable form, which meant that the leaching of total chromium was still high. Furthermore, although citric acid was able to effectively reduce Cr(VI) in the soil, that Cr mainly existed in a soluble form that increased its mobility in the soil. Therefore, further treatment is needed to enhance the stability of chromium in soil and ensure environmental safety.

3.3 The effect of sintering on chromium stabilization

As can be seen in Fig. 4, sintering temperature had an obvious stabilizing effect on Cr. The leaching of total Cr and of Cr(VI) from soil without reduction treatment decreased with increasing temperature from 600°C to 1000°C. When the sintering temperature reached 1000°C, the leaching of total Cr and of Cr(VI) were reduced from 1768.83 mg/kg and 1745.13 mg/kg to 74.24 mg/L and 54.24 mg/L, respectively (Fig. 4(a)–4(d)). At the same temperatures, the residual Cr increased from 5.83% to 94.80% (Fig. 4(e)), indicating that the high temperature sintering process greatly enhanced the stability of the Cr (VI) in the soil. However, these leaching rates for chromium in the soil without reduction treatment after sintering still exceeded safety standards for landfills.

In the process of sintering, the trends in leached total chromium and hexavalent chromium of soil reduced by $FeSO_4$ ($FeSO_4$ -Rsoil) and soil reduced by Na_2S (Na_2S -Rsoil) were basically the same. At 600°C, there were increases in the Cr(VI) leaching from both $FeSO_4$ -Rsoil and Na_2S -Rsoil, increases that almost equaled the increase of total Cr leaching, as can be seen in Figs. 4(b) and 4(c). This may have been because some Cr(III) was oxidized to Cr(VI) in the weak oxidizing environment created at 600°C. Previously research on municipal solid waste incineration (MSWI) has shown that a portion of the slightly soluble Cr_2O_3 was converted to soluble K_2CrO_4 , which resulted in the increase of Cr leaching during sintering (Wang et al., 2001). The changes in Cr speciation composition in $FeSO_4$ -Rsoil and Na_2S -Rsoil at 600°C (Figs. 4(f) and 4(g)) showed increases in acid-soluble Cr and residual Cr. The increase in acid-soluble Cr may have been caused by the oxidation of Cr(III) to the soluble Cr

(VI), and the increase in residual Cr resulted from the formation of Cr_2O_3 . However, there was a decrease in reducible Cr and oxidizable Cr as organic matter was decomposed and Cr(III) was oxidized. These trends were consistent with the observed changes in Cr leaching.

In contrast, soil reduced by $C_6H_8O_7$ ($C_6H_8O_7$ -Rsoil) did not experience the same reductions in toxicity as $FeSO_4$ -Rsoil and Na_2S -Rsoil after the sintering reaction. Sintering $C_6H_8O_7$ -Rsoil at 600°C oxidized some of the Cr(III) to Cr(VI), increasing the Cr(VI) concentration which increased leaching potential. On the other hand, a lot of organic-Cr(III) was transformed to free Cr(III) after sintering, free Cr(III) strongly binds to soils resulting in a reduction in mobility, decreasing the concentration of total Cr leaching and acid-soluble Cr in $C_6H_8O_7$ -Rsoil at 600°C (Figs. 4(d) and 4(h)).

For all the samples, the best stabilization effects on Cr after sintering were observed when the temperatures reached 1000°C. As shown in Figs. 4(b)–4(d), the total Cr and Cr(VI) leaching from $FeSO_4$ -Rsoil and $C_6H_8O_7$ -Rsoil both met the safety standards for the disposal of general industrial solid wastes, but the Cr(VI) leaching from the Na_2S -Rsoil was still higher than 1.5 mg/kg.

Previous studies have investigated the fate of chromium during the sintering treatment of the fly ash generated during municipal solid waste incineration (Sørensen et al., 2001; Hu et al., 2013). Those studies recommended controlling the sintering atmosphere by enriching it with nitrogen (N_2) and hydrogen (H_2) gas to prevent the oxidation of Cr(III) and thus reduce the Cr concentration in the leachate. In this study, no effort to control or alter the sintering environment was made, which simplified the treatment process and decreased the expense.

