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The behaviour of Al in MSW incinerator fly ash during thermal treatment

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Abstract

Fly ash from municipal solid waste (MSW) incinerators contains leachable metals, including potentially hazardous heavy metals. The metal content of the fly ash can be reduced by thermal treatment, which vaporizes the volatile metal compounds. After heat treatment of fly ash at 1000°C for 3 h, less metal was able to be leached from the thermally treated ash than from the ash without thermal treatment. Al and Cr were the exceptions. These metals were more soluble in the ash that had been thermally treated. This paper focuses on the leaching behaviour of Al only. Both simple and sequential extraction leaching tests showed that the leachable Al for the heat-treated fly ash is about twice that of the untreated fly ash. The sequential test further revealed that (i) the majority of the leachable Al is associated with Fe–Mn oxides in the fly ash, and (ii) most of the unleachable Al resides in the silicate matrices of the heat-treated and untreated fly ash. Pure chemicals, Al_2O_3, CaO and $CaCl_2$, simulating the relevant ingredients in the fly ash, were used for studying their reactions at 1000°C. The aluminum compounds were identified by X-ray Diffraction (XRD). Two new chemical phases produced by the thermal treatment were identified; $Ca(AlO_2)_2$ and $12CaO \cdot 7Al_2O_3$. Their formation suggests a mechanism whereby thermal treatment of fly ash would produce more soluble Al. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Energy from waste incineration has several attractive features as a municipal solid waste (MSW) disposal management strategy. In addition to producing energy, the

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thermal treatment reduces the volume of the waste (from trash to ash) by about 90% [1]. During incineration, the waste is converted to a residue containing almost no combustible matter and to gases emitted into the air. The coarse residue is collected from the bottom of the furnace, while the finer particulate matter, entrained by the air stream is trapped in the air pollution control devices. These finer particulates, called fly ash, are enriched with heavy metals such as lead, cadmium and zinc [1,2], which can leach into soil and ground water if the ash is disposed of in an unlined landfill. Leaching of heavy metals from the fly ash in a landfill to the environment has been a concern and received considerable attention [1,3,4]. Although the fly ash has been enriched in heavy metals, the primary matrix material is inert silicate [2,5]. One method to reduce the content of the heavy metals in fly ash is by means of heat treatment, which vaporizes the volatile heavy metal compounds [6,7], and allows separation of the contaminants from the fly ash matrix. The treated fly ash residue thus has a lower heavy metal content available for leaching. Simple heat treatment does not always produce good separation however. A more effective way to reduce the heavy metal content is to heat the fly ash in the presence of a chlorinating agent [8]. The method exploits the volatile nature of metal chlorides. By heating the fly ash with $CaCl_2$ at a high temperature (1000°C) for 3 h, the heavy metals are almost completely converted to volatile metal chlorides, as described earlier [9].

Massillamany [6] thermally treated a fly ash sample from a US energy from waste mass burn facility using various temperatures and lengths of time. No chemical additions were made to the fly ash. In a subsequent leaching test following the leaching extraction procedure (LEP) [10] using 0.5 N acetic acid solution, less metal leached out from the heat-treated ash than from the ash without heat treatment (see Table 1). However, there were exceptions. Al and Cr became more leachable from the ash that had been heat treated. The reason for this leaching behaviour of Al is the subject of the current work.

Although the work focuses on one ash source, the same leaching behavior of Al was found in two other fly ash samples, one from Canada and one from France. Massilla-

Table 1
Metal concentrations in leachate[a] before and after thermal treatment of fly ash[b] at 1000°C for 5 h (this table is quoted from Ref. [6])

Element	Untreated fly ash (mg/l)	Heat-treated fly ash (mg/l)	Regulatory limit[c] (mg/l)
Al	1.8	3.0	–
As	0	0	5.0
Cd	5.6	0	0.5
Cr	0.1	1.9	5.0
Cu	0.2	0.1	–
Pb	1.7	0	5.0
Zn	164.4	19.0	–

[a] The leachate was tested by the standard testing procedure according to Ontario Ministry of Energy and Environment (MOEE) Regulation 347.
[b] This fly ash sample was obtained from electrostatic precipitators in a MSW energy from waste incinerator in the USA.
[c] These limits are quoted from MOEE Regulation 347.

many [6] reported in his thesis that these untreated fly ashes from Canadian, French and American sources had leachable Al concentrations of 0.3, 2.1 and 1.8 ppm, respectively. After heat treatment at 1000°C for 5 h, the leachable Al concentrations increased to 0.6, 2.4 and 3.0 ppm for the three ashes. This was not a desirable outcome of the thermal treatment process, which supposedly reduces the leachable metal.

