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The role of temperature on Cr(VI) formation and reduction during heating of chromium-containing sludge in the presence of CaO

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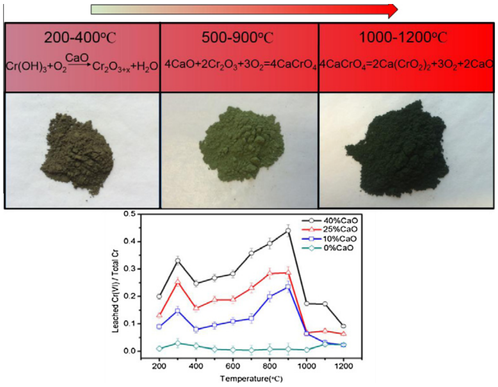
HIGHLIGHTS

- CaO results in Cr(III) being oxidized to Cr_2O_{3+x} annealed at 200–400 °C.
- Most of Cr_2O_{3+x} would be reduced into Cr_2O_3 over 400 °C.
- Part of $CaCrO_4$ is reduced to $Ca(CrO_2)_2$ at 1000–1200 °C.
- $Ca(CrO_2)_2$ is oxidized reversibly to $CaCrO_4$ annealed at 1200 °C over 1 h.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the temperature dependence of Cr(VI) formation and reduction in the presence of CaO was examined during the thermal treatment of sludge that contains chromium. thermogravimetry–differential scanning calorimetry and X-ray diffractometry were used to characterize the thermal behavior and phase transformation, respectively. Na_2CO_3 leaching procedure was employed to determine the amount of Cr(VI). The result showed that CaO promoted Cr(III) oxidation, however, its influence is very dependent on heating temperature, with the extent of the effect varying with temperature. From 200–400 °C, the presence of CaO facilitated formation of intermediate product Cr_2O_{3+x} containing Cr(VI) during dehydration of chromium hydrate, while Cr_2O_{3+x} would decompose as temperature over 400 °C, accompanied by part of Cr(VI) being reduced to Cr(III). From 500 to 900 °C, Cr(III) reacted with CaO to form a leachable $CaCrO_4$ product. This product was stable and a prolonged heating time did not reduce the amount of Cr(VI) significantly. At 1000–1200 °C, part of $CaCrO_4$ was reduced to $Ca(CrO_2)_2$ in 1 h. While extended heating time above 1 h resulted in the $Ca(CrO_2)_2$ being oxidized reversibly to $CaCrO_4$ at 1200 °C. Since $CaCrO_4$ is thermodynamically less stable over 1000 °C, MgO could induce $CaCrO_4$ to be reduced into $MgCr_2O_4$ at around 900 °C, lower than that for the reduction from $CaCrO_4$ into $Ca(CrO_2)_2$. It suggested that adding MgO might be a potential approach for inhibiting Cr(VI) formation during heating sludge containing chromium.

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1. Introduction

As a hazardous metal that is subject to potential bioaccumulation, chromium (Cr) can enter the body, including the digestive tract, respiratory tract, and the skin (Agree and Toffoli, 2009; Huggins et al., 1999). Its hexavalent state, Cr(VI), is highly water-soluble and toxic, and can accumulate in the body and damage the liver, kidney, and other organs. Conversely, its trivalent state, Cr(III), is an essential trace micronutrient for carbohydrate metabolism in low doses (Chen et al., 2012; Jiao et al., 2011; Stam et al., 2011; Wang et al., 2001). Chromium is present in wastewater generated from printed circuit board manufacturing, electroplating, leather tanning, paint production, and printing operations (Erdem and Özverdi, 2008; Sreeram and Ramasami, 2003). Common Cr(VI)- and Cr(III)-containing wastewater treatment strategies include Cr(VI) reduction to low toxicity Cr(III), and its subsequent removal by precipitation and coagulation (Esmaeili and Vazirinejad, 2005). However, these treatments result in the production of large amounts of chromium-containing bearing sludge which requires additional treatment (Swarnalatha et al., 2006, 2008).

The main disposal method for hazardous metals sludge is to stabilize or solidify the solid waste using cement before landfill (Barbir et al., 2012; Swarnalatha et al., 2006, 2008; Wells et al., 2014). However, large amounts of cementitious material are required to produce solidified waste that is strong enough to prevent the leaching of hazardous metals from broken products, and this increases the volume of cement required for landfill (Filibeli et al., 2000; Swarnalatha et al., 2006, 2008). Limited landfill sites and increased amounts of waste sludge have hastened efforts to adopt more effective technologies.

