



Thermal stabilization of chromium slag by sewage sludge: Effects of sludge quantity and temperature

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Abstract

To investigate the feasibility of detoxifying chromium slag by sewage sludge, synthetic chromium slag containing 3% of Cr(VI) was mixed with sewage sludge followed by thermal treatment in nitrogen gas for stabilizing chromium. The effects of slag to sludge ratio (0.5, 1 and 2) and temperature (200, 300, 500, 700 and 900°C) on treatment efficiency were investigated. During the mixing process before thermal treatment, 59.8%–99.7% of Cr(VI) was reduced, but Cr could be easily leached from the reduction product. Increasing heating temperature and decreasing slag to sludge ratio strengthened the reduction and stabilization of Cr(VI). When the slag to sludge ratio was 0.5 and thermal treatment temperature was 300°C, the total leached Cr and Cr(VI) declined to 0.55 mg/L and 0.17 mg/L respectively, and 45.5% of Cr in the thermally treated residue existed as residual fraction. A two-stage mechanism was proposed for the reduction and stabilization of Cr.

Key words: chromium slag; sewage sludge; reduction; detoxification; thermal treatment; leached concentration

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Introduction

Chromium exists mainly in two oxidation states, Cr(III) and Cr(VI), in the natural environment. Cr(III) at trace concentration is essential in human nutrition as well as for animals and plants, while Cr(VI) is a strong oxidizing agent and a carcinogen. Chromium slag from chromate or metallic chromium manufacturing plants is one of the most hazardous solid wastes because of its high content of dissolvable Cr(VI). The continuous Cr(VI) leaching from chromium slag could cause serious contamination to its surrounding environment, such as underground water (Shi and Kan, 2009). It was reported that the accumulative amount of chromium slag was more than 6 million tons in China in 2005, among which only 2 million tons were treated in different extends and the other 4 million tons were simply deposited (State Environmental Protection Administration of China, 2005). Thus, there is an urgent requirement for chromium slag treatment with regard to environmental protection and human health concern. One of the most common ways to deal with these wastes is to reduce Cr(VI) to Cr(III), which is less toxic and more easily removed or immobilized (Wang and Li, 2004). Ferrous sulfate is often used for remediation of Cr(VI) contaminated wastewater and soils, but Fe(II) could precipitate under the alkaline environment of chromium slag, thus hindering the reduction process (Geelhoed et al., 2003).

Remediation of chromium slag by calcium polysulfide is also widely studied (Graham et al., 2006; Wazne et al., 2007). The analyses indicated that Cr(VI) reduction was not complete and the leached Cr would raise again about 15 months later (Wazne et al., 2007). Many studies have shown that organic matters could reduce Cr(VI) (Kozjuh et al., 2000; Wang and Li, 2004; Park et al., 2008a), however, they mostly paid attention to the reduction percentage of Cr(VI) and did not investigate the leachability and mobility of Cr(III) transferred from Cr(VI) in the products.

Thermal treatment can not only reduce Cr(VI) but also stabilize Cr(III) in the matrix, such as kaolin (Wei et al., 2002), clay (Cheng et al., 2005), electroplating sludge (Espinosa et al., 2001; Li et al., 2007). Sewage sludge is a kind of solid waste containing significant amount of organic matters, therefore, it can be possibly used to reduce Cr(VI). At the same time, thermal treatment enhances the reduction effect via shortening the reducing time and ensuring the stability of Cr in the treated residue. Therefore, in this study, thermal reduction of synthetic chromium slag in nitrogen gas was conducted using sewage sludge as reductant, in order to (1) determine the possibility of chromium slag detoxification by sewage sludge, (2) discuss the effects of sludge quantity and temperature on thermal reduction of chromium slag, and (3) investigate the stability of Cr in the thermally treated residues and the possible mechanism(s) for thermal stabilization of Cr by sewage sludge.

