

Chromium behavior during thermal treatment of MSW fly ash

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Received 15 April 2001; received in revised form 21 August 2001; accepted 22 August 2001

Abstract

Energy-from-waste incineration has been promoted as an environmentally responsible method for handling non-recyclable waste from households. Despite the benefits of energy production, elimination of organic residues and reduction of volume of waste to be landfilled, there is concern about fly ash disposal. Fly ash from an incinerator contains toxic species such as Pb, Zn, Cd and Cr which may leach into soil and ground water if landfilled.

Thermal treatment of the fly ash from municipal solid waste has been tested and proposed as a treatment option for removal of metal species such as Pb, Cd and Zn, via thermal re-volatilization. However, Cr is an element that remains in the residue of the heat treated fly ash and appears to become more soluble. This Cr solubilization is of concern if it exceeds the regulatory limit for hazardous waste. Hence, this unexpected behavior of Cr was investigated. The initial work involved microscopic characterization of Cr in untreated and thermally-treated MSW fly ash. This was followed by determining leaching characteristics using standard protocol leaching tests and characterization leaching methods (sequential extraction). Finally, a mechanism explaining the increased solubilization was proposed and tested by reactions of synthetic chemicals. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: MSW fly ash; Thermal treatment; Chromium speciation

1. Introduction

Incineration is considered an attractive method of simultaneous energy production and municipal solid waste MSW reduction. The latter is important because available landfill sites rapidly reach their capacity and the approval of new sites is increasingly unpopular [1]. Incineration requires extensive off-gas treatment and one of the materials captured

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from the off-gas is fly ash. This fly ash is enriched in some toxic metals such as Pb and Cd because these species in the solid waste can be volatilized at the incineration temperatures, and on cooling, condense onto the surface of the fly ash [2–5]. Thus, fly ash disposal must be carefully managed and is a liability for this management option [6].

As a consequence, to make incineration more acceptable, treatment methods must be developed to make the fly ash safe for landfill or construction use. One such method is thermal treatment which involves heating the fly ash to high temperatures ($>700^{\circ}\text{C}$). The treatment re-volatilizes these toxic surface species and removes them from the ash, making them less available for leaching. In addition, chlorination may be included in the thermal treatment since it induces the formation of volatile chloride salts and enhances the evaporation of the metal contaminants [7,8]. Condensation of the volatilized metal salts allows capture and concentration of these species.

Jakob et al. [2] reported that for Pb and Cd, and to a lesser extent for Zn, heating of fly ash to 1000°C , caused volatilization, while Kirk and Graydon [9] reported that roasting the fly ash with chloride was an effective way for removing a wide range of contaminants including Zn, Cd, Pb and Cu. Massillamany [10] found that thermal treatment at 1000°C for 3 h reduced the acid leachable content of these metals. He also reported that for Cr, the thermal treatment increased the leachate concentration by about 20 times for three different fly ash sources. This is not a desirable outcome of the thermal treatment process. The investigation of this behavior of Cr is the subject of this paper.

2. Experimental

2.1. Materials

Since a variety of fly ash samples had shown the effect of increased Cr solubilization after thermal treatment, only one type of fly ash was used in this study. The sample was obtained from a USA facility using MSW as a fuel source. The facility generated steam and electricity along with flue gases, from which fly ash was collected by an electrostatic precipitator.

2.2. Sampling

Samples of the bulk ash were tumbled in a rotary mixer, then were coned and quartered, and divided into three portions, each portion being handled differently: one portion remained untreated (UF); the second portion was thermally-treated (TF); and the third portion was mixed with calcium chloride before being thermally-treated (CF). Each of these prepared samples was again coned and quartered and triplicates of 1 g amounts of each were weighed out into 30 ml Nalgene wide-mouth polyethylene bottles for leaching tests.

2.3. Apparatus and instrumentation

Porcelain crucibles, 15 ml, graphite crucibles, 8 ml, a muffle furnace, Hotpack Model 4601, and a rotary extractor, KBU Model VS309 were used.