Scanning electron microscopic analysis of the heat-treated ash carried out in this laboratory [2] showed that thermal treatment caused many of the silicate spheres found in fly ash to break and expose more surface area. Massillamany [6] explained that the heat treatment exposes more aluminum silicate to the leachate solution and thus may explain the increase in aluminum extraction. The explanation was tentative. Further investigation into this matter, particularly for possible chemical transformations, was needed. In order to obtain more information on how the Al is bound and distributed within the fly ash, a sequential extraction procedure was incorporated in the current work. Furthermore, pure chemicals were used to test reaction hypotheses, and the reaction products were examined by powder X-ray Diffraction (XRD).

2. Experimental

2.1. Sample and sample treatment

The sample used in this study was fly ash from the flue gas of a US MSW incineration plant captured by an electrostatic precipitator (ESP). Grab samples of the ash collected from the ESP were passed through a 20-mesh sieve, and mixed well by a tumbling mixer in the laboratory. The major chemical composition of the fly ash was determined by a bulk chemical analysis using XRD [2] as shown in Table 2.

The well-mixed fly ash sample was divided into two portions. One portion remained untreated, the other was heat treated in a muffle furnace at 1000°C for 1 h. This temperature and time had been shown in previous work [9] to volatilize sufficient heavy metals to meet environmental regulations. Little change occurred with longer heating times. Each sample was to be subjected to sequential extraction analysis.

Table 2
Chemical composition of the fly ash (this table is quoted from Ref. [2]

Major elements elements as oxides	Wt.%	Other elements	Wt.%
SiO_2	39.1	Cl	2.4
CaO	15.0	Zn	0.84
Al_2O_3	13.6	Pb	0.40
SO_3	6.9	Cd	0.014
Na_2O	5.5		
Fe_3O_4	3.2		
TiO_2	2.8		
MgO	2.7		
K_2O	2.3		
CO_2	0.71		

2.2. Reagents

All chemicals used were analytical grade and water was passed through a reverse osmosis unit and then deionized. Nitric acid (70%, w/w) was used to prepare a 5% (v/v) solution. Lithium metaborate ($LiBO_2$) was used for fusion of the unextractable residues. Al_2O_3, CaO, and $CaCl_2$ were used for study of chemical reactions during the thermal treatment. An analytical standard stock solution of 1000 ppm Al was serially diluted to working standard solutions.

2.3. Apparatus and instrumentation

Graphite crucibles, 8 ml, porcelain crucibles, 15 ml, and a muffle furnace, Hotpack Model 4601 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; and an X-ray diffractometer, Siemens Model D 5000.

2.4. Sequential extraction procedure

In order to determine the distribution of Al in the fly ash, 0.5-g samples were extracted with various media in sequence according to the method proposed by Tessier et al. [11]. The five fractions obtained from the extraction are (A) exchangeable fraction, (B) carbonates bound fraction, (C) fraction bound to iron and manganese oxides, (D) oxidizable fraction, and (E) residual fraction, which is accomplished by fusion of the unextractable residue with lithium metaborate followed by acid dissolution.

2.5. Fusion procedure

The dried unextractable residue was mixed with 0.5 g of lithium metaborate flux in a plastic dish. The mixture was transferred to a graphite crucible and was fused at 950°C in a muffle furnace for 5 min. The molten bead was poured into a beaker containing 30 ml of 5% HNO_3 and dissolved with the aid of a magnetic stirrer. The solution, containing some loose graphite particles, was filtered and made up to 50 ml with water.

2.6. Parameters of experiments for study of chemical reactions

Al_2O_3: 204.0 mg (about the same amount of Al in the fly ash sample used for leaching test) was used in each test.

$CaCl_2$: 222.2 mg (equimolar to Al_2O_3) was used in a test.

CaO: 112.0 mg (equimolar to Al_2O_3) was used in a test.

Heating: 1 h at 1000°C.

Dissolution : After heating, the sample in a porcelain crucible was leached with water by standing overnight. The supernatant solution was decanted for Al analysis by atomic absorption spectroscopy. The water insoluble mass was then leached with 5% HNO_3 for 1 h, and the solution was also analyzed for Al.