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1 Materials and methods

The sewage sludge sample was collected from the aeration basin of a municipal wastewater treatment plant in Shanghai, China, and dewatered within 30 min with a centrifuge (5000 r/min, 15 min). The sludge contained 93.2% of water, 3.0% of ash, and 3.8% of organic matters by wet weight (or 55.9% by dry weight). The C and N contents in the sludge by dry weight were 33.5% and 6.2% respectively, measured by an elemental analyzer (Vario EL III, Elementar, Germany). The Cr content in the sludge was 0.049 mg/g by dry weight, analyzed by an inductively coupled plasma spectrometer (ICP) (ICP-optima 2001DV, Perkin-Elmer, USA) after aqua regia/HF digestion. The synthetic chromium slag containing 3% of Cr(VI) was prepared by mixing 11.2 g of K_2CrO_4 with 88.8 g of SiO_2 , which is the main composition of chromium slag (Ding and Ji, 2003; HJ/T301-2007). The sludge and synthetic slag were homogeneously mixed in a mortar with the mass ratio of slag to sludge 0.5, 1, and 2 (denoted as S0.5, S1, and S2, respectively) by dry weight. After mixing, the slurry was dried at 75°C for 3 days (He et al., 2000). Each of the dried mixture was well ground and stored hermetically at 4°C before thermal treatment.

The thermal treatment tests were performed in an electric-heated tubular furnace, in which all the air was displaced with N_2 before the experiments. The dried synthetic chromium slag placed in a porcelain boat was heated in the furnace from room temperature to an established temperature by 10°C/min in N_2 atmosphere (50 mL/min), and kept for 0.5 hr. After that the tube was cooled to the ambient temperature with nitrogen.

The total Cr and Cr(VI) content in the samples and thermally treated residues were analyzed by an ICP after aqua regia/HF digestion and alkaline digestion (US EPA Method 3060A), respectively. The leaching test was conducted according to the Chinese national standard "solid waste extraction procedure for leaching toxicity-sulphuric acid & nitric acid method" (HJ/T299-2007). The concentrations of total Cr and Cr(VI) in the leachate were determined by the ICP and colorimetric method using 1,5-diphenylcarbazide (APHA et al., 1998) respectively. The modified sequential extraction procedure first devised by European Community Bureau of Reference was carried out, which consisted of three extraction steps (exchangeable and weak acid soluble fraction; reducible fraction; oxidizable fraction) and a residual digestion step (residual fraction) (Rauret et al., 1999). The thermogravimetric (TG) analysis was performed in a thermogravimetric analyzer (SDT Q600, TA Instruments-Waters LLC., USA), with the heating rate 10°C/min from room temperature to 900°C, in N_2 atmosphere at 50 mL/min. The mineralogical composition was identified by an X-ray diffractometer (XRD) (D/max 2550, Rigaku Corporation, Japan).

All the reagents used in the experiments were of analytical grade.

2 Results and discussion

2.1 Effect of the slag to sludge ratio on Cr(VI) reduction

Figure 1 shows the content of total Cr and Cr(VI) in the dried samples with different slag to sludge ratios. Before the thermal treatment, 99.7%, 94.7%, and 59.8% of Cr(VI) were reduced for the S0.5, S1, and S2 sample, respectively. It was clear that the higher proportion of sludge was in the sample, the more Cr(VI) was reduced. The organic matter in the sewage sludge could react as a Cr(VI) reductant in the mixture. When Cr(VI) came in contact with organic substances or biomaterial, Cr(VI) could be not only bound on the surface but also reduced to Cr(III) (Elangovan et al., 2008; Gao et al., 2008; Yang and Chen, 2008). Organic reductant could provide electron-donor groups which can reduce Cr(VI) with two reduction mechanisms. In mechanism I (direct reduction), Cr(VI) is directly reduced to Cr(III) by contacting with electron-donor groups. Mechanism II (indirect reduction) consists of three steps: (i) the binding of anionic Cr(VI) to positively charged groups, (ii) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups, and (iii) the release of the reduced-Cr(III) or the complexation of the reduced-Cr(III) with adjacent groups (Park et al., 2008a, 2008b). For the Cr(VI) reduction into Cr(III) in the synthetic chromium slag, electrons as well as protons were required, which was supplied by the electron-donor groups and hydroxyl in the sludge.