Analytical instruments used include: an atomic absorption spectrometer, Perkin-Elmer Model 703; an inductively coupled plasma spectrometer, Spectro Analytical Instruments Model Spectro flame P; an X-ray diffractometer, Siemens Model D 5000; and a Hitachi 570 scanning electron microscope with EDX.

2.4. Thermal treatment

The fly ash samples for thermal treatment were weighed (≈ 5 g) and placed in a porcelain crucible. Those samples requiring calcium chloride were mixed with analytical grade CaCl_2 in a 15:1 (w/w) before transfer to the crucibles. The samples were placed in a preheated muffle furnace at 990 ± 10 °C for 1 h.

Synthetic samples used for investigating chemical reactions were analytical grade Cr_2O_3 , CaCl_2 and CaO . Since the Cr content in the fly ash was much lower relative to the chloride content either with or without chloride addition, a 1:2 (w/w) of Cr_2O_3 to either CaCl_2 or CaO was used to provide sufficient Cr in the tests. The heating time was reduced to 30 min to avoid formation of a fused residue. The synthetic chemical tests provided a means to demonstrate the possibility of specific chemical reactions.

2.5. Parameters for experiments using synthetic chemicals

- Cr_2O_3 : An amount of 0.050 g was used in each test.
- CaCl_2 : An amount of 0.100 g was used in a test.
- CaO : An amount of 0.100 g was used in a test.
- *Heating*: For 30 min at 1000 °C.
- *Dissolution*: After thermal treatment, the sample in the porcelain crucible was leached with water by standing overnight. The supernatant solution was decanted for Cr analysis by atomic absorption spectroscopy. The water insoluble mass was then leached with 5% HNO_3 for a period of 1 h, and the solution was also analyzed for Cr.

2.6. Characterization

The three samples (UF, TF, and CF), as described in Section 2.2, were examined by scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX) and optical microscopy. Synthetic chemicals were used for X-ray diffraction (XRD) analysis to identify the compounds formed after thermal treatment, since the fly ash samples had too little Cr for XRD analysis. Scans were performed at a speed of $2^\circ/\text{min}$ using an X-ray diffractometer employing $\text{Cu K}\alpha$ radiation at 40 kV and 15 mA. Once the 2θ peaks were obtained, a manual matching was done with literature values [11,12].

2.7. Single-step leaching tests

Acetic acid was added to each of the ash replicates in a 20:1 (v/w) as described in the toxicity characteristic leaching procedure (TCLP) [13] and the leaching extraction procedure (LEP) [14] using rotary extraction. The protocol leach tests were conducted based on a scaled mass of solids (1 g).

The leachate derived from the tests was centrifuged at high speed for 5 min and filtered via syringe through 0.45 μm filter discs and acidified with concentrated nitric acid to a $\text{pH} < 2$. The samples were refrigerated at 4 °C until analysis by atomic absorption spectrometry was carried out.

2.8. Determination of Cr in the fly ash residue after leaching

The residues left after the leaching test were analyzed for Cr using lithium metaborate (LiBO_2) fusion technique for sample dissolution [15]. The procedure was as follows: the residue was air dried and weighed into an 8 ml graphite crucible. An amount of 1 g of LiBO_2 was added and the contents were mixed. The mixtures were heated in the muffle furnace at 950 °C for 10 min or until molten; the molten bead was poured into a beaker containing 50 ml of 5% nitric acid and dissolved with the aid of a magnetic stirrer. The Cr in the solution was determined by inductively coupled plasma spectroscopy.

2.9. Sequential leaching test

Five fractions of Cr in the fly ash were isolated using various leaching agents in sequence based on the sequential extraction procedure proposed by Tessier et al. [16] except that five 0.5 g fly ash replicates were used instead of the 1 g sample size suggested. These five fractions were (a) exchangeable fraction, (b) carbonates bound fraction, (c) fraction bound to iron and manganese oxides, (d) fraction bound to organic matter, and (e) residual fraction, which was unextractable. To bring the Cr in this residual fraction into solution to be analyzed, the residue was fused with LiBO_2 followed by acid dissolution instead of the suggested HF-HClO_4 digestion of the residue, since the fusion method is more effective and rapid than the acid digestion for dissolution of residues.

