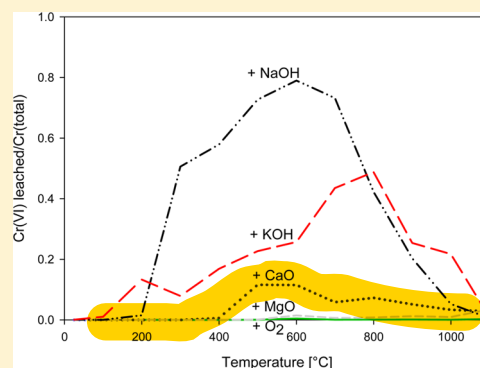


Heating Temperature Dependence of Cr(III) Oxidation in the Presence of Alkali and Alkaline Earth Salts and Subsequent Cr(VI) Leaching Behavior

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ABSTRACT: In this paper, the temperature dependence of Cr(III) oxidation in high temperature processes and the subsequent Cr(VI) leaching was studied using synthetic mixtures. It was experimentally shown that in the presence of alkali and alkaline earth salts, oxidation of Cr(III) takes place, consistent with thermodynamic calculations. Heating of synthetic mixtures of Cr₂O₃ and Na, K, or Ca salts led to elevated leaching of Cr(VI); in the presence of Na, more than 80% of the initial Cr(III) amount was converted to Cr(VI) at 600–800 °C. Kinetic experiments allowed explanation of the increase in Cr(VI) leaching for increasing temperatures up to 600–800 °C. After reaching a maximum in Cr(VI) leaching at temperatures around 600–800 °C, the leaching decreased again, which could be explained by the formation of a glassy phase that prevents leaching of the formed Cr(VI). By way of illustration, Cr(VI) formation and leaching was evaluated for a case study, the fabrication of ceramic material from contaminated sludge. Based on the proposed reaction mechanisms, countermeasures to prevent Cr oxidation (addition of NH₄H₂PO₄, heating under inert atmosphere) were proposed and successfully tested for synthetic mixtures and for the case study.



INTRODUCTION

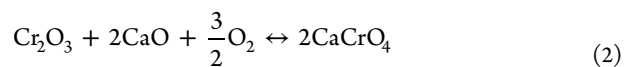
In our recent research, we observed that (i) when expressed as a fraction of the total Cr content, Cr(VI) leaching from bottom ash of a fluidized bed waste incinerator was six times higher than from fly ash, and that (ii) when contaminated sludge was heated in order to obtain a ceramic material, leaching of the mobile and toxic Cr(VI) exceeded the regulatory limit value, at some temperatures (600–700 °C) even by 50 times. As Cr(VI) leaching from the unheated material was below the limit value, this indicates that Cr(VI) is formed during thermal treatment.

Several papers report on elevated Cr leaching or on oxidation of Cr(III) to Cr(VI) and subsequent leaching after high temperature processes but do not explain its causes. After thermal treatment of contaminated sludge in view of recycling,^{1,2} combustion of waste, coal, or biomass,^{3–7} and after other high temperature processes such as cement production,^{8–10} elevated Cr or Cr(VI) leaching was observed. Moreover, Cr(VI) formation may be responsible for enhanced corrosion of stainless steel during high temperature processes.¹¹

It is well-known that Cr(VI) is more mobile than Cr(III),¹² so increased leaching observed in the literature is probably related to oxidation of Cr(III) to Cr(VI). Moreover, Cr(VI) is highly toxic and is ranked as the second most important oxyanion (after arsenic) on the CERCLA 2011 Priority List of Hazardous Substances. Reaction 1, the oxidation of Cr(III) to Cr(VI) in the presence of ambient air does not occur at temperatures below 1500 °C,¹³ as will be shown by experiments and thermodynamic calculations in this paper.



Therefore, Paoletti¹³ hypothesized that Cr(III) (i.e., Cr₂O₃) is oxidized to Cr(VI) in the presence of oxygen and CaO according to reaction 2. This hypothesis was based on TGA observations, where a weight gain was observed starting at a temperature of around 500 °C.



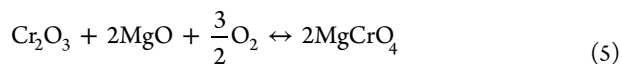
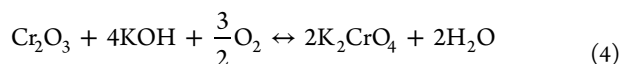
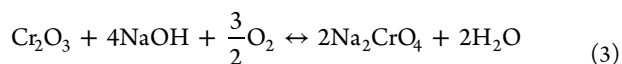
Other researchers^{5,11,14–16} pointed out that in the presence of salts of alkali and other alkaline earth metals, the oxidation of Cr(III) to Cr(VI) by oxygen is also made possible. Whereas Cr(III) oxidation and subsequent Cr(VI) leaching was thus mentioned on several occasions, a systematic description and explanation of the dependence on the oxidation temperature is still lacking. The goal of this paper is to present a framework for understanding Cr(VI) formation in the presence of salts of alkali and alkaline earth metals and its subsequent leaching. Therefore, apart from reactions 1 and 2, three other reactions, 3–5, will be considered:

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Synthetic mixtures are used to study the temperature dependence of the described reactions, and the results are compared with thermodynamic calculations. The synthetic mixtures are also used to carry out kinetic experiments. By way of illustration, the formation of Cr(VI) during thermal treatment of contaminated industrial sludge is quantified and explained. It is shown that a better understanding of the reactions responsible for Cr oxidation may afford effective countermeasures against Cr(VI) formation and leaching.