2.7. X-ray powder diffraction (XRPD) analysis

Chemical phases in a sample were identified by XRPD, using Cu Kα radiation (34 kV, 20 mA). Once the diffraction pattern was obtained, both manual matching of the peak positions and a computer-aided search for the compounds were performed. The results were presented in an intensity -2θ format.

3. Results and discussion

3.1. Effect of thermal treatment on sequential extraction

To determine the Al distribution in the ash and the change of the distribution pattern after the thermal treatment on the fly ash, each of the fly ash samples (untreated and heat treated) was extracted following the sequential extraction procedure. The results, averages of five replicates, are shown in Table 3.

The results of the sequential extraction test provided the following information.

(1) The fractions A and B represent the water soluble and acid soluble portions of the aluminum species and correspond to the LEP test. The results support Massillamany's finding, that the leachable Al for the heat-treated fly ash is about twice the amount for the untreated fly ash. This increase in leachability is found despite the shorter thermal treatment time used in this work.

(2) The majority of the leachable Al (fraction C) is associated with Fe–Mn oxides in the fly ash and this fraction increases substantially with thermal treatment. There also was an increase in Al extracted after the oxidation step (fraction D).

(3) Most of the Al still resides in the inert silicate matrices (fraction E) of the untreated and heat-treated fly ash. After heat treatment, there is a reduction of the

Table 3
Al distribution in the leachates using sequential extraction of the fly ash, (μg Al/g fly ash)[a]

Fraction	Untreated fly ash	Heat-treated fly ash
A	200	500
B	700	1600
C	6600	16,100
D	1600	6900

Condition	Al leached (%)	
	H$_2$O	5% HNO$_3$
(1) Al$_2$O$_3$, no heating	< 0.01	0.08
(2) Heating Al$_2$O$_3$	< 0.01	0.08
(3) Heating Al$_2$O$_3$ with CaO	0.61	18.35
(4) Heating Al$_2$O$_3$ with CaCl$_2$	0.37	13.07

[a]Values are the mean of 5 determinations. Determination errors for fractions A and B are $\pm 20\%$ and for fractions C and D are $\pm 10\%$.

amount of Al associated with the silicate phase (fraction E) and an increase in the more soluble fractions.

## 3.2. Study of chemical reactions at an elevated temperature

The leaching results suggest that there must be a chemical transformation taking place for aluminum in the thermal treatment. Aluminum in fly ash has been reported to be found both as alumina and aluminum silicates by Henry et al. [12] using Fourier transform infrared spectroscopy and by our study using light microscopic analysis [2]. One hypothesis was that since fly ash contains alkaline-earth metal oxides, they may react with alumina at 1000°C to form calcium aluminate, $Ca(AlO_2)_2$. A possible reaction is:

$$Al_2O_{3(s)} + CaO_{(s)} \rightarrow Ca(AlO_2)_{2(s)} \quad \Delta G^{\circ}_{1000°C} = -45.1 \, kJ. \tag{1}$$
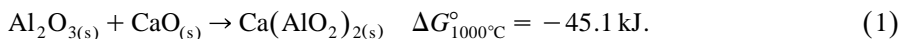
Chloride is also found in fly ash (2.4% in the sample), so that reactions with chloride and chlorine should be considered. When roasting the fly ash sample with a chlorinating agent, such as $CaCl_2$, in air at 1000°C, $AlCl_3$, a soluble compound, may form according to the following reaction:

$$Al_2O_{3(s)} + 3CaCl_{2(l)} \rightarrow 2AlCl_{3(g)} + 3CaO_{(s)} \quad \Delta G^{\circ}_{1000°C} = 552 \, kJ. \tag{2}$$
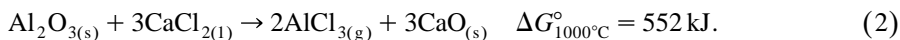
The positive ΔG° value indicates the reaction is not favourable and this is supported by experimental data. Furthermore, $AlCl_3$ sublimes readily at 190°C [13] and cannot be retained in the residue if produced. Previous work [14] showed that all the Al was retained in the residue and no Al was found in the volatile matter when the fly ash was roasted at 1000°C. Thus, reaction (2) does not appear to be significant. Alternatively, the reaction may proceed as:

$$Al_2O_{3(s)} + CaCl_{2(l)} + 1/2O_2 \rightarrow Ca(AlO_2)_{2(s)} + Cl_2 \quad \Delta G^{\circ}_{1000°C} = 60.9 \, kJ. \tag{3}$$
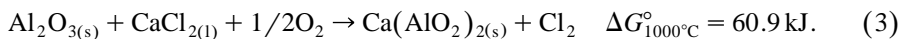
Again the ΔG° is not favourable.