3. Results and discussion

3.1. Characterization

The nature of the chromium content of the fly ash was not known, so that a preliminary characterization was carried out to identify chromium sources. The untreated ash was light gray in appearance and had interspersed in it white specks. There were also black particles present, indicative of unburnt carbon arising from the incineration process. Once thermal treatment was complete there was a change in appearance of the fly ash. The light-gray ash became golden-brown and was also coarser in texture than the initial residue. The loss in mass due to thermal treatment was approximately 5%.

SEM/EDX analysis was conducted to determine the distributions and associations of Cr in fly ash and an elemental analysis done to show the content of Cr. The Cr concentration in the fly ash is generally in the range of 300–600 $\mu\text{g/g}$ which is too low for SEM/EDX analysis on the fly ash directly. Since little Cr (<1%) was lost from the sample due to leaching, the leached ash residues were essentially chromium enriched and were used for this analysis. Polished thin sections were made with surfaces carbon-coated for SEM/EDX

examination. The scans were conducted on an area of $0.8 \text{ mm} \times 1 \text{ mm}$ (a magnification of 120 times). On a given area, 30 scans were collected in order to distinguish true levels of Cr from background signals. Also, elemental distribution maps were made for Si, Ca, K, Al, Fe, Zn and either S or Cl to show the associations of Cr in the analyzed particles.

The mappings were conducted at higher magnifications between 500 and 2000 times when there was difficulty in detecting Cr. The X-ray mapping showed the presence of the respective elements as differences in coloration relative to the background of the picture.

The SEM/EDX spot analysis was done to determine Cr distribution in the ash matrix. Identifying an element present in levels less than 1% relies on localized distributions of the element. The detection limit for Cr in the fly ash matrix was 0.2–0.3% and the presence of localized Cr was facilitated by identification of the element by X-ray mapping.

Lower magnification maps were initially conducted, and in most instances yielded no useful information. Higher magnification maps were then used. At these magnifications, information was obtained on the distribution and concentration of the element and was supplemented by spot analysis of a given point (about a $1\text{--}2 \mu\text{m}$ region).

In the untreated, but leached fly ash, Cr was only found in a small ($2\text{--}5 \mu\text{m}$), rounded porous particle whose borders were irregular and ill defined. Light microscopy confirmed the presence of Cr as the green chromic oxide with some iron present. The Cr was not found within any other particles in the untreated residue either as discrete high concentrations or as regions of lower yet detectable concentrations prior to heat treatment.

In the thermally-treated fly ash, Cr was found in a number of concentrated, more easily located regions. The Cr-bearing particles were a Ca–Al silicate sphere and a slab (Fig. 1), a K–Al silicate rhomboid mantled by Ca (Fig. 2(a) and (b)), and an alumina cenosphere and an alumina mass (Fig. 3). The Cr was usually concentrated in sub-micron particles often at the edge of the particle, and within the particle as well. There was also a frequent association of Cr with Zn. Presumably, the elevations of Cr on particle surfaces and within porous particles are attributed to the migration by diffusion of Cr into adjacent particles during thermal treatment which would be aided by any liquid phases present at such high temperatures. This migration effect was clearly seen for Ca which was widely distributed in the bulk and had diffused $3\text{--}5 \mu\text{m}$ into Si-bearing phases, e.g. quartz and silicate spheres.

Cr was difficult to detect in the thermally-treated fly ash with CaCl_2 . No isolated Cr-bearing particles remained after thermal chloridization. Some Cr ($\approx 12\%$) will be shown to have become soluble and consequently leached from the residue, thus, reducing surface concentrations and apparently bulk concentrations. The results indicate that CaCl_2 allows wide spread mobilization and distribution of Cr in the fly ash after thermal treatment.

