Behaviour of metals under the conditions of roasting MSW incinerator fly ash with chlorinating agents

Chris C.Y. Chan, Donald W. Kirk *

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 3E5

Abstract

A total elemental analysis was performed on a municipal solid waste (MSW) fly ash sample, before and after it was treated at 1000°C, to reveal the metal distribution between the volatile matter and the ash residue. Metals such as Pb, Zn, Cd, and to a lesser degree, Cr, Mn and Ni, were volatilized. Addition of chlorinating agents generally increased the volatility of certain elements. More acid resistant compounds were formed in the ash residue after the heat treatment using $CaCl_2$ as a chlorinating agent. The efficiencies of volatilization of the metals, using Cl_2 as a chlorinating agent, were generally higher compared with using $CaCl_2$. However, $CaCl_2$ was found to be a more selective chlorinating agent for volatilizing the heavy metals of concern, i.e., Pb, Cd, Zn and Cu. The efficiencies of volatilization of the recovered metals were approximately proportional to their standard free-energy changes ($\Delta G°$) for the corresponding chlorination reactions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Municipal solid waste (MSW) fly ash; Roasting; Chlorinating agent; Heavy metal; Volatilization efficiency

1. Introduction

Fly ash from municipal solid waste (MSW) incinerators is potentially a hazardous material due to its elevated levels of leachable heavy metals, such as Pb and Cd [1,2]. Effective handling and safe disposal of the fly ash depends upon thorough understanding

---

* Corresponding author. 200 College St., Toronto, Ontario, Canada, M5S 3E5. Tel.: +1-416-978-7406.

of its chemical properties. On the profitable side, MSW fly ash can be considered a mineral resource due to the enrichment of some metals which have economic values if they are separated. The extraction of these metals requires knowledge of how the elements are bound in the ash. Recently, a method was developed in our laboratory [3] for removal of the heavy metals from the fly ash. The method is based on the volatilization of the heavy metals as chlorides by way of roasting of the fly ash with a chlorinating agent. Not all the metals in fly ash are in chloride form. Many studies indicate that although heavy metals exist in fly ash mainly as chloride, some occur as oxide, sulphate, silicate, and complex compounds [1,4]. These compounds have very different thermal behaviour. In general, chlorides have lower melting and boiling points than oxides and sulphates. Upon heating, sulphates usually decompose to form oxides [5]. Consequently, the metals in chloride form are likely to be removed easier than the metals in oxide or sulphate form. To be effectively volatilized, the metals have to be in or converted to chloride form. The addition of a chlorinating agent is to convert the metals into the chloride form for subsequent volatilization.

In order to better understand the thermal behaviour of these metals in fly ash, accurate information about the metal content in fly ash and in the volatile matter from roasting is required. Difficulty of obtaining complete aqueous digestion of MSW fly ash has been noted by several workers [6,7]. Although Cahill and Newland [8] found that the strong acid digestion $(HF–HClO_4)$ dissolved the ash particles completely and provided total metal concentrations, Fernandez et al. [9] reported that strong acid digestion (with aqua regia/HF and $HF/HClO_4$) dissolved the sample 'almost totally.' The fact remains that after digestion of the fly ash sample with whatever kind of strong acid, some residue, no matter how minute, is always retained. The incomplete digestion can lead to inaccurate analytical results, and thus erroneous interpretation.

This paper presents the results of complete elemental analyses of fly ash using the sample dissolution technique of strong acid digestion in combination with fusion of the acid resistant residue to account for the total elemental content. The efficiencies of volatilization of metal chlorides from using $CaCl_2$ and Cl_2 as chlorinating agents were compared. In addition, the efficiencies of volatilization of metal chlorides were correlated with the standard free energy changes for their chlorination reactions.

2. Experimental

2.1. Heating apparatus and analytical instruments

A tube furnace; Carbolite Model Tzf 12/75, with a programmed temperature controller, Model 808 P; a quartz tube, 100 cm long and 3 cm i.d. to contain the sample boat and to confine the heating space; a gas absorber containing 5% HNO_3 to absorb the volatile metal chlorides; air supply from a cylinder; Teflon beakers, 30 ml capacity, for digestion of samples with HF and other acids; graphite crucibles, 8 ml size, for fusion of acid resistant residues in a muffle furnace; atomic absorption spectrometer, Perkin-Elmer Model 703; inductively coupled plasma spectrometer, Spectro Analytical Instruments Model Spectroflame P; X-ray diffractometer, Philips Model PW 1120-60.