Incineration as an attractive alternative method is becoming more popular throughout the world (Tang et al., 2008). It is expect that its role will increase in future because it is a convenient means to achieve a large reduction of sludge volumes by approximately 90%, recovery of flue gas energy, destruction toxic constituents thermally, and sterilization bacteria. However, since some toxic metals (Pb, Cd, and Cr) can be volatilized at high temperature (Hu et al., 2013a, 2013b; Tahiri et al., 2007), incineration requires extensive off-gas treatment with one of the materials captured from the off-gas being fly ash (Kirk et al., 2002; Tang et al., 2008). CaO was usually injected to remove hazardous metals emissions and remove sulfur dioxide from incineration flue gas (Chen et al., 1998; Hu et al., 2013a, 2013b). On the other hand, as lime was usually used to neutralize acidic chromium-containing wastewater, there is a large amount of calcium hydrate in chromium-containing bearing sludge, which would dehydrate and form CaO during thermal treatment. Therefore, Ca-compounds occupy an important part of the fly ash and bottom ash. Unfortunately, it has been reported that elevated Cr(VI) leaching from residues results after high-temperature processing in the presence of CaO (Chen et al., 2012, 2013; Hu et al., 2013a,b; Pillay et al., 2003). Verbinnen found that toxic Cr(VI) leached in amounts that are higher than the regulatory limit when they used chromium-containing sludge to prepare ceramic materials (Verbinnen et al., 2013). Hu et al. reported that the leaching concentration of Cr(VI) from municipal solid waste fly ash increased sharply after thermal processing and confirmed that CaO plays a significant role in the formation of Cr(VI)(Hu et al., 2013a, 2013b). Chen compared CaO performance with that of two other basic metal oxides (Fe_2O_3 and MgO), and found that it was more likely to react with Cr(III) to form the corresponding chromates (Chen et al., 2013). Although some researchers have mentioned that CaO facilitates Cr(III) oxidation, the knowledge on the reaction between chromium hydrate and CaO is insufficient. A detailed description of Cr(VI) formation and reduction during heating of chromium-contains sludge in the presence of CaO is therefore required.

The objective of this study was to explain the effect of heating temperature on Cr(VI) formation and reduction in the presence of CaO during heating to provide new knowledge on the formation mechanism of Cr(VI) and its variation with increase in temperature. The thermal behavior and phase transformation of the mixtures (simulated sludge and CaO) during heating were characterized by thermogravimetry–differential scanning calorimetry (TG–DSC) and X-ray diffractometry (XRD), respectively. X-ray photoelectron spectroscopy (XPS) and Fourier transform-infrared spectroscopy (FT-IR) were used to determine the Cr-bearing species. Subsequent Cr(VI) leaching was used to display quantitatively the amount of Cr(VI) formed with temperature by using the Na_2CO_3 leaching procedure. Kinetics experiments were used to study the extent of various reactions, and improve the understanding of increases and decreases in Cr(VI) formation with heating time.

2. Materials and methods

2.1. Material preparation

To simplify the complex composition of chromium-containing sludge, a simulated chromium-containing sludge was prepared by adjusting the pH of a $CrCl_3$ solution to between 7 and 8 using ammonia while stirring. The precipitate, which includes chromium hydroxide and soluble salts, is regarded as simulated chromium-containing sludge. Desalination process was carried out by washing the solid with deionized water before sintering for six times. The mixture was centrifuged at 500 rpm for 10 min and filtered (Hsieh et al., 2013; Wei et al., 2014). The desalinated simulated sludge was dried at 105 °C for 24 h and ground to pass through a 74 μm sieve. The sludge chemical composition as determined by X-ray fluorescence (9800XP + ARL) is given in Table S1. To eliminate $CaCO_3$ disturbances to the thermal behavior of the mixture, the received CaO was fired at 950 °C for 6 h to decompose the $CaCO_3$ residue completely (Lee and Nassaralla, 2006). The obtained simulated chromium-containing sludge was mixed well with CaO in the corresponding mass fractions (0%, 10%, 25%, and 40%), and homogenized by mortar grinding. All chemical reagents (Sinopharm Chemical Reagent, China) were of analytical reagent grade.

The contact area between powders was increased by pelletizing into a small 13-mm-diameter cylindrical disk at 10 MPa for the sintering process. During sintering, solids were placed in a muffle furnace in which the temperature was increased at 5 °C/min to the target temperature, and maintained at this temperature for 1 h. For the kinetic experiments, samples were placed in a preheated oven at the desired temperature. After sintering, samples were removed and air-quenched in the sample holder in air at room temperature, and then ground to a powder by mortar for XRD analysis and leaching.

2.2. Analysis

The thermal behavior and solids mass loss was characterized by TG–DSC (STA 449C Netzsch) in air. The increasing rate of heating was 20 deg/min. The phase transformation under different sintering conditions was monitored by XRD (X'TRA, ARL) using a Cu X-ray tube operated at 40 kV and 40 mA, 2θ scans were collected from 10° to 80°, and the step size was 0.02°. Qualitative analysis was accomplished by matching XRD patterns with the powder diffraction files database of the International Center for

Diffraction Data. Infrared spectroscopy experiments were performed using an FT-IR spectrometer (NICOLET NEXUS870 Thermo) from 400 to 4000 cm^{-1}. Powder samples were mixed with KBr to form pellets. XPS spectra were recorded using an ESCA spectrometer (PHI 5000 VersaProbe, Ulvac-PHI, Physical Electronics), equipped with a non-monochromatic Al Kα X-ray source.

Since Cr(VI) salts are soluble over a broad pH range but Cr(III) compounds have limited solubility under neutral and alkaline conditions (Verbinnen et al., 2013), their difference in solubility of Cr(III) and Cr(VI) could be used to extract Cr(VI) from fired samples. In this study, the ratio of Cr(VI) leached to total chromium can provide an indication of the amount of Cr(III) that has been oxidized to Cr(VI) after heating. Cr(VI) leaching from the sintered products was carried out using 0.1 M Na_2CO_3 according to previous studies (Panichev et al., 2005, 2008). Approximately 0.25 g of sintered samples was weighed in a 100 mL glass beaker to which 25 mL of 0.1 M Na_2CO_3 solution was added. After boiling on a hot plate for 15 min, the slurry was filtered using 0.2 μm syringe filters and diluted to 100 mL with deionized water. The chromium concentration was determined by flame atomic absorption spectrophotometry (M6 Thermo).