3.4 The mechanism of Cr stabilization with sintering after reduction

The phase changes observed in the reduced purple soil during the sintering process were closely related to the mineral composition of the soil. XRD and XRF analysis of the original soil had already shown that the purple soil was rich in SiO_2 and other minerals. When the sintering temperature reached 1000°C, the diffraction peaks of SiO_2 (A) and $Na(Si_3Al)O_8$ (B) were obviously reduced, which indicated that quartz and albite both melted at the high temperature (Fig. 5). By comparing Figs. 1 and 5, we see that the peaks representing Fe_2O_3 and pyroxene minerals had all but disappeared after sintering, but a new peak representing Cr_2O_3 had appeared. This may indicate that Fe_2O_3 and pyroxene minerals transitioned to form new minerals with Cr, and the new minerals did not necessarily have clear peaks in the XRD pattern of the sintered soils.

Figure 6 is a representative graph that shows the thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of the Cr-contaminated soil. With a heating rate of 10 K/min, there were three obvious

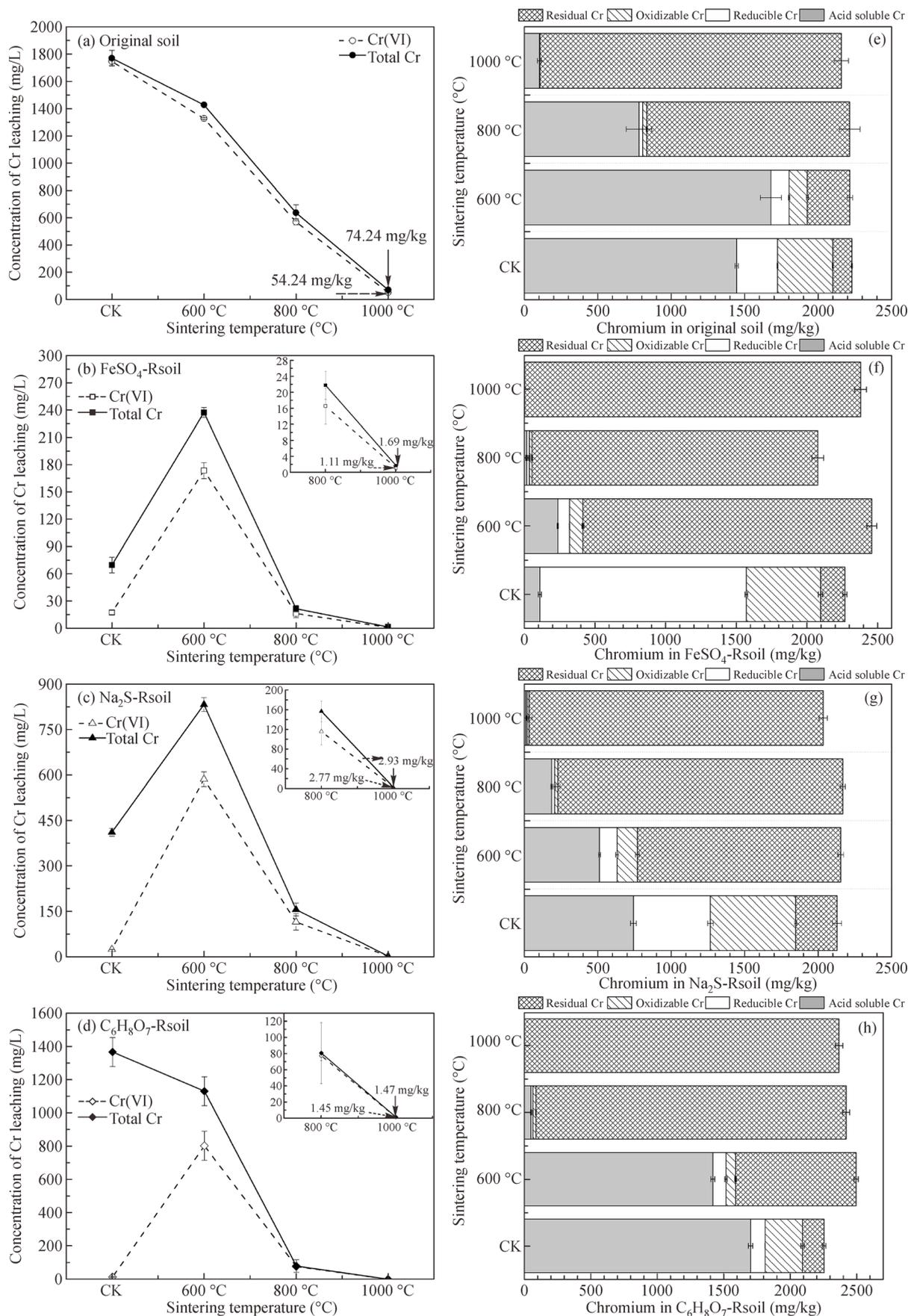


Fig. 4 The effects of sintering temperature on chromium leaching concentration (a, b, c, d) and Cr speciation (e, f, g, h) of original soil, FeSO₄-Rsoil, Na₂S-Rsoil, C₆H₈O₇-Rsoil.