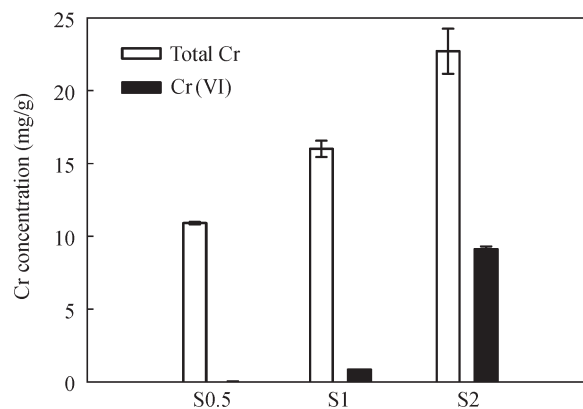


Fig. 1 Total Cr and Cr(VI) content in the dried mixtures of slag and sludge.

2.2 Effect of the slag to sludge ratio on Cr stabilization

All the three mixture samples were identified as hazardous before thermal treatment with regard to leaching toxicity (Table 1), but after treated at 300°C, the leached concentration of total Cr and Cr(VI) decreased by 95.2% and 69.4% for sample S0.5, 96.4% and 96.4% for sample S1, and 97.9% and 99.8% for sample S2. With the increase of sludge proportion in the samples, both the leached ratio and concentration of total Cr decreased significantly,

Table 1 Leached concentration of total Cr and Cr(VI) from the samples before and after treated at 300°C*

Samples	Leached Cr(VI) (mg/L)			Leached total Cr (mg/L)		
	Before thermal treatment	After thermal treatment	Limit value (mg/L)	Before thermal treatment	After thermal treatment	Limit value (mg/L)
S0.5	0.55	0.17	5	45.8 (4.20%)	2.20 (0.14%)	15
S1	99.2	3.56	5	427 (26.7%)	15.3 (0.70%)	15
S2	965	1.95	5	1450 (63.8%)	30.1 (1.07%)	15

* Values in parenthesis are the ratios of total leached Cr to total Cr in the samples, and the leached concentration exceeding the related limited value (GB 5085.3-2007) are expressed as black bold.

whether before or after thermal treatment. The leached ratios of total Cr fell from 26.7% (S1) and 63.8% (S2) to less than 1.10%, and the leached concentrations of Cr(VI) fell from 99.2 mg/L (S1) and 965 mg/L (S2) to 3.56 mg/L and 1.95 mg/L respectively after heating (Table 1). The more sludge in the sample, the less Cr leached from the thermally treated products.

From Fig. 2, Cr in each sample converted from more easily leachable fractions (exchangeable and weak acid soluble fraction, and reducible fraction) to less leachable fractions (oxidizable fraction and residual fraction). The percentages of the more easily leachable fractions decreased from 27.87%, 43.55%, and 70.49%, to 5.27%, 4.14%, and 2.69% for S0.5, S1, S2, respectively. Before thermal treatment, the increase of slag to sludge ratio caused the more Cr of exchangeable and weak acid soluble fraction. It is noteworthy that after thermal treatment, the exchangeable and weak acid soluble Cr was below 0.30% for all the samples, resulting in a significant decline of Cr leachability. Thermal treatment, even at a lower temperature such as 300°C, could obtain a satisfied reduction and stabilization result. Low slag to sludge ratio can make Cr more stable through shifting Cr to oxidizable and residual fractions.

2.3 Effect of heating temperature on Cr(VI) reduction

Figure 3 presents the ratio of Cr(VI) content to total Cr content in sample S1 and its thermally treated residues. The ratio of Cr(VI) to total Cr in the dried S1 sample was as high as 5.3%, but after thermal treatment, the ratio