MATERIALS AND METHODS

Synthetic mixtures were prepared by mixing 5 wt % of Cr(III) oxide (Cr_2O_3 , Sigma-Aldrich) with 95 wt % of potassium hydroxide (KOH, Merck Eurolab), sodium hydroxide (NaOH, Fisher), magnesium oxide (MgO, Sigma-Aldrich), or calcium oxide (CaO, Chem-Lab). The finely divided mixture was homogenized by thoroughly mixing, and 1 g was placed on sand in a ceramic crucible. The crucibles were placed in a muffle furnace that was heated with a heating rate of approximately 10 °C/min until the desired temperature (100–1100 °C) was reached. They were kept at this temperature for half an hour and afterward allowed to cool in the furnace. For kinetic experiments, the mixtures were introduced in a preheated muffle furnace at the desired temperature, removed from the oven after a given time period (1 min to 12 h), and allowed to cool at room temperature.

Industrial sludges originating from the cleaning of soils (with different origin and contaminants, but all mainly inorganic), were dried at 105 °C until constant weight, ground, and then mixed in equal quantities. After homogenization, an appropriate amount (about one-third of the sludge mass) of water was added to allow good pelletization. Spherical pellets with an average diameter of 1.5 cm and an average weight of 5 g were produced and dried at 105 °C. The pellets were then introduced in the oven using the “rapid sintering”¹⁷ technique. This method requires that the samples are placed in a preheated oven at the desired temperature and kept at this temperature for a given period, in this case at temperatures between 200 and 1100 °C for half an hour. After this period, the samples were removed from the oven and allowed to cool at room temperature.

After cooling, the samples were ground and leached with double deionized water (Millipore Milli-Q) on a shaking device (Gerhardt Laboshake, 160 rpm) for 24 h with a liquid/solid ratio of 10 (pellets) or 100 (synthetic mixtures, a higher ratio was chosen to ensure that leaching was not limited by solubility). After leaching, the samples were filtered over a 0.45 μm membrane filter (Chromafil), and the relevant metal concentrations were measured by ICP-MS (Thermo Xi series). Cr(VI) concentrations were measured spectrophotometrically (Shimadzu 1601) using the diphenylcarbazide method.

To study the effect of phase crystallinity on the leaching of Cr, pure K_2CrO_4 was heated for 30 min at temperatures ranging from 500 to 1100 °C, and after cooling, the sample was leached for 24 h with ultrapure water at an L/S ratio of 1000.

In experiments to prevent Cr(III) oxidation, an excess (twice the weight of the mixture) of $\text{NH}_4\text{H}_2\text{PO}_4$ was added to a 5% Cr_2O_3 –95% NaOH mixture, which was then heated at 800 °C for 10 min. To contaminated sludge, 7% $\text{NH}_4\text{H}_2\text{PO}_4$ was added, and the sample was heated at 700 °C for 30 min. To test heating under an inert atmosphere, a sample of the contaminated sludge was heated at 700 °C for 30 min in a furnace through which a constant stream of nitrogen was flowing.

The crystal structure of the samples was determined by XRD (Philips PW1830) using monochromated Cu K α radiation, generated at 45 kV and 30 mA. Measurements ranged from $2\theta = 5^\circ$ to 75° , with a step size of 0.02° .

Thermodynamic calculations were performed using data from the FactSage database and relevant literature sources^{18–23} for data that were not in the FactSage database.

RESULTS AND DISCUSSION

Synthetic Samples. In Figure 1, the ratio of the Cr(VI) amount leached after heating to the initial Cr amount in the

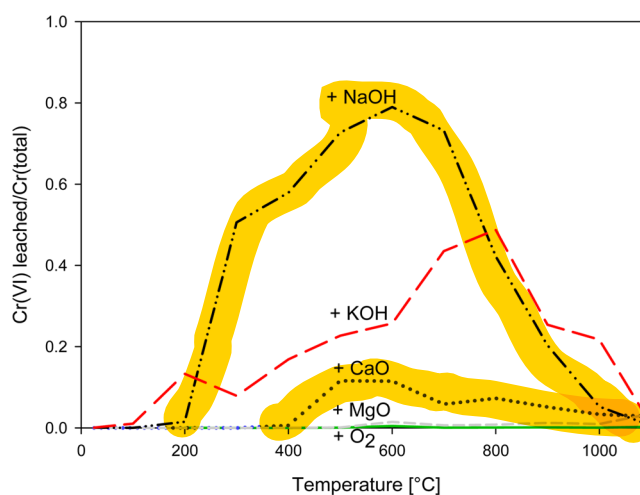


Figure 1. Leaching of Cr(VI) as a function of heating temperature in the presence of NaOH, KOH, CaO, or MgO or without other oxides/hydroxides added.