2.2. Reagents

All chemicals used were analytical grade and water was passed through a reverse osmosis unit and deionized. Nitric acid (70%, w/w), hydrofluoric acid (49%, w/w), and perchloric acid (60%, w/w) were used for digestion of samples; lithium metaborate (LiBO$_2$) for fusion of acid resistant residues; 1000 ppm standard solutions of Pb, Cu, Zn, Cd, Cr, and Mn; chlorinating agents included calcium chloride and chlorine gas supplied from a small cylinder.

2.3. Sample

The fly ash used in this study was from the flue gas of a MSW incineration plant captured by electrostatic precipitators. Grab samples of the ash collected from the electrostatic precipitator were passed through a 20 mesh sieve, and mixed well by a tumbling mixer in the laboratory.

2.4. Procedures for roasting samples and collection of volatile matter

2.4.1. Roasting with CaCl$_2$

A sample and the chlorinating agent (CaCl$_2 \cdot$ 2H$_2$O) which was in powder form, were weighed out. They were thoroughly mixed and transferred to a sample boat. The sample boat was then pushed with a steel rod into the mid-section of the quartz tube. (The set-up of the roasting system and the general roasting parameters were the same as described in a previous paper [3]).

During roasting of the fly ash, air was introduced into the furnace at a flow rate of 150 ml/min to entrain the volatile matter. On leaving the furnace, part of the volatile matter condensed on the wall of the quartz tube outside the heating zone and on the condensation tube; the rest of the volatile matter was absorbed in 5% (v/v) HNO$_3$ solution in a scrubber. After the roasting, the condensed volatile matter was dissolved in 5% (v/v) HNO$_3$. It was combined with the solution in the scrubber. The combined solution contained all the volatile matter, and the elements in the solution were determined by instrumental analytical techniques.

2.4.2. Roasting with Cl$_2$ gas

Same as in Section 2.4.1 except Cl$_2$ gas was used instead of CaCl$_2$. Chlorine from a small cylinder was introduced into the pre-heated furnace with the sample in place at 900°C. The air carrier flow rate was the same at 150 ml/min. Within the next 10 min, the temperature of the quartz tube reached 1000°C. The chlorine flow rate was controlled by a chlorine resistant regulator. At the end of roasting, the chlorine flow was turned off.

2.5. Procedure for determination of total elemental content in fly ash

A 0.5 g sample of fly ash was digested with approximately 6 ml of the concentrated acid mixture, HNO$_3$:HF:HClO$_4$ (4:2:1) in a Teflon beaker on a hot plate and heated to

near dryness until dense white fumes appeared. The contents were digested once more with approximately 4 ml of the acid mixture, and heated to near dryness. One milliliter of HNO_3 was added followed by 1 ml of water. The contents were heated for a few minutes, then cooled and diluted with approximately 30 ml of 5% (v/v) HNO_3. The solution was filtered through a Whatman No. 4 filter paper, and made up to 50 ml with water (solution 1).

The undissolved residue, although minute, contained some refractory chemical compounds that should be accounted for if an accurate analysis is desired. To determine the chemical elements in this acid resistant matter, the following steps were followed. The dried residue was mixed with 0.5 g of lithium metaborate flux in a plastic dish. The mixture was transferred to an 8 ml 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 (solution 2).

Solution 1 along with solution 2 were used for determination of the chemical elements which accounted for the total content of the elements in the fly ash sample.

2.6. Procedure for X-ray powder diffraction (XRPD) analysis

Chemical phases in a sample were identified by XRPD, using Cu-Kα radiation (34 kV, 20 mA). The diffraction pattern was captured on a film in a Guinier-de Wolff focusing camera. The film data were digitized using a photo densitometer; and the results were compared with the standard data sets using the Rigaku IBM search match program.

3. Results and discussion

3.1. Chemical content of the fly ash

Before starting the study of the thermal behaviour of the metals in fly ash, the total content of the elements in the fly ash sample was needed. By comparison with their original amounts, the degree of change or removal of the metals due to the thermal treatment could be quantified.

Following the procedure for determination of total content of chemical elements, a fly ash sample was digested and the insoluble residue was fused and dissolved. The solutions were analyzed for chemical elements using inductively coupled plasma spectrometry (ICP). The sum of the content of an element in both solutions accounted for the total content of the element in the fly ash sample. The results for 32 elements are shown in Table 1.