2.3. Thermodynamic calculation

Thermodynamic calculations were performed with relevant thermodynamic data, which were obtained from previous relevant references (David, 2005; Lee and Nassaralla, 2001, 2006; Liang and Che, 1993; Qi et al., 2011).

3. Results and discussion

3.1. Effect of heating temperature on Cr(VI) leaching behavior

The ratio of Cr(III) that is oxidized with increasing temperature is shown in Fig. 1, about 3% of Cr(III) was oxidized and leached from the sludge without CaO when the heating temperature was less than 1100 °C. However, large amounts of Cr(VI) were leached when the simulated sludge contained CaO, and the amount of Cr(VI) leached was proportional to the CaO content. The Cr(VI) leaching curve could be divided into three zones: (1) 200–400 °C, where Cr(VI) leaching increased with temperature to 300 °C and then decreased at 400 °C; (2) 500–900 °C, where Cr(VI) leaching increased with increasing temperature; and (3) 1000–1200 °C, where Cr(VI) leaching decreased.

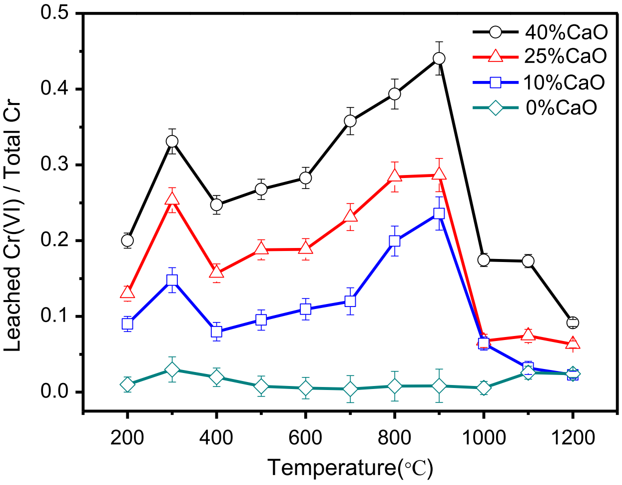

Fig. 1. Cr(VI) leaching behavior of heated pure simulated sludge and mixtures of simulated sludge and CaO.

In general, chromium hydroxide dehydrates to form chromium oxide (Cr_2O_3) after thermal treatment (Wang et al., 2001), and small amounts of Cr(VI) was detected when there was no CaO. However, a large amount of Cr(VI) was leached from heated mixtures of simulated sludge and CaO at 200 °C and 300 °C. To confirm this observation, we also investigated the leaching behavior of Cr(VI) from heated oxide mixtures (Cr_2O_3 + CaO) with the same proportion of CaO (Fig. S1). A similar varying tendency of Cr(VI) was observed above 400 °C. However, small amounts of Cr(VI) were leached below 400 °C, which suggests that this phenomenon was only detected in the mixture of simulated sludge and CaO.

3.2. Temperature dependence of pathways governing Cr(VI) formation and reduction

The reaction that occurred during the heating of Cr(III) and CaO was monitored by thermal analysis. Peaks and troughs on the DSC curves represent endothermic/exothermic changes during heating. Fig. 2(a) shows that the mass increase of simulated sludge without CaO in air is not detected. Peaks (1) and (4) are assigned to the evaporation of absorbed water and the transfer of substance from the amorphous to the crystalline state (Kopylovich et al., 2003; Li et al., 2012; Papassiopi et al., 2014; Yao et al., 2003). However, all mixtures of simulated sludge and CaO exhibited distinct thermal behavior compared with pure simulated sludge, which implies that some reaction occurred that involved CaO. The thermal behavior can be explained over three temperature ranges (200–400 °C and 500–900, and 1000–1200 °C) as proposed in Section 3.1.

3.2.1. Temperature range: 200–400 °C

XRD was used to analyze the phase transformation that occurred in a mixture of simulated sludge and CaO during heating, with the results presented in Fig. 3. Only very small amounts of $CaCrO_4$ were detected at 200 °C and 300 °C. This observation does not agree with those that show that large amounts of Cr(VI) are formed in this temperature range (Fig. 1) and implies that some Cr(VI) must be derived from amorphous Cr(VI) species. Fig. 2 shows that one broad exothermic trough at 250–350 °C (peak (2)) and one endothermic peak at approximately 400 °C (peak (3)) were associated with a small mass increase and loss, respectively. However, these two peaks were not detected from the thermal behavior of oxide mixtures (Cr_2O_3 + CaO) (Fig. S2). It appears that these two peaks correspond to reactions that occurred only in mixtures of simulated sludge and CaO, and are related to the formation of amorphous Cr(VI) species that were only found only in mixtures of simulated sludge and CaO.

XPS analysis was used to investigate the variation in valence of chromium and the chromium speciation (see Fig. 4). Cr(VI) formed from 200 °C and its content increased with temperature to 300 °C. However, part of the Cr(VI) was converted reversibly to Cr(III) at 400 °C. This observation is consistent with the leaching experiment results (Fig. 1), and implies that a reaction with Cr(VI) reduction may occur at around 400 °C. It is reasonable that there are two reactions, which correspond to Cr(III) oxidation and Cr(VI) reduction, respectively. In addition, Cr(IV) is detected at 200 °C and 300 °C, but disappears over 400 °C, possibly indicating the formation of mixed-valence chromium oxide, which would decompose as temperature increases to 400 °C (Harrison et al., 1998; Si et al., 2011). Simulated sludge samples heated at various temperatures were analyzed by FT-IR technique and the result is shown in Fig. 5(a). The band at 1620 cm^{-1} is due to the bending modes of non-dissociated water molecules connected with chromium ions, and with the rise of annealing temperature, this band decreases gradually in intensity until disappears at 300 °C (El-Sheikh and Rabah, 2013, 2014; Yao et al., 2003). Temperature higher than 300 °C in air, Cr(III)–O (538.6 cm^{-1}) would convert into two weak