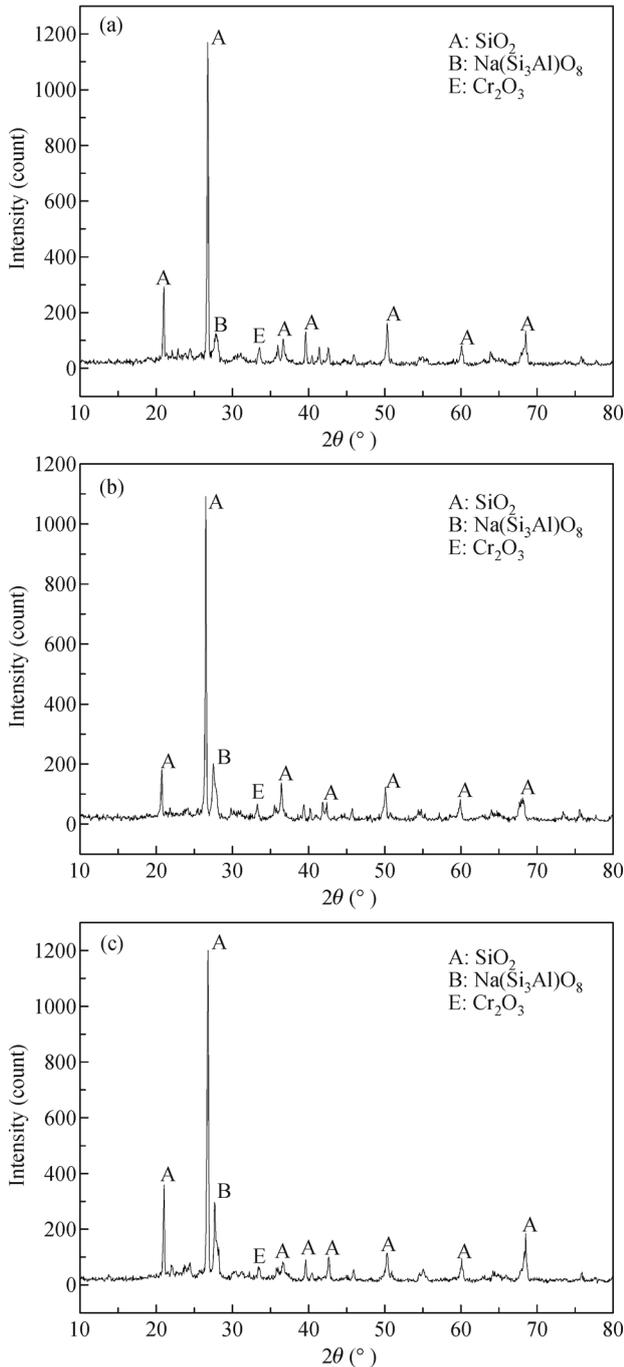


Fig. 5 X-ray diffraction pattern of FeSO_4 -Rsoil (a), Na_2S -Rsoil (b), $\text{C}_6\text{H}_8\text{O}_7$ -Rsoil (c) after sintering at 1000°C .

endothermic DSC peaks, around 66°C , 533°C , and 870°C . Furthermore, at these three temperatures in the TG curve obtained during the thermal processing of Cr-contaminated soil, the weightlessness rate increased markedly (Wei, 2012). Several endothermic peaks accompanied by weight loss were observed during the heating procedure: (1) from ambient temperature to 180°C , the evaporable water was gradually volatilized and the organic matter was decom-

posed; (2) the weight loss between 180°C and 640°C was mainly due to the dehydroxylation of calcium hydroxide and the crystal shape change of quartz; and (3) the weight loss from 640°C to 940°C corresponded to calcium carbonate decomposition. There was a correlation between the changes in the crystal shape of quartz and calcium carbonate decomposition and Cr stabilization. The TG-DSC curve predicted that the crystalline structure of quartz changed when the sintering temperature was greater than 533°C , meaning that a small amount of SiO_2 reacted with Cr and formed residual Cr. There was an obvious endothermic peak around 870°C related to the fusing of quartz and calcium carbonate in soil. Therefore, a large amount of the liquid phase was generated at 1000°C , giving rise to the mineralization of Cr, and formation of more stable chromic substances. This was consistent with the observation that almost all chromium had taken a residue form at 1000°C .