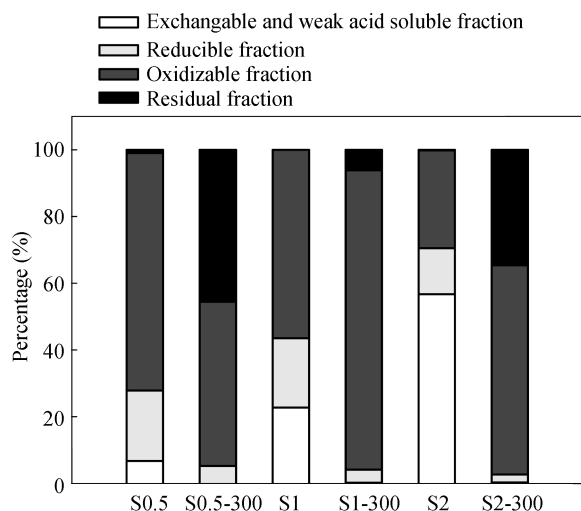


Fig. 2 Speciation of the mixed samples with different slag to sludge ratios and the thermally treated residues at 300°C (e.g., S0.5–300).

decreased significantly, from 1.68% at 200°C to 0.45% at 300°C, while varied a little from 500 to 700°C. Thermal treatment induced the Cr(VI) reduction and the increase of thermal treatment temperature could enhance the reduction level.

2.4 Effect of heating temperature on Cr stabilization

Figure 4 shows the leached concentration of total Cr and Cr(VI) in S1 and its thermally treated residues. It can be concluded that Cr leached from the thermally treated residues was greatly influenced by the heating temperature. Higher temperature resulted in markedly less leached concentration of Cr. Although 94.7% of Cr(VI) was reduced in sample S1 before thermal treatment (Fig. 1), the leached

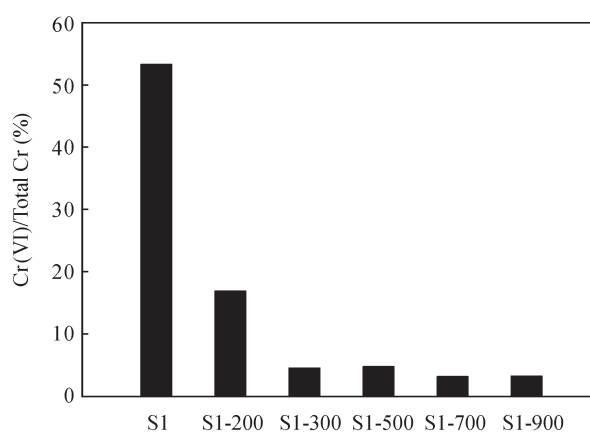


Fig. 3 Cr(VI) to total Cr ratio of the sample S1 and its thermally treated residues. The values 200–900 following S1 indicate the heating temperatures.

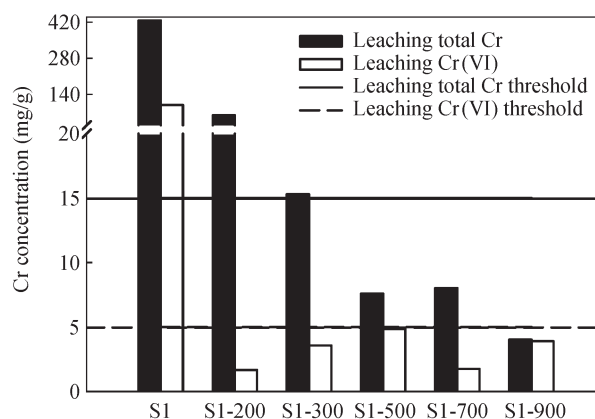


Fig. 4 Leached concentration of total Cr and Cr(VI) from the sample S1 and its thermally treated residues. The values 200–900 following S1 indicate the heating temperatures.

concentration of total Cr and Cr(VI) was still very high, 427 mg/L (26.7% of total Cr in the sample) and 99.2 mg/L, respectively (Table 1). That was far beyond the limit values for hazardous waste (GB 5085.3-2007). Because most Cr(III) converted from Cr(VI) before thermal treatment was simply bound to the negative charged groups in the sludge, such as carboxyl and sulphonate groups (Park et al., 2008b), it could be easily leached out. However, when the sample was heated at 300°C, the leached concentration of total Cr and Cr(VI) significantly decreased to 15.3 mg/L and 3.56 mg/L, which almost reached to the limit values for hazardous waste (GB 5085.3-2007).