synthetic samples is plotted against the heating temperature. As all Cr(VI) salts that might be formed in these experiments are very soluble over a broad pH range, and Cr(III) salts are hardly soluble at neutral and alkaline pH values, the ratio of Cr(VI) leaching to total Cr could be considered an indication of the total Cr(III) amount that has been oxidized to leachable Cr(VI) after heating. At high temperatures however, this is not correct, as will be shown later. From the graph, it appears that Cr_2O_3 as such is not oxidized. Also, the presence of MgO leads to little oxidation: at 1100 °C, only 3.5% of the initial Cr(III) amount is leached as Cr(VI).

The graph corresponding to Cr(VI) leaching after heating in the presence of CaO, KOH, and NaOH shows a different behavior. Due to the addition of CaO, 12% of the initial amount of Cr(III) is leached as Cr(VI) between 500 and 600 °C. The presence of KOH leads to leaching of 49% at 800 °C, and with the addition of NaOH even 79% of Cr(III) leaches as Cr(VI) at 600 °C. The higher maximum leaching concentrations and the earlier start of increased Cr(VI) leaching for NaOH and KOH (200–300 °C vs 500 °C) in comparison to CaO can be explained by the lower melting temperature of

NaOH and KOH (318 and 406 °C, respectively) in comparison to that of CaO (2572 °C), which improves contact between (molten) hydroxides and Cr₂O₃. The three graphs show a maximum at 600–800 °C. At higher temperatures, Cr(VI) leaching decreases until it reaches values between 0.5 and 3% at 1100 °C. Thermodynamic calculations and kinetic experiments were performed to explain this behavior.

Thermodynamics. The reaction Gibbs free energies for reactions 1–5 were calculated as a function of temperature and are shown in Figure 2. The results indicate that the oxidation of

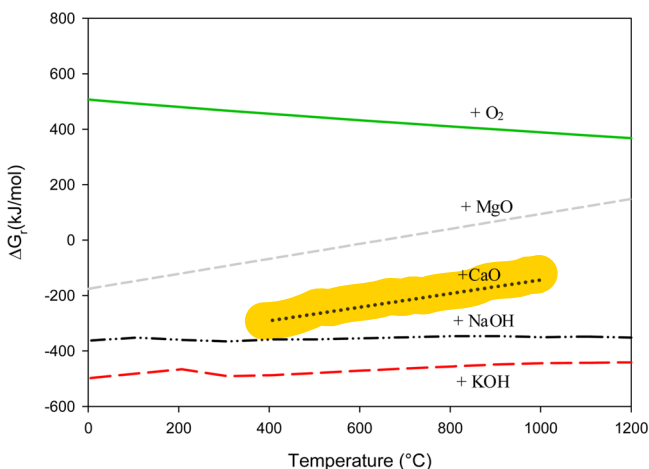


Figure 2. Reaction Gibbs free energies as a function of temperature for the formation reactions of chromates starting from Cr₂O₃, or Cr₂O₃ mixed with NaOH, KOH, CaO, or MgO.

Cr₂O₃, Cr₂O₃ + ³/₂O₂ ↔ 2CrO₃, does not take place in the temperature range studied (0–1200 °C), as the reaction Gibbs free energy is positive over the entire range. Oxidation in the presence of MgO is thermodynamically feasible for temperatures up to 650 °C, but the reaction Gibbs free energy is less negative than for the reaction in the presence of CaO, KOH, or NaOH. For the latter reactions, the reaction Gibbs free energy is negative over the whole temperature range studied. These results correspond very well with Figure 1 at the temperatures where maximum leaching was observed (600–800 °C).

The reaction Gibbs free energies for the formation of the respective chromates and chromites of calcium and sodium are shown in Figure 3. The thermodynamic data show that in the case of CaO, the formation of calcium chromate is favored over the formation of calcium chromite at temperatures up to 1000 °C. At higher temperatures, there is a lack of accurate thermodynamic data, but the trend of the Gibbs free energies suggests that the formation of calcium chromite might become dominant at temperatures higher than 1300 °C.

For sodium (shown as an example in Figure 3) and potassium (not shown), the reaction Gibbs free energies for chromite formation are much higher than for chromate formation, meaning that the formation of chromates is favored.