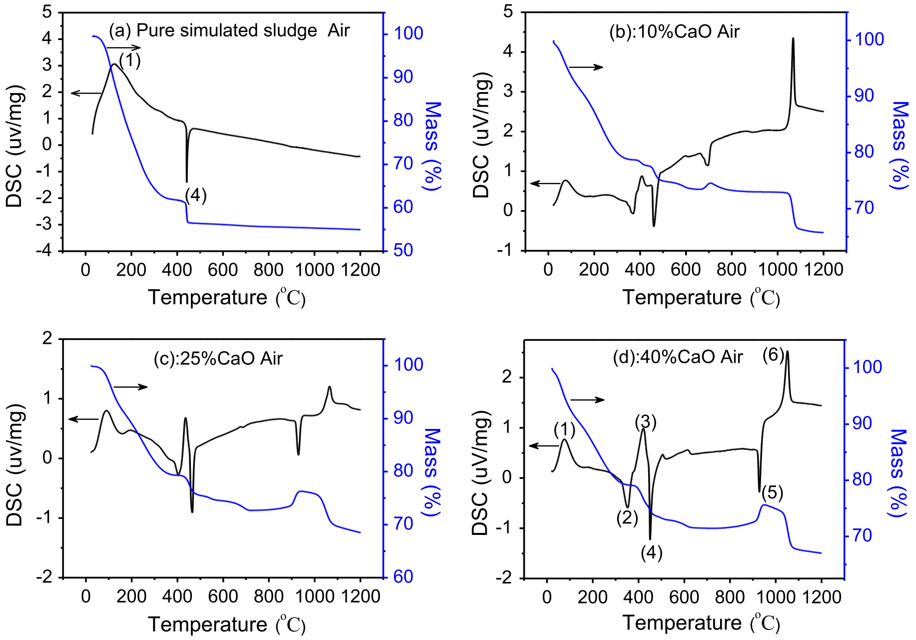

Fig. 2. TG and DSC curves of pure simulated sludge and simulated sludge containing CaO in air.

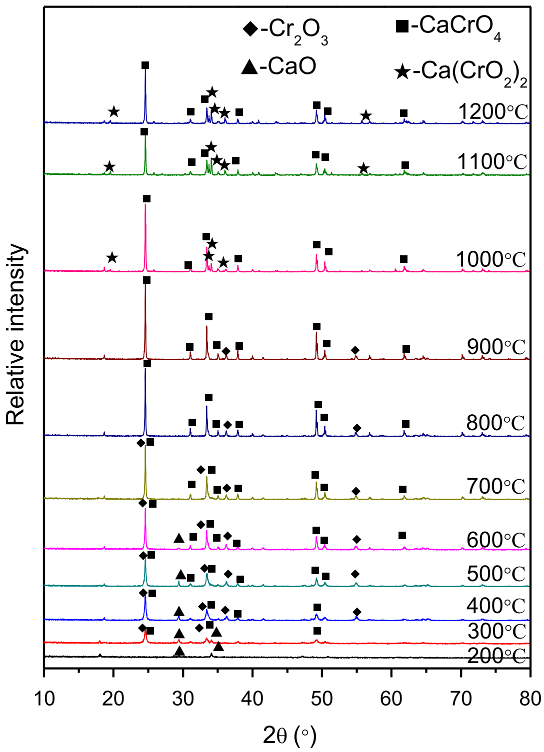

Fig. 3. XRD patterns for products from simulated sludge containing CaO (40%) at 200–1200 °C.

bands at 410 cm^{-1} and 440 cm^{-1} and two strong bands at 566.9 cm^{-1} and 620.7 cm^{-1} (Barbu et al., 2012, 2013; El-Sheikh and Rabah, 2013; Li et al., 2012), these bands are characteristic of Cr_2O_3. The band of 940 cm^{-1} is assigned to the vibration of Cr(VI)–O from CrO_3 (Pei and Zhang, 2013; Yao et al., 2003). As the temperature up to 500 °C, the band located at 940 cm^{-1} disappears, which indicates that CrO_3 would be reduced with the increasing temperature. When CaO added into sludge system, an intensive band at 938 cm^{-1} assigned to Cr(VI)–O formed from 200 °C and its amount increases with temperature rising to 300 °C (Fig. 5(b)) (Stefanescu et al., 2011; Ştefănescu et al., 2013; Barvinschi et al., 2013). This observation was consistent with the result of leaching experiment (Fig. 1). Similarly, with the temperature higher than 400 °C, the intensity of band at 938 cm^{-1} assigned to Cr(VI)–O would weaken, suggesting that part of CrO_3 would be reduced (El-Sheikh and Rabah, 2014). Additionally, a new absorption band at around 1100 cm^{-1} appears in residues heated above 400 °C, which can be attributed to vibrations of the Cr(VI)–O bond from the corresponding metal chromates $CaCrO_4$ (El-Sheikh and