As shown in Fig. 5, there was 20.4% of exchangeable and weak acid soluble Cr which can be easily leached from the waste, and no residual fraction of Cr existed in the sample S1. But with the increase of thermal treatment temperature, the Cr of exchangeable and weak acid soluble fraction shifted to oxidizable and residual fractions, especially for the sample S1-900, 98.5% was residual fraction which is immobile. Similar result was obtained by Zorpas et al. (2001), who observed that up to 87.0% of Cr contained in the sewage sludge would transform from other fractions to residual fraction when the sludge was heated in kiln at 900°C. It is clear that the distribution of Cr had close relationship with the leaching results (Fig. 4), the more Cr in the residual fraction, the less Cr leached from the sample. The increase of temperature benefited to the stabilization of Cr in the thermally treated residues.

2.5 Possible stabilization mechanism(s) of Cr by thermal treatment with sludge

Figure 6 shows the XRD patterns for the sample de-S1 (the mixture of SiO₂ and sludge at 1:1 by weight, without spiking of Cr), S1 and its thermally treated residues. The characteristic peaks for quartz could be detected for all the samples, because the matrix of the synthetic chromium slag was SiO₂. Although most Cr existed as residual fraction (Fig. 5) after thermal treatment, especially at 700 and 900°C, no significant peaks for Cr-containing minerals

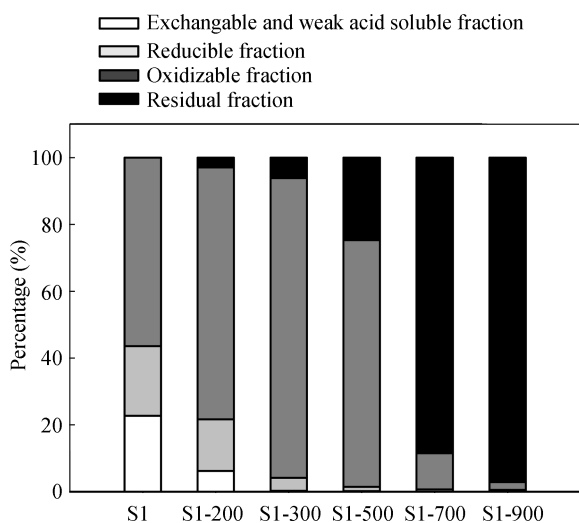


Fig. 5 Speciation of the sample S1 and its thermally treated residues. The values 200–900 following S1 indicate the heating temperatures.