If either reaction (1) or (3) takes place, Al should be able to be detected in the leachate of the thermally treated fly ash, since $Ca(AlO_2)_2$ is soluble in water [13]. The fact that Al was leached from the heat-treated fly ash does not necessarily reveal the soluble salt phase nor confirm the presence of $Ca(AlO_2)_2$. The leachable Al fraction is much less than 1% wt. of the sample, and the analytical tools, such as XRD, could not identify the new phase in the residue. Therefore, synthetic samples (pure chemicals) had to be used for testing to uncover the chemical reactions. For the synthetic samples, heating and leaching were conducted in the same porcelain crucible to avoid the risk of sample loss due to sample transfer, and a simple water leach and dilute acid (5% HNO_3) leach were used. An initial experiment of heating Al_2O_3 in a muffle furnace at 1000°C for 1 h followed by the leaching indicated that no appreciable amount of Al was in the leachates. The result was expected since Al_2O_3 is insoluble in water and dilute acids. Next, experiments were carried out in the same way by heating Al_2O_3 with equimolar

CaO or $CaCl_2$ to determine whether reaction (1) or (3) might be initiated. This was followed by leaching the solid products first in water and then in 5% HNO_3, and the concentrations of Al in the leachates were determined (see details in Section 2.6). The soluble Al, in terms of percent of total Al, obtained under different test conditions are shown in Table 3.

Conditions (1) and (2) show that heating Al_2O_3 alone does not alter its insoluble nature; heating with CaO or $CaCl_2$ (conditions (3) and (4)), show that a small amount of Al ($< 1\%$) was water soluble, but about 10% to 20% of the Al_2O_3 was converted to an acid soluble aluminum compound.

Next, additional thermally treated products were prepared using the same conditions as above for compositional analysis. The solid products from heating synthetic mixtures of (i) Al_2O_3 with CaO and (ii) Al_2O_3 with $CaCl_2$ were examined by powder XRD. Figs. 1 and 2 are the powder XRD spectra. For heating with CaO, case (i), two new chemical phases were identified, $Ca(AlO_2)_2$ and $12CaO \cdot 7Al_2O_3$. An unidentified cubic phase also was found. For heating with $CaCl_2$, case (ii) only the phase of $12CaO \cdot 7Al_2O_3$ was identified; and as expected, $AlCl_3$ was not found. Both chemical phases are soluble in water and in acidic solution [15]. The reason why the water leach does not result in much solubilization is understandable. The water leachate of the heat-treated sample is quite alkaline due to the presence of CaO in the sample, which likely prevents the Al compounds from dissolution. Nitric acid removes the CaO and exposes the soluble Al species. The XRD results demonstrate that reaction (1) could occur, but do not support reaction (3), since no $Ca(AlO_2)_2$ was found in the $CaCl_2$ reaction. These findings are consistent with the thermodynamic data, which indicate that reaction (1)
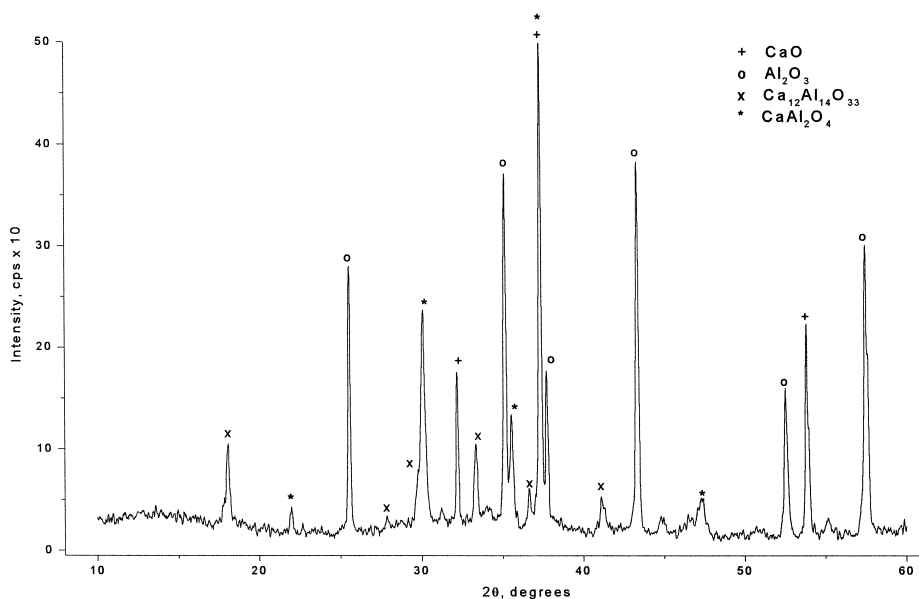