Kinetics. Thermodynamics alone does not suffice to describe the shape of the curves in Figure 1. Reaction Gibbs free energies as a function of temperature, as in Figure 2, do not explain the increase or the decrease of the Cr(VI) leaching as a function of temperature in Figure 1. Therefore, a kinetic study was performed using the synthetic mixture of Cr₂O₃ and NaOH, which showed the highest leaching in the earlier tests. Kinetic studies were performed in two temperature intervals:

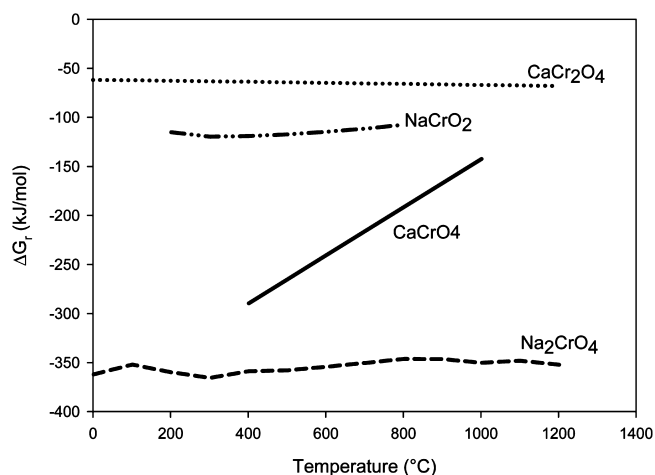


Figure 3. Reaction Gibbs free energy as a function of temperature for the formation of calcium and sodium chromates and chromites.

(1) at 300, 500, and 700 °C, where the Cr(VI) leaching from Figure 1 increases as a function of temperature, and (2) at 700, 800, and 900 °C, where the Cr(VI) leaching decreases again.

In Figure 4, the leaching of Cr(VI) as a function of heating time is shown for three different temperatures: 300, 500, and

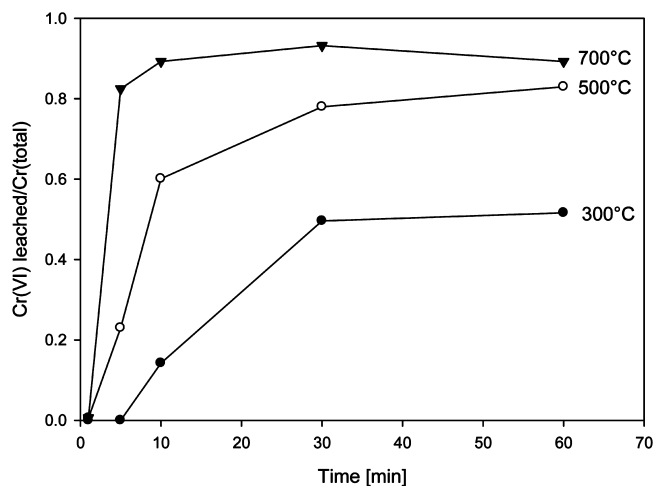


Figure 4. Cr(VI) leaching as a function of heating time for three temperatures (300–700 °C) for a 95% NaOH–5% Cr₂O₃ mixture.

700 °C. For a given heating time (e.g., 30 min), the leaching increases from 300 to 700 °C, and maximum leaching is reached faster at higher temperatures. At 300 °C, the Cr(VI) leaching is 52% of the initial Cr content after 60 min; at 500 and 700 °C, the leaching reaches 83 and 89%, respectively. The higher leaching at 500 and 700 °C after 60 min is related to the fact that above the melting temperature of NaOH (318 °C) contact between molten NaOH and Cr₂O₃ improves, resulting in a higher leaching for the time intervals shown. The leaching ratios after 30 min from Figure 4 can be related to those from Figure 1 at the same temperatures. It can be concluded that kinetics are able to explain the oxidation behavior up to 700 °C.

At temperatures above 700 °C, the amount of leached Cr(VI) for a residence time of 30 min (Figure 1) starts to decrease again. Paoletti suggested that in the presence of CaO, a possible explanation for the reduced Cr leaching at temperatures above 850 °C could be the formation of calcium