Some researchers have found that during the process of fly ash sintering, loose, small particles tended to gather and form larger particles (Liu et al., 2009). More complex aluminosilicates can be produced by increasing the sintering temperature. Above 800°C , the metals Mg, Fe, and Pb can be mixed into the newly formed aluminosilicates, which is consistent with the results of this study.

Compared with the original soil, in reduced soils, the concentration of Cr(VI) was greatly reduced, and Cr(III) was more commonly bound to the soil. However, at 600°C , some of the Cr(III) was oxidized to Cr(VI), but as the temperature increased, the negative effects of this oxidation were obscured as nearly all Cr had taken the residue form. By comparing the SEM images of the original soil, FeSO_4 -Rsoil, and Na_2S -Rsoil (Figs. 7(a)–7(c), respectively), it can be seen that both FeSO_4 -Rsoil and Na_2S -Rsoil were completely fused at 1000°C , while the original soil had almost no melting. Considering that the melting points of quartz and feldspar minerals are higher than 1000°C , the addition of Fe, Na, and other elements may have reduced their melting points by forming low-temperature eutectic materials. Looking at the reduction effect of the three reductants assessed here, it was clear the reduction by citric acid performed best. At 1000°C , the sample surface of the $\text{C}_6\text{H}_8\text{O}_7$ -Rsoil melted, but the surface was porous, which may have been caused by escaping carbon dioxide during the pyrolysis process (Fig. 7(d)). The addition of citric acid also made the soil melt easier in comparison to the original soil. In contrast to the reduced soils, the concentration of Cr leached from the original soil still did not meet the safety standards after sintering at 1000°C , probably because the soil had not fully wrapped the Cr in minerals and the Cr(VI) content was too high, making it difficult to bind compared with Cr(III).

It can be seen from Figs. 4(e)–4(h) that the residual Cr content of the four soil samples increased continuously between 600°C and 1000°C . Taking the FeSO_4 -Rsoil as an example, SEM analysis showed tiny dispersed particles

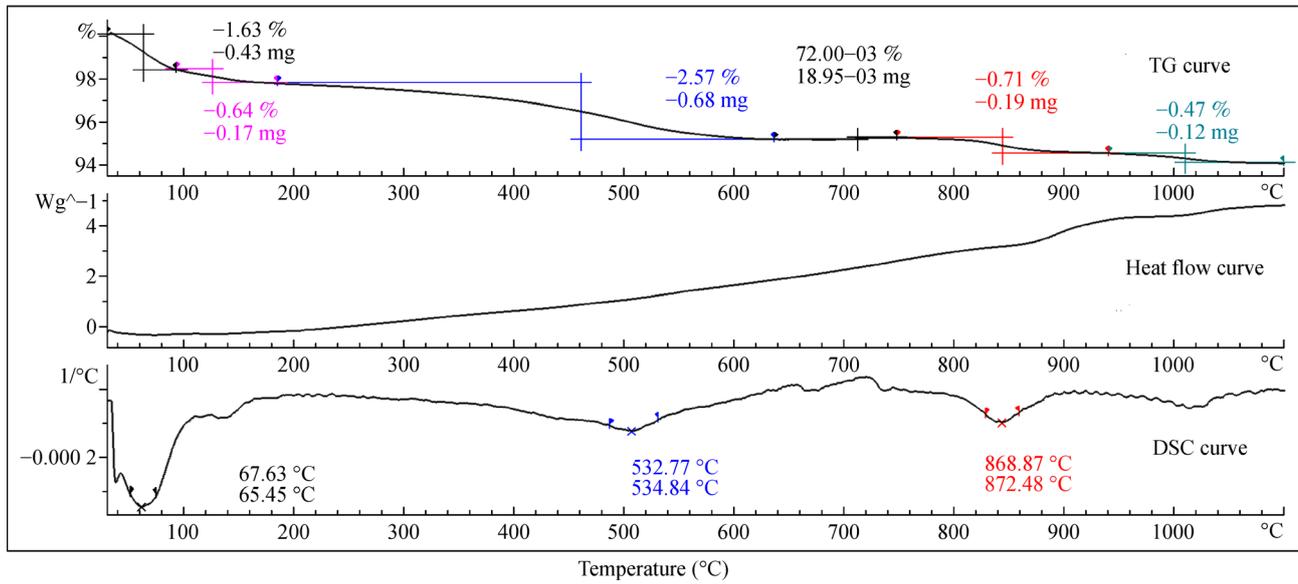


Fig. 6 TG and DSC curves of the Cr-contaminated soil.