3.2. Leaching analysis

Both the TCLP and LEP tests provided similar results for the leaching behavior of Cr after thermal treatment as seen in Table 1. The Cr extracted from the thermally-treated ash was greater than from the untreated residue and was within a factor of 10 of being classified hazardous. The CaCl_2 thermally-treated samples also had increased Cr solubility to about the same extent.

It should be noted that the TCLP procedure was influenced by the formation of silica gel in the leachate creating filtration difficulty and possibly absorption of solubilized Cr

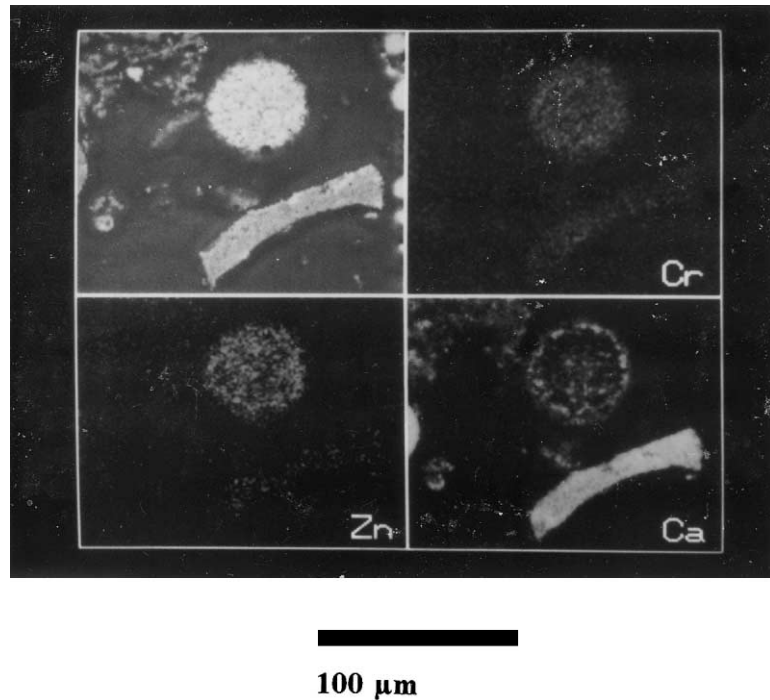


Fig. 1. Elemental mapping of a Ca-silicate sphere and slab in thermally-treated and sequentially-leached fly ash.

[17]. Since the regulation limits for Cr leachability in a non-hazardous solid is 5 ppm, the increased solubilization after thermal treatment is of concern.

The results of the residue analysis show that TCLP extraction of the untreated ash yielded no significant leaching of Cr, less than 1% of the total Cr in the ash being extracted; while the heat treated samples had 11–13% Cr extracted. The results support earlier observations [6] that Cr becomes more leachable after thermal treatment.

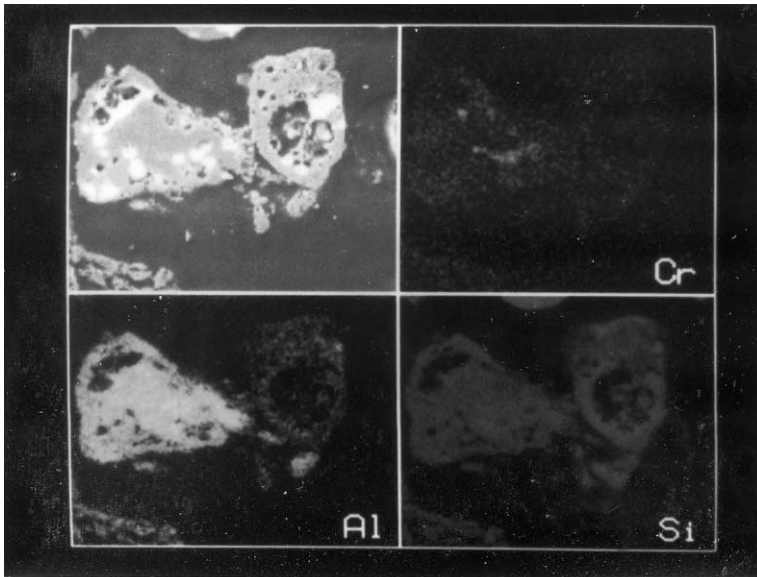
The sequential extraction procedure was used to give insight into the distribution of Cr within the fly ash. The method is beneficial in that it goes beyond the single-step leaching tests to provide more information on the characteristics of the leachability. The results