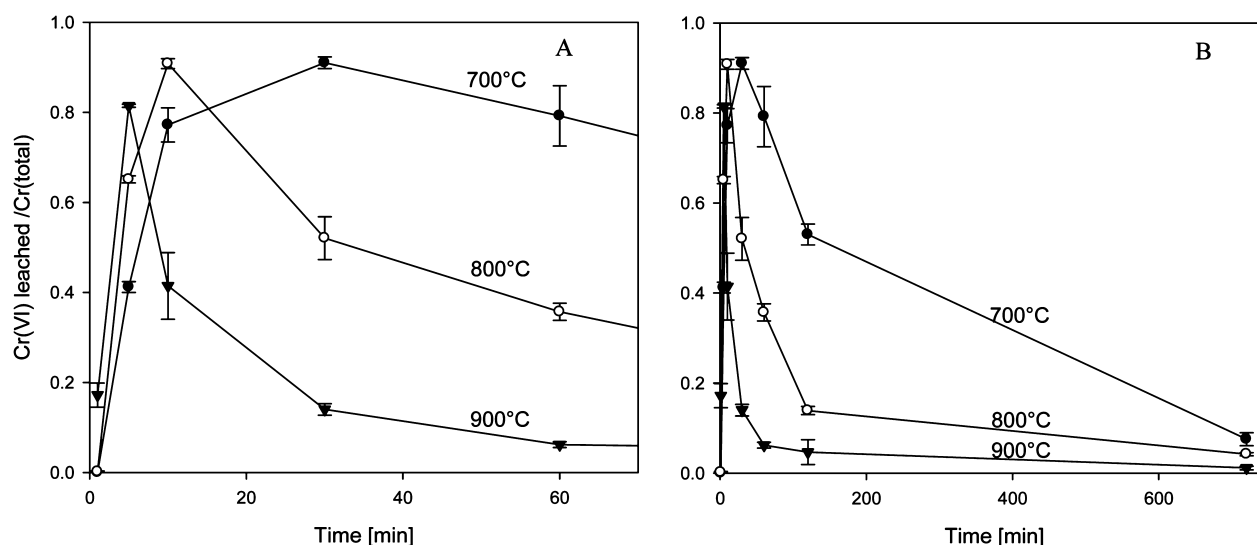


Figure 5. Cr(VI) leaching as a function of heating time (A, 0–60 min; B, 0–12 h) for three temperatures (700–900 °C) for a 95% NaOH–5% Cr₂O₃ mixture.

chromite, competing with the formation of calcium chromate. However, the present thermodynamic calculations (Figure 3) indicate that chromite formation in the presence of alkali and alkaline earth salts is less favorable than chromate formation at temperatures up to 1200 °C, so that the decrease in Cr(VI) leaching cannot be explained by the formation of these chromites.

Figure 5A and B show the results of kinetic experiments at three different temperatures (700, 800, and 900 °C) for residence times between 1 min and 12 h. In Figure 5A, an enlargement of Figure 5B for residence times up to 60 min is shown. For all three temperatures, a maximum in leaching is observed (81–91%). Again, the maximum is reached faster at higher temperatures, in agreement with the observations from Figure 4. After the maximum has been reached, the Cr leaching decreases significantly at 800 and 900 °C. After 60 min at 900 °C, the Cr leaching is reduced to 6% and at 800 °C to 36%, but at 700 °C it is still 80% of the initial amount of Cr.

In Figure 5B, results for residence times up to 12 h are shown. From these results, it is clear that also at 700 °C, the Cr leaching decreases, but this decrease starts later and is slower than at 800 and 900 °C. After 12 h, the leached percentage of the initial Cr amount is below 8% for all three temperatures.

As previously explained, thermodynamic calculations indicate that chromates are still formed at these temperatures (700–900 °C). This is confirmed by observation of the color of the heated samples: as Cr₂O₃ is converted to CrO₄²⁻, its color changes from green to yellow. Although leaching at elevated temperatures (e.g., for the sample heated for 60 min at 900 °C) is low, the samples are still as yellow as at lower temperatures where high Cr(VI) leaching was observed, indicating that Cr(VI) is present but does not leach. The decreased Cr(VI) leaching can be explained as follows: after heating and removal of the samples from the oven, the samples are rapidly cooled at room temperature, resulting in the formation of an amorphous, glassy chromate phase, from which leaching of Cr(VI) is prevented. It is clear from Figure 5B that the formation of the glassy phase is slower than the oxidation of Cr(III) to Cr(VI) at 700–900 °C.

The temperature at which Cr(VI) leaching starts to decrease from Figure 1 can now be linked with the melting temperature of the chromates. In the presence of NaOH, the leaching of

calcium chromate starts to decrease after 600 °C; in the presence of KOH, the decrease starts after 800 °C, whereas the melting temperatures of Na₂CrO₄ and K₂CrO₄ are 792²⁴ and 980 °C,¹¹ respectively. The temperature difference between the points where the leaching starts to decrease is comparable to the temperature difference between the melting points. The presence of NaOH or KOH, which are known to be fluxing agents, explains the fact that the temperatures at which the leaching starts to decrease are lower for the synthetic mixtures than for the pure compounds.

To confirm this theory, the leaching of pure K₂CrO₄, after heating for 30 min at temperatures ranging between 500 and 1100 °C, was evaluated. The percentage of the total Cr amount that is leached is shown in Figure 6. It can be concluded that at temperatures above the melting temperature of K₂CrO₄ (980 °C), the leaching of Cr is strongly reduced.