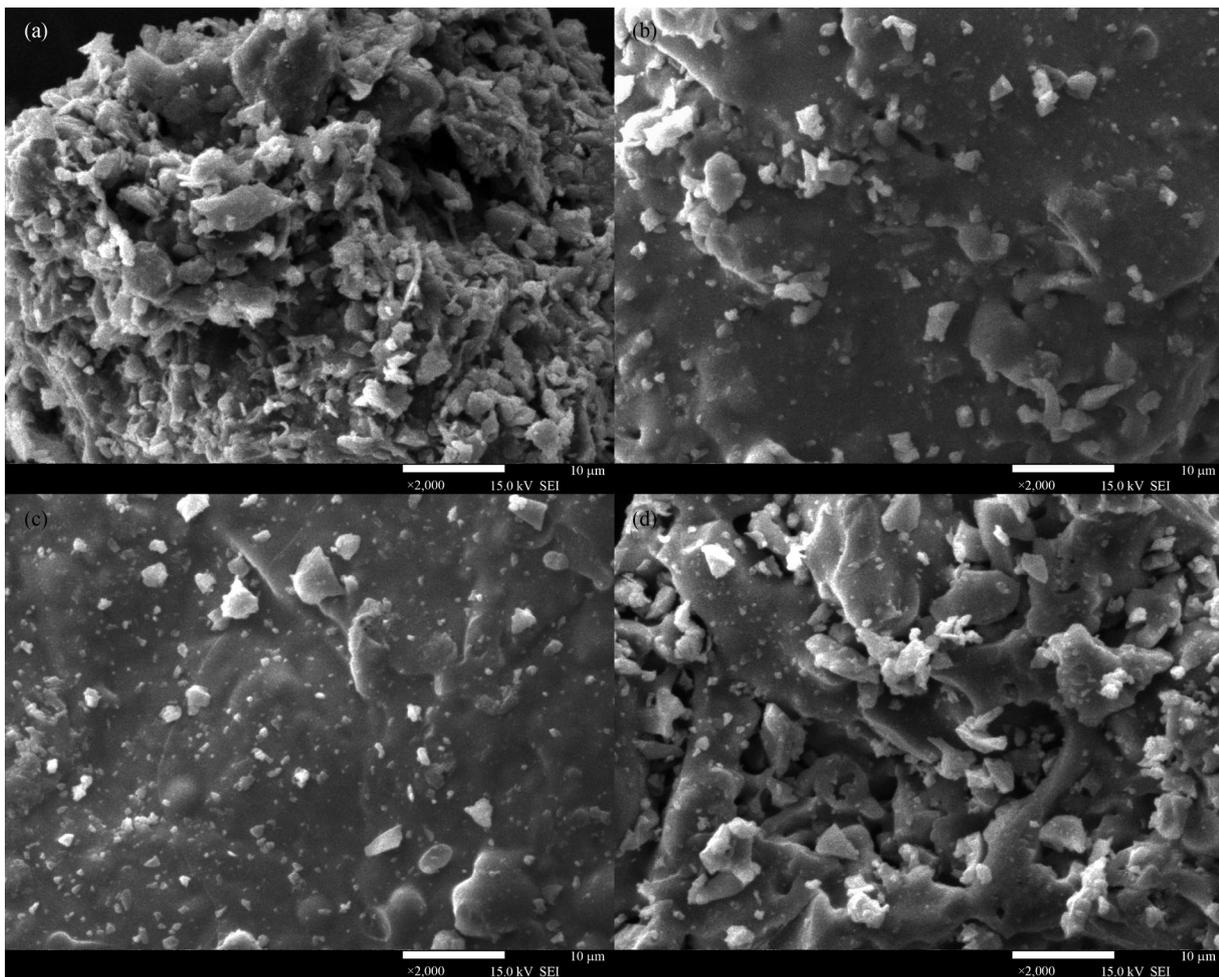


Fig. 7 The SEM image of original soil (a), FeSO_4 -Rsoil (b), Na_2S -Rsoil (c), $\text{C}_6\text{H}_8\text{O}_7$ -Rsoil (d) after sintering at 1000°C .

combining to form larger particles as the sintering temperature increased (Fig. 8). Moreover, when the temperature reached 1000°C, and the soil particles were in a high temperature liquid phase, the cohesive action of

the soil particles was further strengthened, and the diffusion of the liquid by capillary action resulted in the recombination of the separated small particles to form a dense structure.