Table 1
Cr ($\mu\text{g}/\text{ml}$) in leachate from fly ash using standard leaching protocols^a

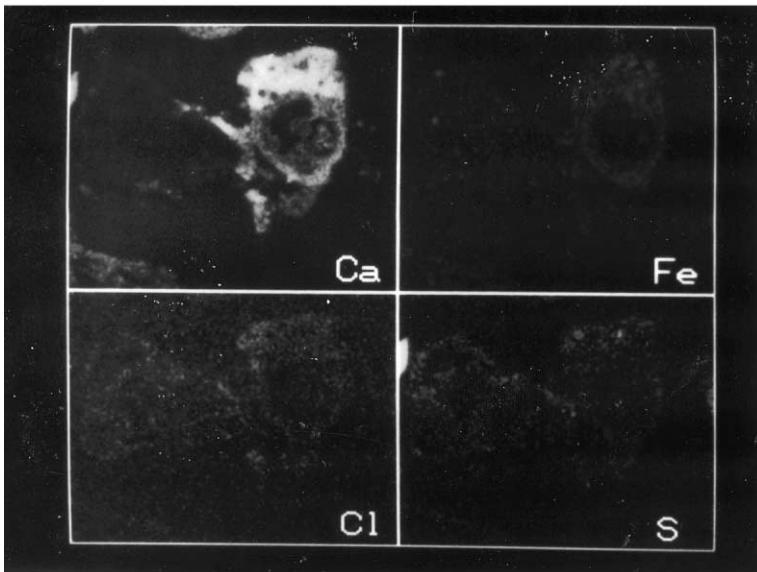
Fly ash	TCLP ^b	LEP ^b
Untreated	0.2 (4)	0.3 (5)
Heat treated	2.3 (47)	1.4 (27)
Chlorinated	1.2 (23)	1.5 (30)

^a Determination error is $\pm 10\%$.

^b Values in brackets are μg Cr leached/g fly ash.



(a)



(b)

Fig. 2. (a and b) Elemental mapping of a K-Al silicate rhomboid in thermally-treated and sequentially-leached fly ash.

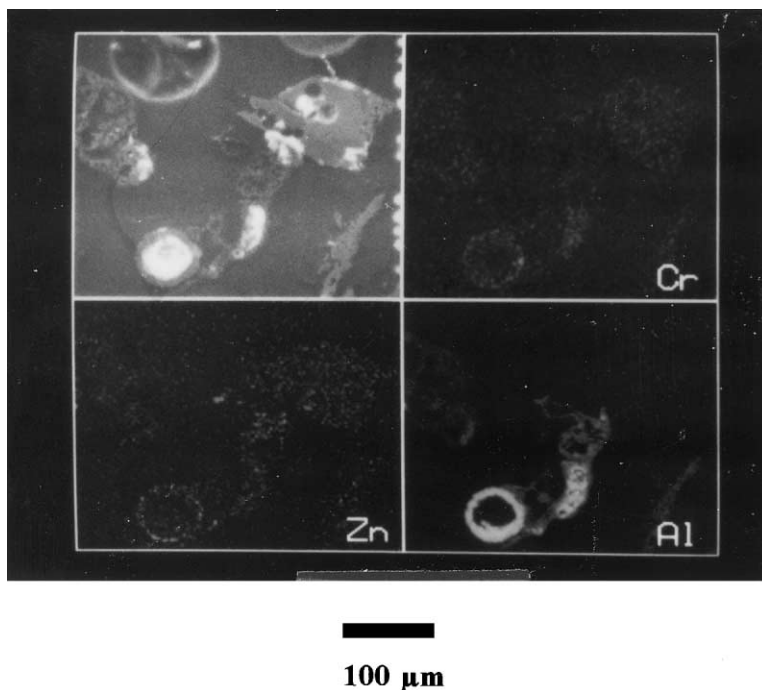


Fig. 3. Elemental mapping of an alumina cenosphere and in thermally-treated and sequentially-leached fly ash.