It can be concluded from this section that the increased leaching concentrations for increasing temperatures up to 600–800 °C shown in Figure 1 could be explained by kinetics. The decrease in Cr(VI) leaching, observed after the maximum leaching was reached, was explained by the formation of a

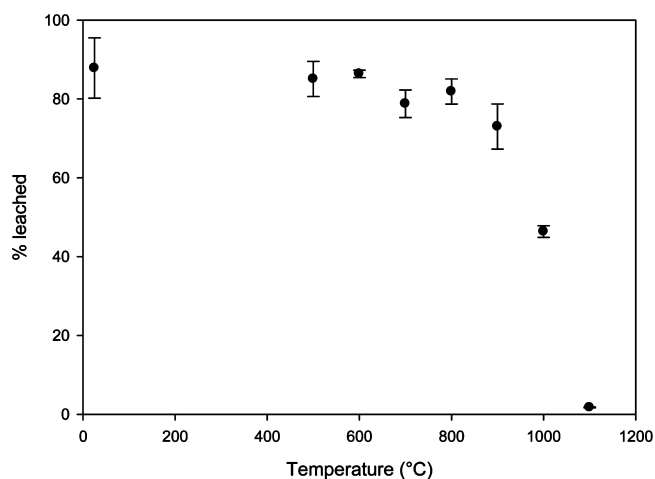


Figure 6. Percentage of Cr(VI) leached after heating K₂CrO₄ for 30 min at 500–1100 °C.

glassy chromate phase, which was formed faster at higher temperatures.

On the basis of reactions 2–5, countermeasures to prevent Cr leaching can be tested. First of all, if no oxygen is present during heating, Cr(III) will of course not be oxidized to Cr(VI). This possibility will be tested in the next section. Second, the alkali and alkaline earth salts can also be bound to other compounds (additives), to prevent them from participating in reactions 2–5. As an additive, $\text{NH}_4\text{H}_2\text{PO}_4$ was chosen because it is thermodynamically less stable than alkali and alkaline earth phosphates, which are in turn more stable than their respective chromates, so the alkali and alkaline earth metals would preferably bind with phosphate, instead of participating in reactions 2–5. The amount of $\text{NH}_4\text{H}_2\text{PO}_4$ that was added (7%) was comparable to the total amount of Ca, Mg, Na, and K in the sludge. The addition of $\text{NH}_4\text{H}_2\text{PO}_4$ reduced Cr leaching from 92% (without addition, Figure 5A) to only 1.4%. This test shows that the earth and alkaline earth salts can be bound to other compounds to prevent them participating in reactions 2–5 that give chromates and is another proof that the proposed reaction mechanisms are correct. This countermeasure will also be tested in the next section.

Thermal Treatment of Contaminated Sludge. The contaminated sludge mainly contains tectosilicates (6.0%), phyllosilicates (26.3%), quartz (31.2%), calcite (3.3%), and organic material (11.6%); the remainder is other or amorphous material. Cr(VI) leaching from the pelletized industrial sludge as a function of heating temperature is shown in Figure 7. For

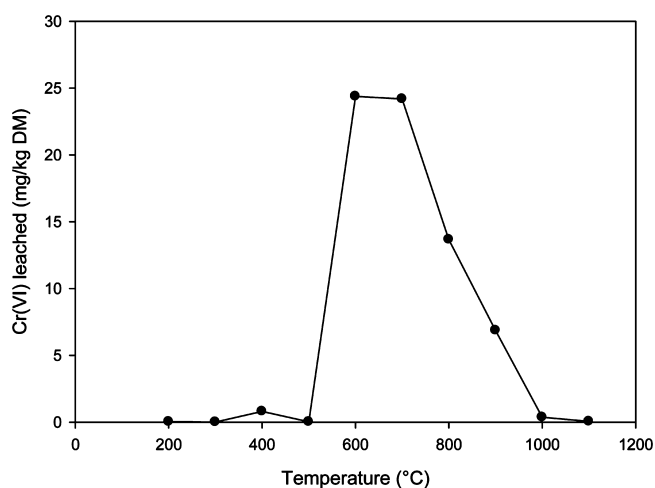


Figure 7. Leaching behavior of Cr(VI) from industrial sludge fired at temperatures between 200 and 1100 °C.

unheated samples and samples heated up to 500 °C, almost no Cr(VI) leaching is detected. Also, no Cr(VI) was detected in a pH-dependent leaching test of the unheated sample for the relevant pH range (7–12.5), carried out in this study. From 500 °C on, Cr(VI) leaching increases and reaches about 25 mg/kg at 600–700 °C, thus exceeding the limit value for use of waste material as a secondary raw material (0.5 mg/kg DM) in Flanders²⁵ significantly, almost 50 times. All of this indicates that Cr(VI) is formed during thermal treatment. Around 13% of the total amount of Cr present in the sludge (184 mg/kg) is leached as Cr(VI) after heating at 600–700 °C. After heating between 700 and 800 °C, the Cr(VI) leaching starts to decrease, but only after heating at 1100 °C is the concentration below the regulatory limit again.