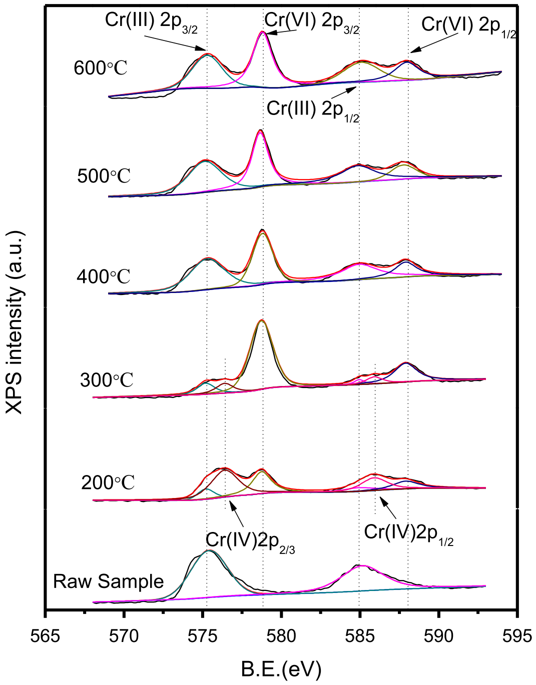

Fig. 4. XPS spectra of heated simulated sludge containing CaO (40%) at 200–600 °C.

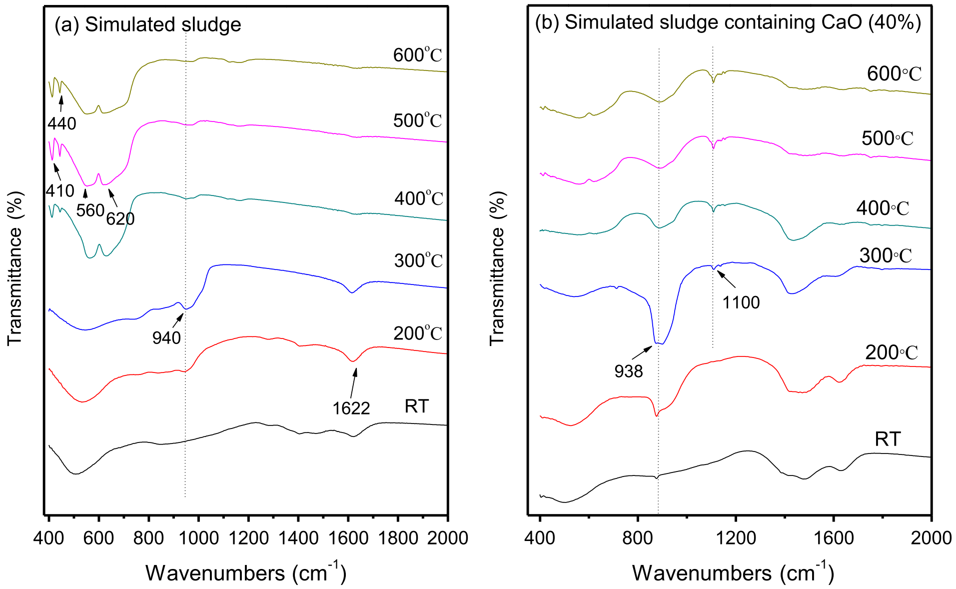

Fig. 5. FT-IR spectra of products from (a): simulated sludge and (b): simulated sludge containing CaO (40%) heated at 200–600 °C.

Rabah, 2014). FT-IR analysis illuminates that during when chromium hydrate transformation to Cr_2O_3, a small quantity of Cr(III) is oxidized to CrO_3, which would be reduce to Cr_2O_3 above 400 °C, however, the presence of CaO significantly results in the formation of more CrO_3.

Every surface chromium ion in the hydrated oxide is surrounded by six ligands, with three lattice oxygen ions and three surface groupings (either OH^- or coordinated water) (Yao et al., 2003). Generally, H_2O is eliminated that was coordinated or has been formed by condensation of two hydroxyls (El-Sheikh and Rabah, 2013). In such a dehydration process Cr^{3+} c.u.s ions (coordinative unsaturated surface ions) would be produced with one coordinative vacancy only. At higher temperatures, more water is removed from the surface and chromium ions with more vacancies could be formed. The removal of water from the surface would lead to surface rearrangement, and the destruction of Cr–O groups with octahedrally coordinated chromium generates higher adsorbing species, such as tetrahedrally coordinated chromium ions. At higher temperatures, ligands of octahedral species are removed from the central ion and migrate to form complex oxide islands with high valency (Yao et al., 2003).