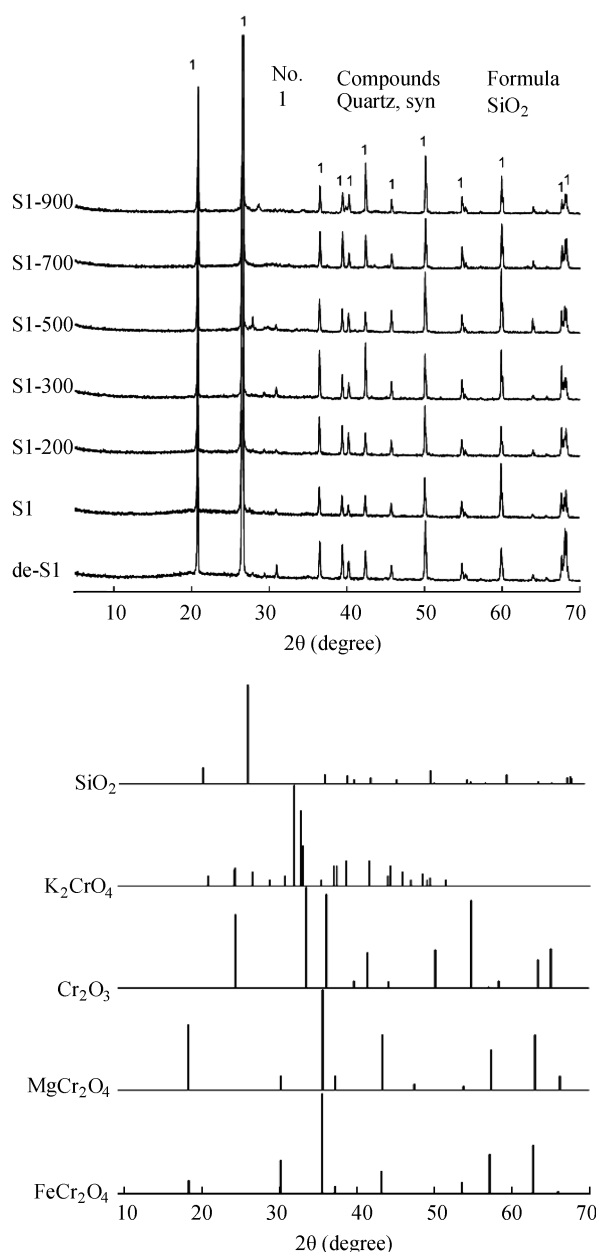


Fig. 6 XRD patterns of the samples.

were detected, indicating that amorphous Cr compounds were formed during the thermal treatment process, since XRD fails to detect amorphous phases.

Figure 7 illustrates the TG curves of the mixed samples. Some differences for the four samples were observed. Firstly, the shoulder at 430°C became more significant with the increase of spiked Cr; secondly, the maximum weight loss of the sample de-S1 occurred at 330°C, with 300°C, 295°C and 290°C for the samples S0.5, S1, S2, respectively. It is clearly that the peak shift to lower temperature. For all the four samples, the first weight loss occurred between room temperature and 180°C. This process was associated to the dehydration of the samples. The second weight loss was observed from 180 to 390°C and it corresponded to decomposition of organics in a wider temperature range, resulting in the different weight loss ratios. Sample S0.5