All the results shown in the tables throughout this work are the mean values of duplicate analysis. Whenever duplicate analysis differed by more than 10%, additional samples were run until the combined error was within ±10%.

Table 1
Chemical contents of 32 elements in fly ash ($\mu g/g$). Elements were determined by ICP following sample dissolution

	Direct digestion (1)	Fusion residue (2)	Total (3)
Pb	3870	<1	3870
Cu	1030	2	1030
Zn	9450	14	9460
Cd	142	<1	142
Cr	230	135	365
Mn	1900	14	1910
Na	49400	66	49500
K	24400	<1	24400
Mg	12200	100	12300
Ca	106000	114	106000
Fe	18500	126	18600
Al	69600	1540	71100
Ti	17700	940	18600
Be	2	<1	2
P	6800	30	6830
Sc	5	<1	5
V	58	<1	58
Co	31	<1	31
Ni	207	<1	207
As	60	<1	60
Sr	444	1	445
Y	8	<1	8
Zr	167	4	171
Mo	43	<1	43
Ag	27	<1	27
Sn	259	71	330
Sb	526	<1	526
Ba	918	16	934
La	18	<1	18
W	21	<1	21
Bi	8	4	12
Hg	0.4	<0.1	0.4

Besides the refractory elements, most of the elements, such as Pb, Cu, Zn, and Cd, were small in quantity in the acid resistant residue (column (2), Table 1). Those small quantities can be ignored when referring to the total content of the elements in the fly ash, if great accuracy is not required. Si, a main ingredient in fly ash, was not included in this analysis, since Si was vaporized as SiF_4 during the digestion of the sample with HF.

A bulk chemical analysis of the fly ash using X-ray technique was done by Graydon and Kirk [1], and the results are given in Table 2. On the left hand side are the major elements expressed as their oxides, Si, Ca and Al being the main ingredients of fly ash. On the right are the minor elements. The last three are the soluble heavy metal salts that constitute the environmentally important species in fly ash.

Table 2
Typical chemical analysis of fly ash[a]

Major elements	Weight (%)	Other elements[b]	Weight (%)
SiO_2	39.1	SO_3	6.9
CaO	15.0	Cl	2.4
Al_2O_3	13.6	CO_2	0.71
Na_2O	5.5	Zn	0.84
Fe_3O_4	3.2	Pb	0.40
TiO_2	2.8	Cd	0.014
MgO	2.7		
K_2O	2.3		

[a]This table is quoted from Ref. [1].
[b]P_2O_5, C, and MnO are not included.

3.2. Effect of thermal treatment on the refractory elements in fly ash

After the fly ash was roasted with $CaCl_2$, the ash was more difficult to digest by acids compared to the fly ash without a heat treatment. It was observed that more acid resistant residue remained after digestion of the roasted fly ash. This indicates that some changes of the non-volatile compounds occurred during roasting. In order to compare these refractory elements before and after the heat treatment, a total elemental analysis in a different way was needed. This was done in the following manner.

A 3 g fly ash sample with the addition of 0.622 g of $CaCl_2 \cdot 2H_2O$ (0.3 g Cl) was heated at 1000°C for 3 h. The volatile matter was captured and dissolved in a 5% HNO_3 solution (solution 1). An aliquot of the ash residue was digested with the acid mixture, HNO_3:HF:$HClO_4$ (4:2:1), and the solution was diluted with 5% HNO_3, (solution 2). The ash residue cannot be completely dissolved by digestion with the acid mixture. This acid resistant matter was treated with fusion followed by dissolution in 5% HNO_3 (solution 3) as described in the procedure for determination of total elemental content in Section 2. The solutions 1–3 were used for determination of the chemical elements by ICP. The results for 32 elements are shown in Table 3, columns (1–3), respectively. The sum of the content of an element in each solution represents the total content of the element in the fly ash. These sums (column (4), Table 3) agree well with the total content obtained by direct digestion method as shown in column (3), Table 1.