Oxygen surface mobility could favor this transformation (Zecchina et al., 1971a, 1971b). The alkaline earth metals have been proven capable of catalytically acting as oxygen-shuttling agent for bulk oxygen activation. And the redox reaction swing between a metallic cation and its metal radical may serve as transmitter for the electron transfer (Chen et al., 2013). In this case, CaO can assist the electron transfer from Cr(III) to O_2 through the conversion of Ca^{2+} into $Ca^{(0)}$. The resulting atomic $Ca^{(0)}$ is swung back to Ca^{2+} by the molecular oxygen to form more vacancies (Chen et al., 2013). Thus, in this study, with increasing heating temperature, the remove water from chromium ions surface would lead to forming chromium ions with more vacancies, and surface ligands rearrangement would result in forming complex oxide islands with high valency. The presence of CaO as transmitter for the electron transfer helps complex oxide islands with high valency absorb oxygen to form more high valency intermediate species Cr_2O_{3+x}, including CrO_3, Cr_3O_8 and Cr_5O_{12} (CrO_3 has been detected in this study, but Cr_3O_8 and Cr_5O_{12} not), which results in an unusual leaching quantity of Cr(VI) at 200 °C and 300 °C (Fig. 1) (Jóźwiak et al., 2004; Labus et al., 2003; Wei et al., 2014; Yao et al., 2003). However, these intermediate products Cr_2O_{3+x} would decompose and transform into Cr(III) with the temperature rising to approximate 400 °C (Jóźwiak et al., 2004; Labus et al., 2003; Wei et al., 2014). Accordingly, Peaks (2) and (3) could be attributed to the formation and decomposition of Cr_2O_{3+x}, respectively (El-Sheikh and Rabah, 2014). Since analytical reagent Cr_2O_3 would not dehydrate, chromium ions surface ligands would not rearrange to form complex oxide islands with high valency. Thus, these special intermediate products are not detected in mixture of Cr_2O_3 and CaO, but only found in mixtures of chromium hydroxide and CaO. The formation of these intermediate products suggests that there is a risk involved in Cr(VI) leaching, when sludge containing chromium and calcium is heated at low temperature (200–300 °C). Though the common incineration temperature is far higher than 200–300 °C, this temperature range is precisely the common operating temperature for thermal drying technology, which is usually used to remove moisture from sludge before incineration (Liu et al., 2014; Zhu et al., 2012). This study indicated that during thermal drying process Cr(III) oxidation is promoted remarkably because of the disturbance of CaO.

3.2.2. Temperature range: 500–900 and 1000–1200 °C

Figs. 2 and S2 present similar thermal behavior at 500–1200 °C. Two peaks (peaks (5) and (6)) are accompanied by a mass increase and decrease, respectively. XRD analysis also shows a similar phase transformation in this temperature range (Figs. 3 and S3). $CaCrO_4$ is the only hexavalent chromium species and its characteristic peak intensity increases with increase in temperature to 900 °C. Combined with thermal analysis results, it is thought that the exothermic peak at 600–900 °C corresponds with a mass increase that could be assigned to Cr_2O_3 oxidation, this oxidation reaction has been examined broadly in previous studies (Hu et al., 2013a, 2013b; Tahiri et al., 2007; Verbinnen et al., 2013) and can be expressed as:

$$4CaO + 2Cr_2O_3 + 3O_2 = 4CaCrO_4 \quad (1)$$

Cr_2O_3 oxidation reaction imply that the common average fuel temperature in solid waste incinerators would be between 800 °C and 1000 °C as this is the range in which Cr(III) is most easily oxidized. Large amounts of Cr(III) may be converted to Cr(VI) and increase the risk of Cr(VI) release.

When the heating temperature is higher than 1000 °C, Fig. 2 showed a new trivalent chromium species $Ca(CrO_2)_2$ was detected. Since a combination of CaO with Cr_2O_3 to form $Ca(CrO_2)_2$ would not lead to mass loss, $Ca(CrO_2)_2$ may result from part of $CaCrO_4$ decomposition with a release of oxygen instead of by CaO combining with Cr_2O_3 directly. This assumption corresponds with an endothermic peak in the TG curve and mass loss in the DSC curve (Fig. S2). The proposed reactions can be expressed by Eq. (2):

$$4CaCrO_4 = 2Ca(CrO_2)_2 + 3O_2 + 2CaO \tag{2}$$

$Ca(CrO_2)_2$ formation decreases the content of Cr(VI) in residuals, which is responsible for decreasing Cr(VI) leaching over 1000 °C (Fig. 1). Moreover, it means that elevating temperature could inhibit Cr(III) from being oxidized. The reduction from $CaCrO_4$ to $Ca(CrO_2)_2$ implies $CaCrO_4$ is thermodynamically less stable at higher 1000 °C, and there is always the trend of $CaCrO_4$ transforming into more stable phase. $MgCr_2O_4$ with a high melting point (2330 °C) performs inert at high temperature, which indicates it is thermodynamically more stable than $CaCrO_4$ (Klyucharov and Eger, 1963). Moreover, in prior studies (Barbu et al., 2012, 2013; El-Sheikh and Rabah, 2013), the decomposition of $MgCrO_4$ into $MgCr_2O_4$ occurs at about 500 °C, far lower than that for the transformation of $CaCrO_4$ into $Ca(CrO_2)_2$, which further suggests the presence of Mg might induce Cr(VI) to be reduced into Cr(III) at lower temperature. Thus, adding MgO might be an approach for decreasing Cr(III) oxidation below 1200 °C, and the possible reaction can be expressed by Eq. (3):

$$4CaCrO_4 + 2MgO = 2MgCr_2O_4 + 4CaO + 3O_2 \tag{3}$$

The reaction Gibbs free energies for Eqs. (2) and (3) were calculated as a function of temperature and are presented in Fig. S4. The Gibbs free energy for Eq. (3) is more negative than that for Eq. (2) at temperature higher 1000 °C, indicating that the reaction (3) may be dominant over reaction (2) at same temperature (at temperature range of 900–1200 °C). Fig. S5 presents XRD patterns of residue for the mixture of $CaCrO_4$ and MgO heated at 600–1200 °C, XRD result confirmed thermodynamic calculation well. MgO results in part of $CaCrO_4$ being reduced into $MgCr_2O_4$ from about 900 °C, lower than that for the transformation from $CaCrO_4$ to $Ca(CrO_2)_2$ (1000 °C). Which indicates the reaction (3) is easier to trigger than reaction (3) at same temperature. Combining results of thermodynamic calculation and XRD analysis, it is reasonable that thermal reduction of Cr(VI) into $MgCr_2O_4$ phase with addition of Mg containing materials (e.g. dolomite) might be the potential remedial approach for inhibiting Cr(VI) formation during heating solid waste containing chromium.