presented in Table 2 show that the water and acid soluble phases (A and B) are relatively small fractions of the total Cr content of the fly ash. Therefore, any treatment, which increases Cr in these fractions, would increase the environmental impact of this waste. There is also a clear trend for all of the fractions (except the inert residual fraction E) that thermal treatment with and without chloride addition, causes an increase in chromium solubilization. Fraction C is associated with the Fe–Mn oxide phases and contains two to three times the Cr available from the first two fractions and is the next most easily leached phase. A similar study of the sequential extraction was performed by Wunsch et al. [18] and similar findings were reported.

Table 2

Cr in five fractions obtained by sequential extraction from fly ash ($\mu\text{g Cr/g fly ash}$)^a

Fraction	Untreated fly ash	Heat treated fly ash	Chlorinated fly ash
A	3.6	11	29
B	4.2	4.2	7.4
C	15	31	53
D	5.5	18	37
E	503	455	361

^a Determination error is $\pm 10\%$.

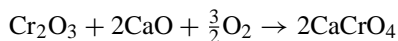
Table 3
Cr leached from Cr₂O₃ under different test conditions

Condition	Cr leached (%)	
	H ₂ O	5% HNO ₃
Cr ₂ O ₃ , no heating	<0.01	0.01
Cr ₂ O ₃ , heating	0.02	<0.01
Heating Cr ₂ O ₃ with CaCl ₂	24.7	2.23
Heating Cr ₂ O ₃ with CaO	40.9	12.8

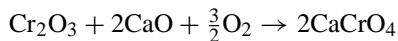
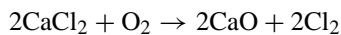
3.3. Synthetic chemical tests

The leaching tests and the characterization study indicate that chromium undergoes a chemical change during the thermal treatment. Neither SEM/EDX nor XRD was able to identify a soluble product using fly ash samples that would account for this behavior. The difficulty was the low concentration of Cr in the fly ash samples. Therefore, synthetic Cr₂O₃ was tested as a representative chromium compound in the fly ash. The Cr₂O₃ alone, and with either CaCl₂ or CaO were thermally-treated, and then leached with water and 5% HNO₃, as described in Section 2.5. The leached Cr, in terms of percent of total Cr, obtained under different test conditions are shown in Table 3. Given that a pure Cr₂O₃ was used, the solubilization (<0.03%), as expected, was very low with or without thermal treatment. Once CaCl₂ is added in the thermal treatment, however, there is a significant increase in solubility (27%). An even larger increase in soluble fraction (54%) is found when CaO is used in place of CaCl₂.

The XRD was conducted on each of the chromic oxide samples. The Cr₂O₃, whether thermally-treated or not, gave the same diffraction patterns as expected from the behavior in the leaching tests (see Table 3). The products from thermally-treated Cr₂O₃ with CaO (Fig. 4, curve 1) and with CaCl₂ (Fig. 4, curve 2) are shown as XRD 2θ values with the peaks identified. Both samples reveal the presence of calcium chromate. This species is soluble and could account for the increase in solubility of the thermally-treated Cr₂O₃ and the Cr in fly ash samples. In the synthetic chemical tests, CaO was more efficient in converting Cr₂O₃ into CaCrO₄. The likely reason is that only a single reaction step is required:



compared to the two stage chloride reactions



Although the reaction mechanism is quite clear for the synthetic chemicals, the fly ash is a much more complex material. Nevertheless, other researchers have suggested the possibility of chromate formation. Shoto and Hattori [19] in a study of solidification of a Cr-containing sludge with a glass matrix Na₂O–CaO–SiO₂ using temperatures in the range of 800–1000 °C