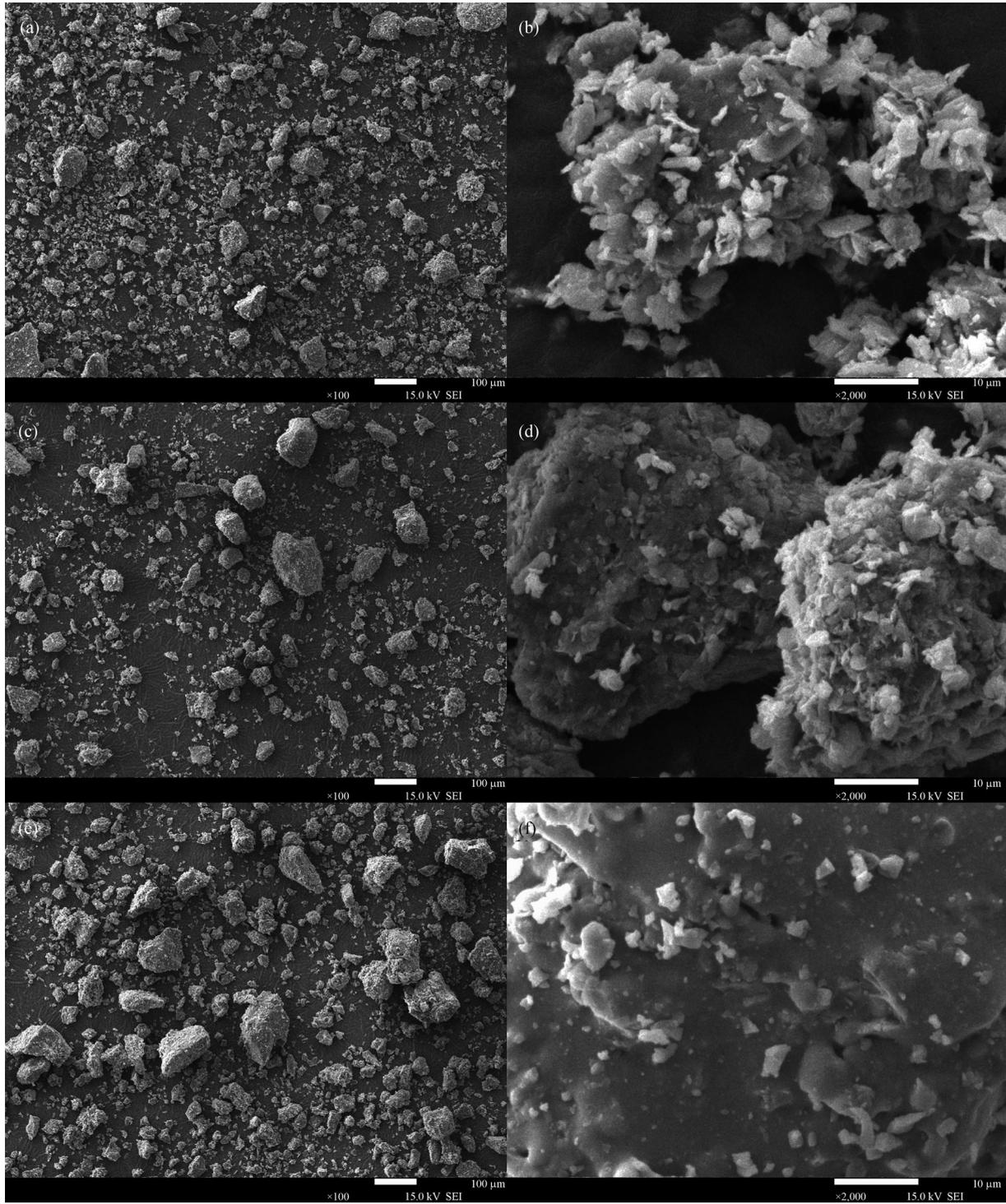


Fig. 8 The SEM image of FeSO_4 -Rsoil (a. $\times 100$ times, 600°C; b. $\times 2000$ times, 600°C; c. $\times 100$ times, 800°C; d. $\times 2000$ times, 800°C; e. $\times 100$ times, 1000°C; f. $\times 2000$ times, 1000°C).