Judging the values in Table 1, column (2) and Table 3, column (3), one can see that the acid resistant matter from both methods (volatilization vs. direct digestion) contained substantial amounts of Mg, Ca, Fe, Al, and Ti. Moreover, the indigestible ash residue from the heat-treated fly ash sample contained more of these elements than the indigestible fly ash sample did. This suggests that after heat treatment with $CaCl_2$, new compounds which are acid resistant in nature, were formed. XRPD analysis showed that more crystalline compounds existed in the heat-treated fly ash sample than in the untreated one. Two chemical phases, pyroxene, $Ca(Mg,Al)(Si,Al)_2O_6$ and anorthite, $CaAl_2Si_2O_8$, were identified in the heat treated sample, but not found in the untreated fly ash. All the elements under study formed more acid-resistant compounds after heat treatment, except Cr and Sn which formed more acid-soluble compounds.

Table 3
Chemical contents of 32 elements in fly ash (μg/g). Elements were determined by ICP following heat treatment and sample dissolution

	Volatile (1)	Ash digest (2)	Fusion residue (3)	Sum (4)
Pb	3670	136	9	3820
Cu	933	138	11	1080
Zn	9130	392	24	9550
Cd	140	4	< 1	144
Cr	24	284	41	347
Mn	746	1110	88	1940
Na	37 300	12 100	513	49 900
K	22 700	1650	103	24 500
Mg	4	9380	2670	12 100
Ca	152	148 000	6190	154 000[a]
				(101 000)[b]
Fe	83	15 900	1770	17 800
Al	1	59 800	9160	69 000
Ti	< 1	16 700	1350	18 100
Be	< 1	4	< 1	4
P	8	6520	125	6650
Sc	< 1	4	< 1	4
V	1	49	6	56
Co	12	21	< 1	33
Ni	58	137	3	198
As	< 1	58	< 1	58
Sr	1	415	14	430
Y	< 1	8	1	9
Zr	< 1	131	46	177
Mo	2	31	5	38
Ag	7	5	1	13
Sn	< 1	346	22	368
Sb	< 1	526	8	534
Ba	3	542	172	717
La	< 1	18	< 1	18
W	< 1	18	< 1	18
Bi	11	< 1	< 1	11
Hg[c]	0.3	< 0.1	< 0.1	0.3

[a] The 0.622 g $CaCl_2 \cdot 2H_2O$ added to the 3 g sample contained 0.158 g of Ca, moisture being excluded. Therefore, the Ca added per gram sample = 158 000 μg × 1/3 = 52 600 μg. This amount should be excluded for mass balance calculation.
[b] That is, 154 000 − 52 600 = 101 000 μg Ca per gram sample.
[c] Hg was analyzed by cold vapour AAS.

It is also interesting to note that the Hg content is very low in the fly ash sample. Hg is an element of environmental concern. When the MSW is incinerated, Hg remains in the gas phase throughout the entire process. It undergoes volatilization but not condensation. The temperature of the exit gas from the incinerator is about 330°C, too high for Hg to condense. The vapour pressures of Hg and $HgCl_2$ at that temperature are 0.57 and 2.09 atm, respectively [10]. As expected, there is little chance for Hg to remain in the fly ash, which is consistent with our finding.

3.3. Chemical phases in the volatile matter

The volatile matter accumulated in the condensation tube was a yellowy and greenish powder. The sample was examined by XRPD. Because of its highly hygroscopic nature, the volatile matter was collected in a dry-air environment, and was immediately sealed by a non-crystalline organic cement to prevent absorption of moisture. Three chemical phases, $Na_2ZnCl_4 \cdot 3H_2O$, K_2ZnCl_4 and KPb_2Cl_5, were identified, the former being the most dominant one. Halite (NaCl), a prominent phase identified in the fly ash, disappeared from the ash residue after heat treatment due to volatilization or reaction. It was not found in the volatile matter except as the double salts. These findings indicate that the volatilized heavy metals, such as Pb and Zn, were in the form of chloride, and in the process of volatilization the metal chlorides tend to form double salts. The double salts exist not only in the volatile matter, but also, to a lesser degree, in the raw fly ash where potassium–zinc–lead chloride and K_2ZnCl_4 were detected by Graydon and Kirk [1]. The suggestion by Jakob et al. [11] that the heavy metals in fly ash can be evaporated as chlorides in air at the roasting temperatures of 850–1030°C is supported by this work.