3.3. *Effect of heating time on Cr(VI) leaching behavior*

To better understand the Cr(III) oxidation behavior at varied temperatures, the effect of heating time on Cr(VI) leaching was carried out at 200, 400, 700, 900, and 1200 °C.

The effect of heating time on Cr(VI) leaching at 200 °C is presented in Fig. 6(a). Cr(VI) leaching increased with heating time from 0.25 h to 4 h and then declined over the same period, with a maximum being reached in approximately 4 h. The XPS results agree with the leaching experiment results (Fig. S6). As mentioned above, Cr(VI) leaching at 200 °C and 300 °C occurs mainly because of Cr_2O_{3+x} formation. A requirement of 4 h to reach a maximum indicates that this reaction may not be rapid at 200 °C. The residual color variations reflect the amount of change in the Cr(VI) residue; mixtures of simulated sludge and CaO were green after being sintered for 0.25 h, and became brown with an increase in residence time to 0.5 h (Fig. S7). This change reveals that Cr_2O_{3+x} began to form from 0.5 h. Upon heating to 6 h, mixtures reversed to a dull green. This concurs with the XPS analysis, which shows that the Cr(III) increases with a decrease in Cr(VI) (Fig. S6), and implies that Cr_2O_{3+x} can be reduced by extending the heating time (Fouad et al., 1999; Hiramatsu et al., 2010). These results suggest that when sludge is heated at low temperature (200–300 °C), an extended heating time lowers the extent of Cr(VI) leaching.

Cr(VI) leaching from products sintered at 400 °C for various times is presented in Fig. 6(b). Within the first hour, Cr(VI) leaching attained a maximum at ~0.5 h and increased again after 1 h with increase in heating time. Fig. S8 shows that the peak intensity of $CaCrO_4$ is lower than that heated for 1 h, however, the increased amount of Cr(VI) leached may be derived from the intermediate product Cr_2O_{3+x} containing Cr(VI). This assumption agrees with color variations of the residue; the solid was still green after being heated for 0.25 h, and turned brown after 0.5 h. However, the decreasing Cr(VI) leaching from 0.5 h to 1 h suggests that Cr(VI) may be reduced to Cr(III), and is attributed to the bleaching of Cr_2O_{3+x}. Compared with the results above (Fig. 6(a)), a higher heating temperature could bleach Cr_2O_{3+x} in a shorter period of time. When the heating time was higher than 1 h, the residue turned dull yellow green instead of dull green, which indicates that some chromate formed (Verbinnen et al., 2013), which is assumed to be $CaCrO_4$ from the XRD patterns (Fig. S8). More $CaCrO_4$ was generated with an increase in heating time, which results in an increase in Cr(VI) leaching after 1 h. Nonetheless, it seems that the $CaCrO_4$ formation speed is slow at 400 °C, most likely because the external energy in this temperature range was insufficient to trigger all atoms to participate in the reaction.

At 700 °C and 900 °C, a similar varying tendency of Cr(VI) leaching was observed in Fig. 6(c) and (d). Maximum Cr(VI) leaching was reached at 2 h and 1 h, respectively. As mentioned above, Cr_2O_3 oxidation is responsible for the increased Cr(VI) leaching in this temperature range (500–900 °C). Maximum Cr(VI) leaching could be achieved at a higher temperature over a shorter period, which indicates that higher temperature could improve this reaction speed. However, it is not good news to reduce Cr(III) oxidation for thermal treatment of sludge containing chromium because a large amount of Cr(III) would be oxidized even in a short time. Cr(VI) leaching would decrease with an extended heating time above 2 h. XRD analysis shows that the main phase is still $CaCrO_4$ and its characteristic peak intensity does not decrease significantly (Fig. S9). Therefore, the change in amount of $CaCrO_4$ is not obvious. A similar phenomenon has been reported by Verbinnen et al. (2013), who considered that fired samples cool down rapidly at room temperature after being removed from the oven and form an amorphous, glassy calcium chromate, which prevents Cr(VI) from being leached (Verbinnen et al., 2013). In this study, a slightly endothermic peak at ~1000 °C corresponds to a significant mass loss as monitored in Fig. 2. Because chromium hydroxide would dehydrate completely to chromium oxide at this temperature and the lime has been fired over time, this reaction with mass loss could not be assigned to chromium hydroxide dehydration and CO_2 escape. Cr(VI) reduction with oxygen release may partly contribute to a decrease in Cr(VI) leaching and mass loss.

At 1200 °C, Cr(VI) leaching declined within 1 h and then increased after 1 h (Fig. 6(e)). As explained previously, $CaCrO_4$ reduction contributes to a decrease in Cr(VI) leaching. However, the Cr(VI) leaching increases over 1 h, which implies that some Cr(VI) must be oxidized to Cr(VI). The residue composition was determined by XRD and shows that the peak intensity of $CaCrO_4$ decreased with heating time up to 1 h (Fig. S10). These results agree with those from the leaching experiments (Fig. 6(e)). The intensity of $CaCrO_4$ increases and that of $Ca(CrO_2)_2$ declines after 1 h, which indicates that part of the $Ca(CrO_2)_2$ was oxidized to $CaCrO_4$ with heating over 1 h. This result suggests that a prolonged heating time of more than 1 h does not favor a lower Cr(VI) leaching.