4 Conclusions

This study has shown that neither reduction treatment nor sintering treatment on their own can stabilize the chromium in heavily Cr(VI)-contaminated soil well enough to meet the safety standards for landfills. Even after treatment with FeSO₄, which performed best in reducing Cr(VI) to Cr(III), only a small portion of the reduced chromium existed in a stable residue state in the soil, meaning that leachate still contained chromium at levels that did not meet the safety standards. The original Cr-contaminated soil, without reduction, was not able to fully fuse and encapsulate the Cr in minerals at 1000°C and the Cr(VI) was less likely than Cr(III) to bind to soil. After an adequate reduction reaction with FeSO₄, Na₂S, or C₆H₈O₇, followed by sintering at 1000°C, the concentrations of total Cr and Cr(VI) found in the soil leachates had dramatically decreased and nearly all the Cr was in the residual form. Indeed, both the total Cr and Cr(VI) leaching from the FeSO₄-Rsoil and C₆H₈O₇-Rsoil after sintering at 1000°C met the safety standards for landfills, however, the Cr(VI) leaching from Na₂S-Rsoil was slightly greater than the acceptable limits (1.5 mg/kg). The reduction of Cr(VI) to Cr(III) reduced the mobility of the chromium in the soil, and at the same time, when sintering temperature reached 1000°C, the soil melted and accelerated the combination and retention of Cr in minerals, forming new, stable, Cr-containing compounds. Treatment of heavily Cr-contaminated soil by combining sintering with a pre-reduction could prove a feasible and cost-effective approach to the remediation of Cr-contaminated soil. The treated soil may also be a resource that can be used for various applications due to its low Cr content leaching and excellent structural characteristics. These results were highly favorable and provide useful insight and direction for the future efforts in stabilization/solidification of Cr(VI) contaminated soil.

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References

- Bakhshi N, Sarrafi A, Ramezani-pour A A (2019). Immobilization of hexavalent chromium in cement mortar: leaching properties and microstructures. *Environmental Science and Pollution Research International*, 26(20): 20829–20838
- Cao X, Guo J, Mao J, Lan Y (2011). Adsorption and mobility of Cr(III)-organic acid complexes in soils. *Journal of Hazardous Materials*, 192(3): 1533–1538
- Chrysochoou M, Ferreira D R, Johnston C P (2010). Calcium polysulfide treatment of Cr(VI)-contaminated soil. *Journal of Hazardous Materials*, 179(1): 650–657
- Coetzee J J, Bansal N, Chirwa E M N (2020). Chromium in Environment, Its Toxic Effect from Chromite-Mining and Ferrochrome Industries, and Its Possible Bioremediation. *Exposure and Health*, 12(1): 51–62
- Covelo E F, Vega F A, Andrade M L J (2007). Competitive sorption and desorption of heavy metals by individual soil components. *Journal of Hazardous Materials*, 140(1–2): 308–315
- Elzinga E J, Cirimo A (2010). Application of sequential extractions and X-ray absorption spectroscopy to determine the speciation of chromium in Northern New Jersey marsh soils developed in chromite ore processing residue (COPR). *Journal of Hazardous Materials*, 183(1–3): 145–154
- Ertani A, Mietto A, Borin M, Nardi S (2017). Chromium in Agricultural Soils and Crops: A Review. *Water, Air, and Soil Pollution*, 228(5): 190
- Eyvazi B, Jamshidi-Zanjani A, Darban A K (2019). Immobilization of hexavalent chromium in contaminated soil using nano-magnetic MnFe₂O₄. *Journal of Hazardous Materials*, 365: 813–819
- Grasso D (1993). *Hazardous Waste Site Remediation*. Boca Raton: CRC Press
- Hsu L C, Liu Y T, Tzou Y M (2015). Comparison of the spectroscopic speciation and chemical fractionation of chromium in contaminated paddy soils. *Journal of Hazardous Materials*, 296: 230–238
- Hu H, Luo G, Liu H, Yu Q, Xu M, Hong Y J (2013). Fate of chromium during thermal treatment of municipal solid waste incineration (MSWI) fly ash. *Proceedings of the Combustion Institute*, 34(2): 2795–2801
- Jiang Y, Xi B, Li R, Li M, Xu Z, Yang Y, Gao S (2019). Advances in Fe(III) bioreduction and its application prospect for groundwater remediation: A review. *Frontiers of Environmental Science & Engineering*, 13(6): 89
- Jurate K, Anders L, Christian M J (2008). Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments: A review. *Waste Management*, 28(1): 215–225
- Kanchinadham S B K, Narasimman L M, Pedaballe V, Kalyanaraman C J J (2015). Diffusion and leachability index studies on stabilization of chromium contaminated soil using fly ash. *Journal of Hazardous Materials*, 297: 52–58
- Kartal S, Aydin Z, Tokalioğlu S J J (2006). Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *Journal of Hazardous Materials*, 132(1): 80–89
- Khan A A, Muthukrishnan M, Guha B K J (2010). Sorption and transport modeling of hexavalent chromium on soil media. *Journal of Hazardous Materials*, 174(1–3): 444–454
- Kožuh N, Štupar J, Gorenc B (2000). Reduction and oxidation processes of chromium in soils. *Environmental Science Technology*, 34(1): 112–119
- Kumpiene J, Lagerkvist A, Maurice C (2008). Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments: A review. *Waste Management (New York, N.Y.)*, 28(1): 215–225
- Lan Y, Li C, Mao J, Sun J (2008). Influence of clay minerals on the reduction of Cr⁶⁺ by citric acid. *Chemosphere*, 71(4): 781–787
- Liu Y, Zheng L, Li X, Xie S (2009). SEM/EDS and XRD characterization of raw and washed MSWI fly ash sintered at different temperatures. *Journal of Hazardous Materials*, 62(1): 161–173