The behavior of the Cr(VI) leaching as a function of temperature is rather similar to the behavior observed for synthetic mixtures of Cr_2O_3 with Ca, Na, or K salts (Figure 1). This indicates that the elevated Cr(VI) leaching in the thermally treated industrial sludge can be attributed to reactions 2–5. Moreover, XRD measurements of the samples showed that the total amount of amorphous material is constant (about 30%) up to 1000 °C and increases to around 60% at 1100 °C. The decrease in Cr(VI) leaching between 700 and 1000 °C can thus not be explained by vitrification of the sample as a whole but should be attributed to the chromates forming a glassy phase from 700 °C on and preventing Cr from leaching, as explained before. In the synthetic samples, Cr(VI) leaching started between 200 and 500 °C, whereas for the contaminated sludge it only started at 600 °C. This can be explained by the presence of organic material in the contaminated sludge (11.5 wt %), which needs to be oxidized first, before Cr(III) can be oxidized to Cr(VI).

The shape of the Cr(VI) leaching as a function of heating temperature from Figures 1 and 7 is comparable to earlier literature findings. Prokisch et al.²⁶ studied the speciation of chromium during sludge incineration at temperatures between 200 and 1200 °C and observed Cr(III) oxidation to Cr(VI), with a maximum in extractable chromate concentration at 500 °C. Wang et al.⁴ studied thermally treated municipal solid waste incinerator fly ash, spiked with Cr_2O_3 , between 600 and 1000 °C and observed elevated Cr(VI) leaching, with a maximum in total Cr leaching at 900 °C. At 800 °C, the Cr_2O_3 peak on the XRD pattern was decreased, while the peak of K_2CrO_4 was increased. Chang et al.¹ sintered metal sludge from industrial wastewater treatment plants mixed with mining residues at temperatures between 850 and 1250 °C in order to obtain lightweight aggregates. A maximum in Cr leaching was observed at 950 °C, and the leaching was strongly reduced at 1250 °C. All of these observations, which were not or only partly explained in literature, can now be explained with the results from this paper.

The countermeasures described in the previous chapter can also be tested for this industrial sludge. Heating under an inert atmosphere at 700 °C for 30 min reduced Cr(VI) leaching, which was 24.2 mg/kg (Figure 7) after heating in ambient air, to 0.42 mg/kg.

A second method that was tested to prevent Cr oxidation is the addition of $\text{NH}_4\text{H}_2\text{PO}_4$, which was shown to be an effective method for the synthetic samples. For the industrial sludge, the measured Cr(VI) leaching was reduced from 24.2 mg/kg in an untreated sample to only 0.018 mg/kg for a sample to which $\text{NH}_4\text{H}_2\text{PO}_4$ was added and which was heated at 700 °C for 30 min.