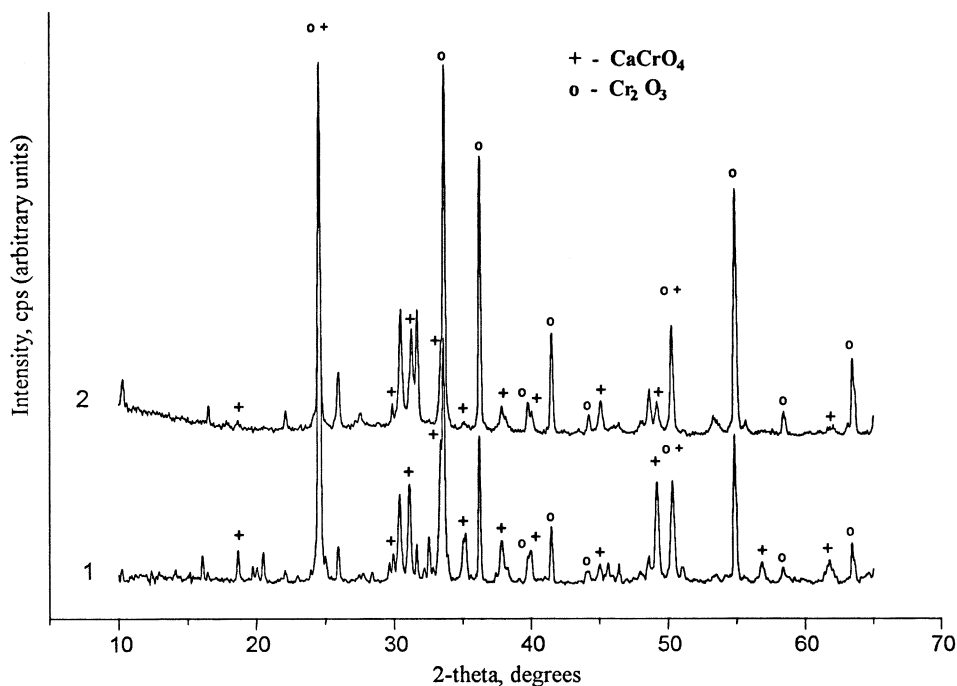


Fig. 4. XRD spectra of thermally-treated synthetic samples at 1000 °C for 30 min: Cr₂O₃ with CaO—curve 1; and Cr₂O₃ with CaCl₂—curve 2.

for 2 h reported that the residual chromium solubility was substantial and probably caused by the formation of a soluble chromate.

4. Conclusions

The Cr content of a fly ash sample from an energy-from-waste incinerator was approximately 500 µg/g. The Cr-bearing material was not uniformly distributed. A porous 2–5 µm particle of Cr₂O₃ was identified. Thermal treatment of fly ash was used to remove volatile metals such as Pb, Cd and Zn, but not Cr. After thermal treatment at 990 °C for 1 h, the fly ash sample revealed a variety of Cr-bearing particles; Cr was found both at the surface and within particles. Thermal treatment of the fly ash sample with added calcium chloride caused the Cr to disperse throughout the sample, so that no Cr-enriched particles were found. Before thermal treatment, Cr in the fly ash was essentially not leachable. However, with thermal treatment, the leachable Cr increased to about 12% of the Cr content. The speciation of the leachable Cr could not be directly identified. However, thermally-treated samples of synthetic chromium oxide with CaCl₂ or CaO produced CaCrO₄ which was leachable. Fly ash contains both CaCl₂ and CaO so that thermal treatment must be applied with caution if there is significant chromium present in the ash.

Acknowledgements

The authors thank Dr. Srebri Petrov, Department of Chemistry, University of Toronto, for his meticulous XRD work and Dr. John Graydon for his detailed SEM/EDX work.

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