3.4. Effect on volatilization using Cl_2 as chlorinating agent

The effect on volatilization of metals from the fly ash depends on many factors as reported in our previous study [3]. Among them are the type of chlorinating agents and
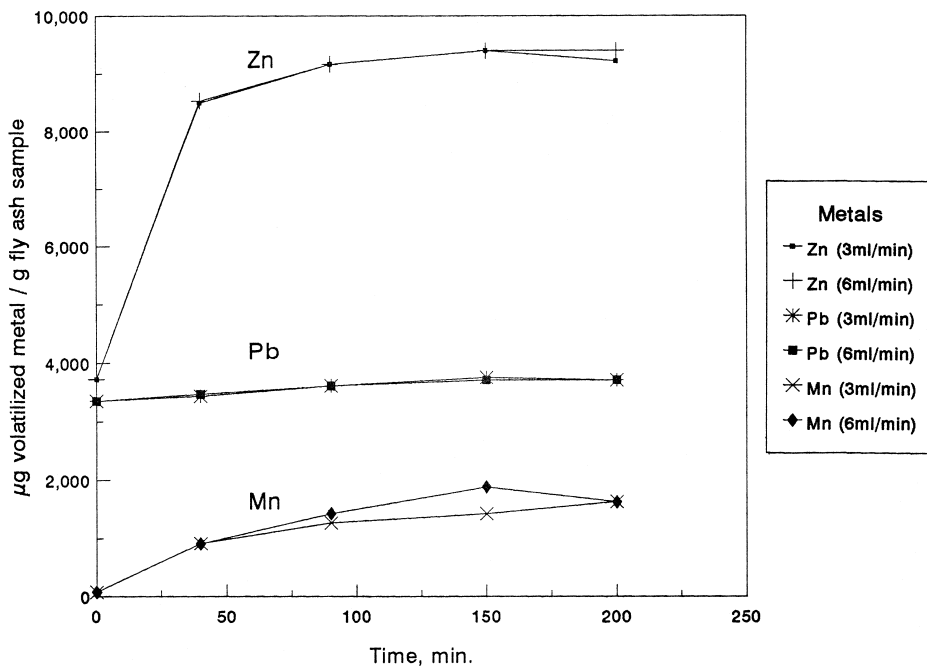

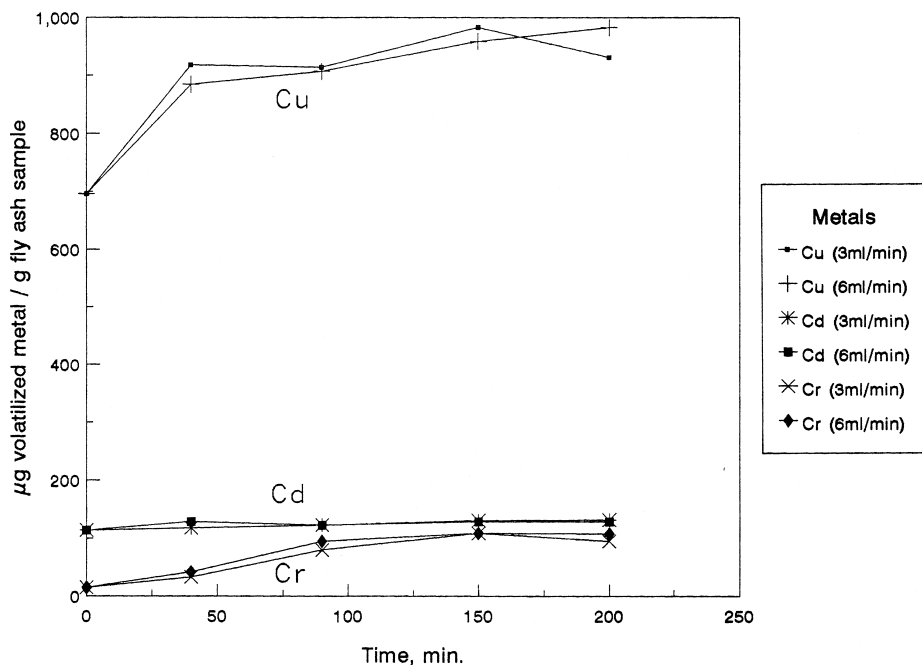Fig. 1. Effect of heating time on Zn, Pb and Mn volatilized. Cl_2 flow rate: 3 ml/min and 6 ml/min.