Cr(VI) formation can thus be reduced by working under inert atmosphere or by adding an appropriate compound that binds the alkali and alkaline earth salts in the sample.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Chang, F. C.; Lo, S. L.; Lee, M. Y.; Ko, C. H.; Lin, J. D.; Huang, S. C.; Wang, C. F. Leachability of metals from sludge-based artificial lightweight aggregate. *J. Hazard. Mater.* **2007**, *146* (1–2), 98–105.
- (2) Xu, G. R.; Zou, J. L.; Li, G. B. Stabilization of heavy metals in ceramsite made with sewage sludge. *J. Hazard. Mater.* **2008**, *152* (1), 56–61.
- (3) Abbas, Z.; Steenari, B. M.; Lindqvist, O. A study of Cr(VI) in ashes from fluidized bed combustion of municipal solid waste: leaching, secondary reactions and the applicability of some speciation methods. *Waste Manage.* **2001**, *21* (8), 725–739.
- (4) Wang, K. S.; Sun, C. J.; Liu, C. Y. Effects of the type of sintering atmosphere on the chromium leachability of thermal-treated municipal solid waste incinerator fly ash. *Waste Manage.* **2001**, *21* (1), 85–91.
- (5) Stam, A. F.; Meij, R.; Winkel, H. T.; van Eijk, R. J.; Huggins, F. E.; Brem, G. Chromium Speciation in Coal and Biomass Co-Combustion Products. *Environ. Sci. Technol.* **2011**, *45* (6), 2450–2456.
- (6) Hu, H.; Luo, G.; Liu, H.; Qiao, Y.; Xu, M.; Yao, H. Fate of chromium during thermal treatment of municipal solid waste incineration (MSWI) fly ash. *Proc. Combust. Inst.* **2013**, *34* (2), 2795–2801.
- (7) Hyks, J.; Nesterov, I.; Mogensen, E.; Jensen, P. A.; Astrup, T. Leaching from waste incineration bottom ashes treated in a rotary kiln. *Waste Manage. Res.* **2011**, *29* (10), 995–1007.
- (8) Vangelatos, I.; Angelopoulos, G. N.; Boufounos, D. Utilization of ferroalumina as raw material in the production of Ordinary Portland Cement. *J. Hazard. Mater.* **2009**, *168* (1), 473–478.
- (9) Sinyoung, S.; Songsiriritthigul, P.; Asavapisit, S.; Kajitvichyanukul, P. Chromium behavior during cement-production processes: A clinkerization, hydration, and leaching study. *J. Hazard. Mater.* **2011**, *191* (1–3), 296–305.
- (10) Chen, Y. L.; Chang, J. E.; Lai, Y. C.; Ko, M. S. Effects of sintering atmosphere on cement clinkers produced from chromium-bearing sludge. *J. Air Waste Manage. Assoc.* **2012**, *62* (5), 587–593.
- (11) Lehmusto, J.; Lindberg, D.; Yrjas, P.; Skrifvars, B. J.; Hupa, M. Thermogravimetric studies of high temperature reactions between potassium salts and chromium. *Corros. Sci.* **2012**, *59*, 55–62.
- (12) McLean, J. E.; Bledsoe, B. E. Behavior of metals in soils. *EPA Ground Water Issue*; Technology Innovation Office, Office of Solid Waste and Emergency Response, University of Minnesota: Minneapolis, MN, 1992.
- (13) Paoletti, F. Behavior of oxyanions forming heavy metals in municipal solid waste incineration. Ph. D. Dissertation, Institute for Technical Chemistry: Karlsruhe, Germany, 2002.
- (14) Xu, H. B.; Zhang, Y.; Li, Z. H.; Zheng, S. L.; Wang, Z. K.; Tao, Q.; Li, H. Q. Development of a new cleaner production process for producing chromic oxide from chromite ore. *J. Clean Prod.* **2006**, *14* (2), 211–219.
- (15) El-Hasan, T.; Szczerba, W.; Buzanich, G.; Radtke, M.; Riesemeier, H.; Kersten, M. Cr(VI)/Cr(III) and As(V)/As(III) Ratio Assessments in Jordanian Spent Oil Shale Produced by Aerobic Combustion and Anaerobic Pyrolysis. *Environ. Sci. Technol.* **2011**, *45* (22), 9799–9805.
- (16) Kirk, D. W.; Chan, C. C. Y.; Marsh, H. Chromium behavior during thermal treatment of MSW fly ash. *J. Hazard. Mater.* **2002**, *90* (1), 39–49.
- (17) Adell, V.; Cheeseman, C. R.; Doel, A.; Beattie, A.; Boccaccini, A. R. Comparison of rapid and slow sintered pulverised fuel ash. *Fuel* **2008**, *87* (2), 187–195.
- (18) Lee, Y. M.; Nassaralla, C. L. Standard free energy of formation of calcium chromate. *Mater. Sci. Eng., A* **2006**, *437* (2), 334–339.
- (19) Rajendran Pillai, S.; Khatak, H. S.; Gnanamoorthy, J. B. Formation of NaCrO₂ in sodium systems of fast reactors and its consequence on the carbon potential. *J. Nucl. Mater.* **1995**, *224* (1), 17–2424.
- (20) Qi, T. G.; Liu, N.; Li, X. B.; Peng, Z. H.; Liu, G. H.; Zhou, Q. S. Thermodynamics of chromite ore oxidative roasting process. *J. Cent. South Univ. Technol.* **2011**, *18* (1), 83–88.
- (21) Jacob, K. T. Potentiometric Determination of the Gibbs Free Energy of Formation of Cadmium and Magnesium Chromites. *J. Electrochem. Soc.* **1977**, *124* (12), 1827–1831.
- (22) Brittain, R. D.; Lau, K. H.; Hildenbrand, D. L. Mechanism and thermodynamics of the vaporization of K₂CrO₄. *J. Electrochem. Soc.* **1987**, *134* (11), 2900–2904.
- (23) Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. Janaf thermochemical tables, 1975 supplement. *J. Coord. Chem.* **1975**, *4* (1), 1–175.
- (24) Tathavadkar, V.; Antony, M. P.; Jha, A. Determination of the free energies of formation of Na₂Cr₂O₄ and Na₂CrO₄ using the sodium-beta''-Al₂O₃ soled electrolyte. In *Light Metals 2002*; Schneider, W. A., Ed.; Minerals, Metals & Materials Soc.: Warrendale, PA, 2002, 31–36.
- (25) Order of the Flemish Government for the establishment of the Flemish regulations relating to sustainable management of material cycles and waste. <http://navigator.emis.vito.be/milnav-consult/drukwerkWettekstServlet?wettekstId=44119&actueleWetgeving=true&date=27-03-2013&appLang=en&wettekstLang=nl>.
- (26) Prokisch, J.; Katz, S. A.; Kovacs, B.; Gyor, Z. Speciation of chromium from industrial wastes and incinerated sludges. *J. Chromatogr., A* **1997**, *774* (1–2), 363–371.