Fig. 1. XRPD spectrum of thermally treated Al_2O_3 with CaO at 1000°C for 1 h.
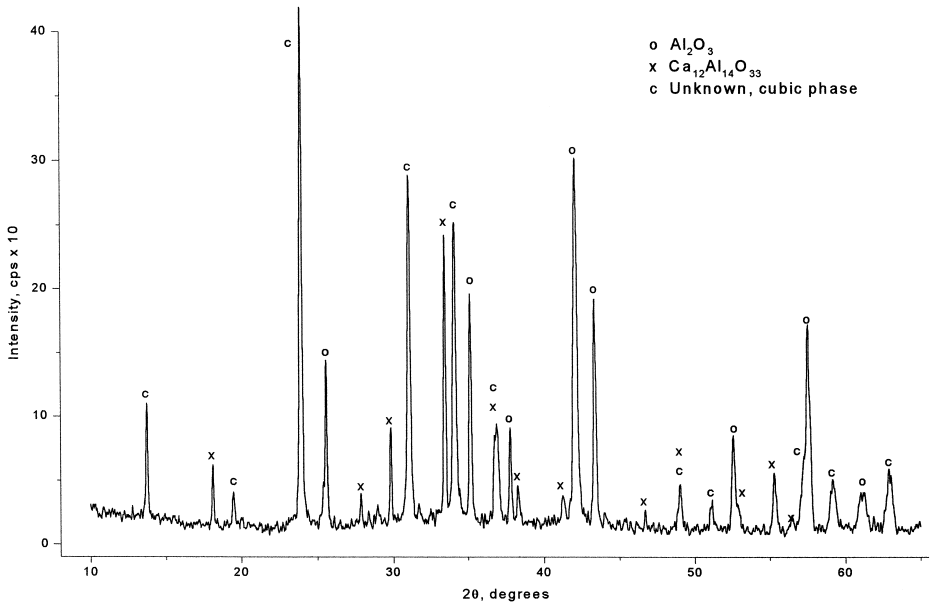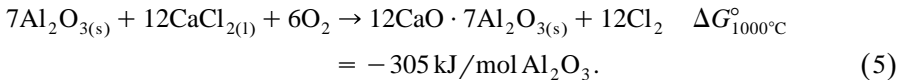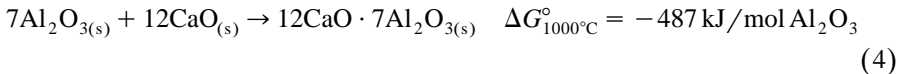
Fig. 2. XRPD spectrum of thermally treated Al_2O_3 with $CaCl_2$ at 1000°C for 1 h.

with a $\Delta G°$ value of -45.1 kJ is favourable while reaction (3) with a $\Delta G°$ of $+60.9$ kJ is not. The XRD results also suggest two additional possible reactions:

$$7Al_2O_{3(s)} + 12CaO_{(s)} \rightarrow 12CaO \cdot 7Al_2O_{3(s)} \quad \Delta G°_{1000°C} = -487 \, kJ/mol \, Al_2O_3 \tag{4}$$

$$7Al_2O_{3(s)} + 12CaCl_{2(l)} + 6O_2 \rightarrow 12CaO \cdot 7Al_2O_{3(s)} + 12Cl_2 \quad \Delta G°_{1000°C}$$
$$= -305 \, kJ/mol \, Al_2O_3. \tag{5}$$

Given the low conversion of Al_2O_3 to a soluble form in the fly ash sample, the relative dominance of reactions (1), (4) and (5) was not able to be resolved.

The work has shown that the behavior of relatively refractory materials such as aluminum oxides or silicates can become more soluble during thermal heating as a result of reaction with calcium compounds because of formation of calcium aluminum oxides. While the extent of soluble oxide formation from fly ash is relatively low, more concentrated forms of aluminum and calcium such as alumina and lime produced 18% soluble Al as calcium aluminum oxides. Thus, the combination of aluminum and calcium wastes in thermal stabilization treatment processes should be carefully investigated.

Acknowledgements

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