Fig. 2. Effect of heating time on Cu, Cd and Cr volatilized. Cl_2 flow rate: 3 ml/min and 6 ml/min.

the quantity of the agents used. A number of solid chlorinating agents, such as $CaCl_2$, $MgCl_2$, NaCl, and $AlCl_3$, have been tested for their effectiveness. In addition, a gaseous chlorinating agent (chlorine) was chosen and its effect on volatilization was tested. The effect on volatilization of six elements (Pb, Cu, Zn, Cd, Cr, and Mn) of concern at reaction periods of 40, 90, 150, and 200 min, with Cl_2 at each of the two flow rates (3 and 6 ml/min), equivalent to 0.02 and 0.04 atm partial pressures, was examined. Chemical analysis of the captured volatile matter was done by atomic absorption spectroscopy (AAS). The quantities of the elements volatilized are plotted as a function of time in Figs. 1 and 2. The figures show that: (i) maximum volatilization of the above elements is reached at about 150 min, and (ii) there is no significant difference in effect on volatilization whether the Cl_2 is at 0.02 or 0.04 atm partial pressure (flow rate at 3 or 6 ml/min).

3.5. Comparison of effect on volatilization using $CaCl_2$ vs. Cl_2

A metal oxide can react with $CaCl_2$ at 1000°C to form metal chloride in two possible ways.

(a) Direct chlorination, where direct contact between the two reactants exists, such as

$$MO + CaCl_2 \rightarrow MCl_{2(g)} + CaO \tag{1}$$

(b) Indirect chlorination, where the overall reaction is separated into two stages.

$$CaCl_2 + \frac{1}{2}O_2 \rightarrow CaO + Cl_2 \tag{2}$$

$$MO + Cl_2 \rightarrow MCl_{2(g)} + \frac{1}{2}O_2 \tag{3}$$

The first stage is generation of chlorine, and the second stage is formation of the volatile metal chloride. The performance of the second stage is very much dependent upon the first stage. If there is not enough Cl_2 produced from the first stage or the Cl_2 is produced too slowly, the second stage would be hindered, and the formation of the metal chloride would be less complete or slow. It is therefore expected that using Cl_2 straight for the chlorination of a metal oxide should be more effective. In order to better understand the chlorination mechanism, it is important to know the difference made, from using a solid chlorinating agent such as $CaCl_2$ against using a gaseous chlorinating agent such as Cl_2. In the latter case, Cl_2 was introduced at the flow rate of 3 ml/min ($p_{Cl_2} = 0.02$ atm) for 3 h. The rest of the heating parameters remained the same as given in Section 2. The ICP analytical results of the volatile matter for 32 elements, using Cl_2 as the chlorinating agent, are shown in Table 4, column 4. The parallel results obtained from using $CaCl_2 \cdot 2H_2O$ are also tabulated in column 3. For comparison of the effectiveness of the two chlorinating agents, a term 'efficiency of volatilization', E, is used which is defined as the percentage of the amount of a metal volatilized.

In general, the E values from using Cl_2 are higher than those from using $CaCl_2$. This suggests that when $CaCl_2$ is used as a chlorinating agent, the reaction (or part of) follows the route of indirect chlorination (Eqs. (2) and (3)). The effectiveness of using Cl_2 relative to $CaCl_2$ for volatilization of the above elements can be summarised as follows.

(1) Of the six elements (Pb, Cu, Zn, Cd, Cr, and Mn) of interest, Cl_2 is about as effective for Pb and Cd, slightly more effective for Cu and Zn, and very much more effective for Cr and Mn (note that Cr is still largely unconverted).

(2) Cl_2 is as effective for Na and K.

(3) Cl_2 is more effective for Mg than for Ca, although both elements have a low efficiency of volatilization.

(4) Cl_2 is significantly more effective for Fe. More than half of the Fe can be recovered compared with practically no recovery at all when $CaCl_2$ is used.

(5) By using Cl_2, the good yields of Co and Ni improve into full recoveries.

(6) Cl_2 is significantly more effective for V, Mo, Sn, and Sb as can be seen, even though these elements are in small quantities in the fly ash.

The other reasons for Cl_2 to be more effective than $CaCl_2$ include the following.