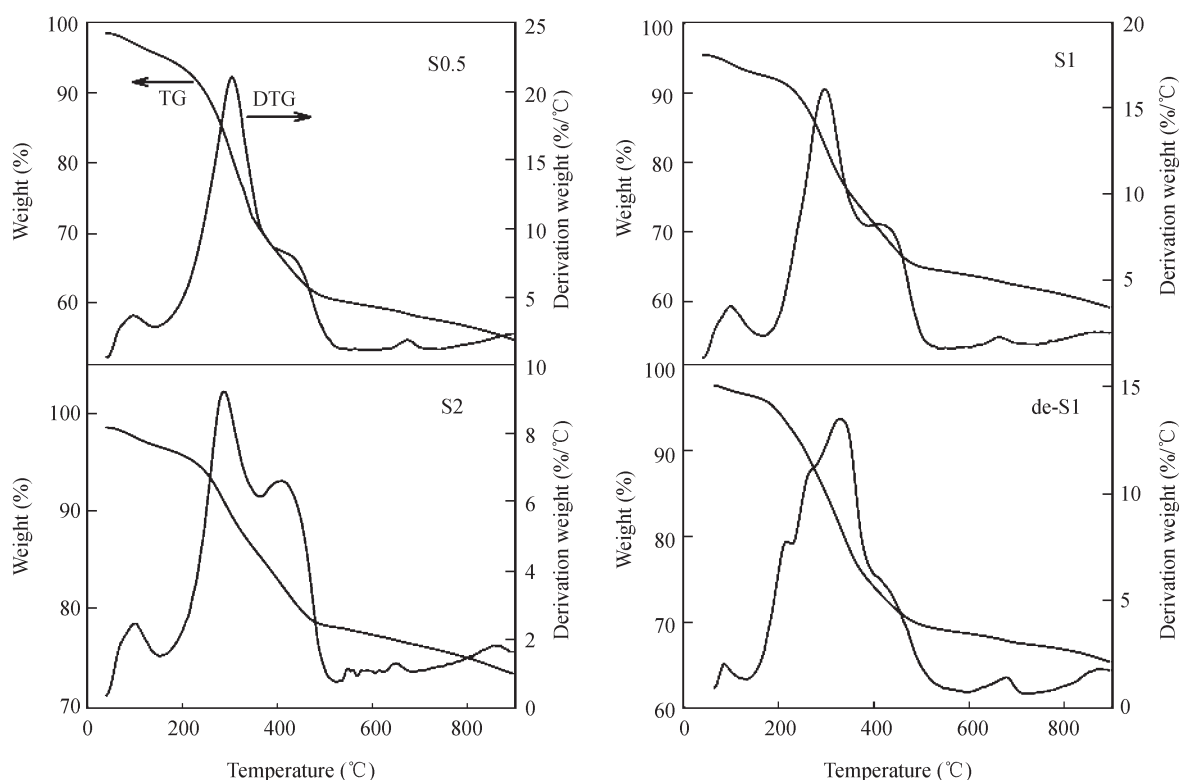


Fig. 7 Thermogravimetric (TG) analysis results of different samples.

lost 26.5% of weight under 180–390°C, while 20.1% for S1 and 10.8% for S2 were obtained.

When S1 was thermally treated at 200°C, the leached concentration of total Cr reached to 59.0 mg/L, but when the temperature came to 300°C, during which the weight loss was 18% and a lot of organics were decomposed, the total leached Cr of the residue of S1 decreased to 15.3 mg/L (Fig. 4) and some Cr transformed to residual fraction (Fig. 2). It could be assumed that when the synthetic slag was mixed with the sludge and dried for 3 days, Cr(VI) can be reduced to Cr(III) which was bound to the negative charged groups in the sludge, then with thermal treatment in nitrogen gas, Cr(III) reduced from Cr(VI) transformed to more stable and immobile compounds, and the residual Cr(VI) continued to be reduced with the decomposition of organic matters. There are also the other two peaks appeared at about 430°C and 670°C, which could correspond to depolymerization of cellulose and decomposition of calcium carbonate or non-biodegradable matters referring to former publications (Font et al., 2001; Thipkhunthod et al., 2006; Shao et al., 2008). At 900°C, the curve of derivability weight inclined to raise again, the sample might be sintered at higher temperature and form spinel structure which will make Cr more stable in the residues (Wei et al., 2006).

3 Conclusions

Cr(VI) in the synthetic chromium slag could be effectively reduced to Cr(III) by sewage sludge. Lower slag to sludge ratio (0.5 by weight) benefited to both the reduction

effect of Cr(VI) and the stability of Cr in the thermally treated residue. Temperature is a key factor for Cr(VI) reduction and stabilization. With the increase of thermal treatment temperature, the leached Cr decreased significantly, especially at temperature above 300°C; and Cr transformed to stable fraction, i.e., oxidizable and residual fractions.

The mechanism for thermal detoxification of Cr by sewage sludge may contain two-stage reaction. First, Cr(VI) was reduced to Cr(III) during the mixing and drying process and Cr(III) was adsorbed on the surface of sludge, and then, Cr(III) transformed to stable compounds with organic matters decomposition at high temperature.

Acknowledgments

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References

- APHA (American Public Health Association), AWWA (American Water Works Association), and WEF (Water Environment Federation), 1998. Standard Methods for the Examination of Water and Wastewater (20th ed.). Washington DC, USA. 366–368.
- Cheng N, Wei Y L, Hsu L H, Lee J F, 2005. XAS study of chromium in thermally cured mixture of clay and Cr-containing plating sludge. *Journal of Electron Spectroscopy and Related Phenomena*, 144–147: 821–823.