- Meegoda J N, Kamolpornwijit W J (2011). Chromium steel from chromite ore processing residue: A valuable construction material from a waste. *Frontiers of Environmental Science & Engineering*, 5 (2): 159–166
- Moon D H, Wazne M, Koutsospyros A, Christodoulatos C, Gevgilili H, Malik M, Kalyon D M (2009). Evaluation of the treatment of chromite ore processing residue by ferrous sulfate and asphalt. *Journal of Hazardous Materials*, 166(1): 27–32
- Pan C, Giammar D (2020). Interplay of transport processes and interfacial chemistry affecting chromium reduction and reoxidation with iron and manganese. *Frontiers of Environmental Science & Engineering*, 14(5): 81
- Qian H, Yanjun W U, Liu Y, Xinhua X U J F O E S (2008). Kinetics of hexavalent chromium reduction by iron metal. *Frontiers of Environmental Science & Engineering in China*, 2(1): 51–56
- Rai D, Eary L E, Zachara J M J (1989). Environmental chemistry of chromium. *Science of the Total Environment*, 86(1–2): 15–23
- Rinehart T L, Schulze D G, Bricka R M, Bajt S, Iii E R B J (1997). Chromium leaching vs. oxidation state for a contaminated solidified/stabilized soil. *Journal of Hazardous Materials*, 52(2/3): 213–221
- Shen Z, Li Z, Alessi D S (2018). Stabilization-based soil remediation should consider long-term challenges. *Frontiers of Environmental Science & Engineering*, 12(2): 16
- Sørensen M A, Mogensen E P B, Lundtorp K, Jensen D L, Christensen T H J (2001). High temperature co-treatment of bottom ash and stabilized fly ashes from waste incineration. *Waste Management (New York, N.Y.)*, 21(6): 555–562
- Taghipour M, Jalali M J C (2016). Influence of organic acids on kinetic release of chromium in soil contaminated with leather factory waste in the presence of some adsorbents. *Chemosphere*, 155: 395–404
- Wang K S, Sun C J, Liu C Y (2001). Effects of the type of sintering atmosphere on the chromium leachability of thermal-treated municipal solid waste incinerator fly ash. *Waste Management*, 21 (1): 85–91
- Wei X, Guo S, Wu B, Li F, Li G (2016). Effects of reducing agent and approaching anodes on chromium removal in electrokinetic soil remediation. *Frontiers of Environmental Science & Engineering*, 10 (2): 253–261
- Wei Y (2012). *Characteristics of Chromium Contaminated Soil and Ceramsite Sintering*. Chongqing: Chongqing University
- Zhang C, Peng P, Song J, Liu C, Peng Y, Lu P J (2012). The BCR method was improved to analyze the chemical morphology of heavy metals in national soil standard materials. *Ecology and Environmental Sciences*, 000(011): 1881–1884
- Zhao Z, An H, Lin J, Feng M, Murugadoss V, Ding T, Liu H, Shao Q, Mai X, Wang N, Gu H, Angaiah S, Guo Z (2019). Progress on the photocatalytic reduction removal of chromium contamination. *Chemical Record (New York, N.Y.)*, 19(5): 873–882