(1) The $\Delta G°$ value for the chlorination reaction is smaller. Take ZnO for example.
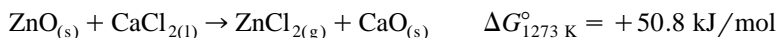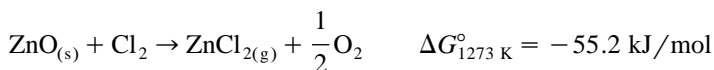
$$ZnO_{(s)} + Cl_2 \rightarrow ZnCl_{2(g)} + \frac{1}{2}O_2 \qquad \Delta G°_{1273\ K} = -55.2\ kJ/mol$$

$$ZnO_{(s)} + CaCl_{2(l)} \rightarrow ZnCl_{2(g)} + CaO_{(s)} \qquad \Delta G°_{1273\ K} = +50.8\ kJ/mol$$

Table 4
Effect of chlorinating agents (Cl_2 vs. $CaCl_2 \cdot 2H_2O$) on volatilization of 32 elements in fly ash sample, heating at 1000°C for 3 h. Values are in $\mu g/g$ sample

Element	Total	Volatile matter		E (%)	
		$CaCl_2$	Cl_2	$CaCl_2$	Cl_2
Pb	3870	3670	3720	94.8	96.1
Cu	1030	933	1010	90.5	98.0
Zn	9460	9130	9500	96.5	100
Cd	142	140	145	98.5	100
Cr	365	24	133	6.5	36.4
Mn	1910	746	2020	39.0	100
Na	49 500	37 330	37 400	75.3	75.5
K	24 400	22 700	22 000	93.0	90.1
Mg	12 300	4	1200	< 0.1	9.7
Ca	105 900	152	1000	< 0.1	0.9
Fe	18 600	83	11 000	0.4	59.1
Al	71 120	1	60	< 0.1	< 0.1
Ti	18 610	< 1	< 1	0	0
Be	2	< 1	< 1	< 0.1	< 0.1
P	6830	8	86	0.1	1.2
Sc	5	< 1	< 1	< 0.1	< 0.1
V	58	1	40	1.7	68.9
Co	31	12	33	38.7	100
Ni	207	58	210	28.0	100
As	60	< 1	10	< 0.1	16.6
Sr	445	1	3	0.2	0.6
Y	8	< 1	< 1	< 0.1	< 0.1
Zr	171	< 1	< 1	0	0
Mo	43	2	40	4.6	93.0
Ag	27	7	10	25.9	37.0
Sn	330	< 1	320	< 0.1	96.9
Sb	526	< 1	480	< 0.1	91.2
Ba	934	3	10	0.3	1.0
La	18	< 1	< 1	< 0.1	< 0.1
W	21	< 1	< 1	< 0.1	< 0.1
Bi	12	< 1	24	< 0.1	100
Hg	0.4	0.3	0.4	75.0	100

The ΔG_f° for $CaCl_{2(l)}$ and $CaO_{(s)}$ at 1273 K are -604.7 and -498.7 kJ/mol, respectively [12]. There is always $-498.7 - (-604.7) = 106$ kJ/mol higher energy required for the chlorination reaction if $CaCl_2$ is used instead of Cl_2.

(2) Cl_2 is particularly effective for volatilizing Fe. The volatile compounds likely are $FeCl_2$ (b.p. 1023°C) and $FeCl_3$ (b.p. 316°C). With $CaCl_2$ as chlorinating agent, however, CaO was produced which could combine with the Fe_2O_3 to form the stable Ca ferrite, $CaO \cdot Fe_2O_3$, thus preventing the Fe from forming the volatile compounds.

Although Cl_2 is more effective for volatilizing almost every element under study, that does not necessarily make it the better choice as a chlorinating agent. In some applications of volatilization, selectivity is a more important factor. If the recoveries are only concerned with certain heavy metals, such as Pb, Cu, Zn, and Cd, which provide an

economic value, and if simple matrices of the volatile matter is desired in order to facilitate subsequent chemical separation, then, $CaCl_2$ would be preferable to Cl_2 as a chlorinating agent as in the case of roasting fly ash.
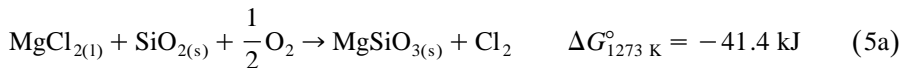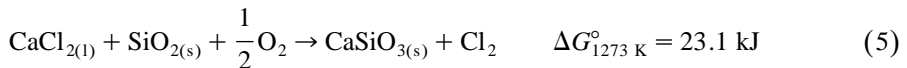
3.6. Silica effect on chlorination

The reaction of chlorination of metal oxides by chlorides can be greatly enhanced by the addition of an acid oxide [13], such as SiO_2, that leads to the formation of silicate.

$$MO_{(s)} + CaCl_{2(l)} + SiO_{2(s)} \rightarrow MCl_{2(g)} + CaSiO_{3(s)} \tag{4}$$
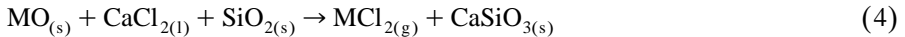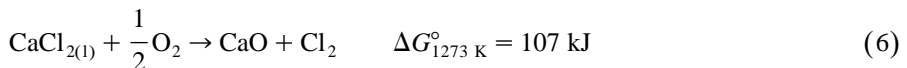
This reaction is used in the recovery of non-ferrous metals from pyrite cinder [13].