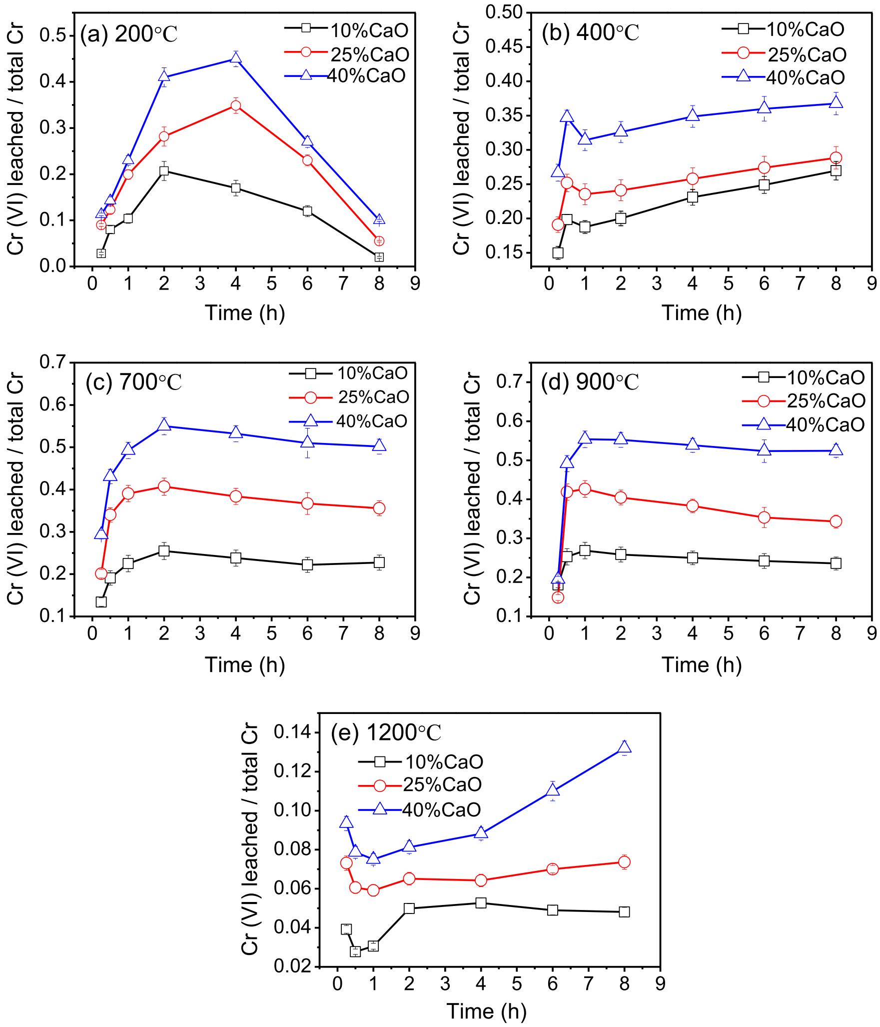

Fig. 6. Cr(VI) leaching as a function of heating time (0.25–8 h) at five temperatures ((a) 200 °C, (b) 400 °C, (c) 700 °C, (d) 900 °C and (e) 1200 °C).

4. Conclusions

The heating temperature dependence of Cr(VI) formation and reduction was investigated during the heating of chromium-containing sludge in the presence of CaO. The presence of CaO promoted Cr(III) oxidation, however, temperature plays an important role in Cr(VI) formation and reduction from 200 to 1200 °C, and its influence varied over different temperature ranges.

From 200 to 400 °C, a large amount of Cr(VI) was formed in 1 h. Most Cr(VI) leaching was derived from intermediate product Cr_2O_{3+x} containing Cr(VI) during dehydration of chromium hydrate. This special phenomenon was only found in mixtures of chromium hydroxide and CaO, but was not detected in mixtures of Cr_2O_3 and CaO. Cr_2O_{3+x} would decompose above 400 °C accompanied by Cr(VI) reduction to Cr(III). At 200 °C, with an extended heating time above 4 h, Cr_2O_{3+x} is reduced slowly to Cr(III) as well.

At 500–900 °C, Cr(III) combined with CaO to produce $CaCrO_4$. A maximum amount of Cr(III) could be oxidized in 1 h at 900 °C, and extending the heating time did not result in a significant reduction in the amount of $CaCrO_4$ in this temperature range. Thus, there is a significant risk that Cr(VI) could be leached in this temperature range.

From 1000–1200 °C, part of $CaCrO_4$ is reduced to $Ca(CrO_2)_2$ and is accompanied by oxygen liberation. This reaction reduces the amount of Cr(VI). Extending the heating time above 1 h, however, does not favor a lower Cr(VI) leaching, because $Ca(CrO_2)_2$ can be oxidized reversibly to $CaCrO_4$ in this temperature range. The reduction of $CaCrO_4$ to $Ca(CrO_2)_2$ implies that $CaCrO_4$ is thermodynamically less stable, and adding MgO could induce part of $CaCrO_4$ to be reduced into more stable phase $MgCr_2O_4$ from 900 °C, lower than that for the transformation from $CaCrO_4$ into $Ca(CrO_2)_2$.

The above results show that, during the heat treatment of sludge that contains chromium, and in the presence of CaO, a prolonged heating time could inhibit Cr(III) oxidation at low temperature (200–400 °C). At high temperature (above 600 °C), an elevated temperature (1000–1200 °C) or the addition of MgO could abate Cr(III) oxidation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.05.097.

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