- Ding Y, Ji Z, 2003. Production and Application of Chromium Compounds. Chemical Industry Press, Beijing.
- Elangovan R, Philip L, Chandraraj K, 2008. Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies. *Journal of Hazardous Materials*, 152(1): 100–112.
- Espinosa D C R, Tenorio J A S, 2001. Thermal behavior of chromium electroplating sludge. *Waste Management*, 21(4): 405–410.
- Font R, Fullana A, Conesa J A, Llavador F, 2001. Analysis of the pyrolysis and combustion of different sewage sludges by TG. *Journal of Analytical and Applied Pyrolysis*, 58-59(1): 927–941.
- Gao H, Liu Y G, Zeng G M, Xu W H, Li T, Xia W B, 2008. Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste-rice straw. *Journal of Hazardous Materials*, 150(2): 446–452.
- Geelhoed J S, Meeussen J C L, Roe M J, Hillier S, Thomas R P, Farmer J G et al., 2003. Chromium remediation or release? Effect of iron(II) sulfate addition on chromium(VI) leaching from columns of chromite ore processing residue. *Environmental Science & Technology*, 37(14): 3206–3213.
- Graham M C, Farmer J G, Anderson P, Paterson E, Hillier S, Lumsdon D G et al., 2006. Calcium polysulfide remediation of hexavalent chromium contamination from chromite ore processing residue. *Science of the Total Environment*, 364(1-3): 32–44.
- He P J, Gu G W, Shao L M, Zhang Y, 2000. Research on low temperature thermo-chemical conversion to oil process for sewage sludge. *Water Science and Technology*, 42(3-4): 301–308.
- Kozýuh N, Sýtupar J, Gorenc B, 2000. Reduction and oxidation processes of chromium in soils. *Environmental Science & Technology*, 34(1): 112–119.
- Li C T, Lee W J, Huang K L, Fu S F, Lai Y C, 2007. Vitrification of chromium electroplating sludge. *Environmental Science & Technology*, 41(8): 2950–2956.
- Park D, Ahn C K, Kim Y M, Yunb Y S, Parka J M, 2008a. Enhanced abiotic reduction of Cr(VI) in a soil slurry system by natural biomaterial addition. *Journal of Hazardous Materials*, 160(2-3): 422–427.
- Park D, Lim S R, Yun Y S, Park J M, 2008b. Development of a new Cr(VI)-biosorbent from agricultural biowaste. *Bioresource Technology*, 99(18): 8810–8818.
- Rauret G, Lopez-Sanchez J F, Sahuquillo A, Rubio R, Davidson C, Ure A et al., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring*, 1(1): 57–61.
- Shao J G, Yan R, Chen H P, Wang B W, Lee D H, Liang D T, 2008. Pyrolysis characteristics and kinetics of sewage sludge by thermogravimetry fourier transform infrared analysis. *Energy Fuels*, 222(1): 38–45.
- Shi H S, Kan L L, 2009. Study on the properties of chromium residue-cement matrices (CRCM) and the influences of superplasticizers on chromium(VI)-immobilising capability of cement matrices. *Journal of Hazardous Materials*, 162(2-3): 913–919.
- State Environmental Protection Administration of China and National Development Reform Commission, 2005. The Scheme for Pollution Treatment of the Chromium Residue. Beijing, China.
- Thipkhunthod P, Meeyoo V, Rangsunvigit P, Kitiyanan B, Siemanond K, Rirksomboon T, 2006. Pyrolytic characteristics of sewage sludge. *Chemosphere*, 64(6): 955–962.
- Wang T G, Li Z H, 2004. High-temperature reduction of chromium(VI) in solid alkali. *Journal of Hazardous Materials*, B112(1-2): 63–69.
- Wazne M, Jagupilla S C, Moon D H, Jagupilla S C, Christodoulatos C, Kim M G, 2007. Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR). *Journal of Hazardous Materials*, 143(3): 620–628.
- Wei Y L, Chiu S Y, Tsai H N, Yang Y W, Lee J F, 2002. Thermal stabilization of chromium(VI) in kaolin. *Environmental Science & Technology*, 36(21): 4633–4641.
- Wei Y L, Hsieh H F, 2006. Effect of humic substance on thermal treatment of chromium(VI)-containing latosol soil. *Journal of the Air & Waste Management Association*, 56(3): 350–355.
- Yang L, Chen J P, 2008. Biosorption of hexavalent chromium onto raw and chemically modified *Sargassum* sp. *Bioresource Technology*, 99(2): 297–307.
- Zorpas A A, Vlyssides A G, Zorpas G A, Karlis P K, Arapoglou D, 2001. Impact of thermal treatment on metal in sewage sludge from the Psittalias wastewater treatment plant, Athens, Greece. *Journal of Hazardous Materials*, B82(3): 291–298.