As a major component of the fly ash [14], silica may enhance the ability of the chlorinating agent in a similar way under oxidizing conditions to release chlorine by forming silicates. For example,

$$CaCl_{2(l)} + SiO_{2(s)} + \frac{1}{2}O_2 \rightarrow CaSiO_{3(s)} + Cl_2 \qquad \Delta G^\circ_{1273\ K} = 23.1\ kJ \tag{5}$$

$$MgCl_{2(l)} + SiO_{2(s)} + \frac{1}{2}O_2 \rightarrow MgSiO_{3(s)} + Cl_2 \qquad \Delta G^\circ_{1273\ K} = -41.4\ kJ \tag{5a}$$

The available Cl_2 then attacks the metal oxides to form metal chlorides as shown in Eq. (3). In fact, reaction (5) was suggested by Deng and Li [15], who used $CaCl_2$ as a chlorinating agent to roast gold ore. Without the aid of SiO_2, the corresponding reactions (6) and (6a) proceed with more difficulty, as the standard free energy changes are greater compared with reactions (5) and (5a).

$$CaCl_{2(l)} + \frac{1}{2}O_2 \rightarrow CaO + Cl_2 \qquad \Delta G^\circ_{1273\ K} = 107\ kJ \tag{6}$$

$$MgCl_{2(l)} + \frac{1}{2}O_2 \rightarrow MgO + Cl_2 \qquad \Delta G^\circ_{1273\ K} = -9.38\ kJ \tag{6a}$$

It conforms to the principle that the more negative the ΔG°, the more stable the product for a chemical reaction. The effect of silica is generally larger for more basic oxides, such as Na_2O and K_2O.

3.7. Relationship between E and ΔG°

Since metal chloride volatilization is considered to be the primary recovery mechanism, the recovery efficiency (E) should be related to the relative stabilities of the metal compound in the fly ash vs. its chloride at the conditions of the thermal treatment. The reaction of a metal chloride with oxygen is reversible:
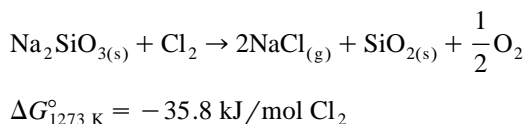
$$MCl_2 + \frac{1}{2}O_2 \rightleftarrows MO + Cl_2$$
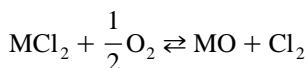
For the generation of Cl_2 by heating a chlorinating agent, the forward reaction is considered; and for chlorination of a metal oxide, the reverse direction is considered. Whichever direction the reaction proceeds depends on the relative stability of the oxide and chloride at the given temperature. This relative stability is reflected by the value of

standard free energy change ($\Delta G°$) for the reaction between metal oxide and chlorine to form metal chloride and oxygen. For the chlorination of metal oxides in fly ash, using $CaCl_2$ as a chlorinating agent (the source of Cl_2) and heating at 1000°C for 3 h, the $\Delta G°$ values for a number of reactions were calculated using the available thermochemical data [12]. For example, $\Delta G°$ for Pb was calculated based on the following equation.

$$PbO_{(s)} + Cl_2 \rightarrow PbCl_{2(g)} + \frac{1}{2}O_2 \qquad \Delta G°_{1273\ K} = -106.2\ kJ/mol\ Cl_2$$
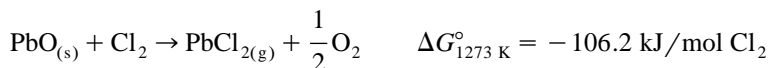
Only those metals which were significant in the fly ash were chosen for this calculation. Silicates are major components of the fly ash. Some are formed by the reaction between a basic oxide (the alkali or alkaline earth oxides) and an acid oxide (silica). For this reason, the reaction between metal silicate and the chlorine (released from $CaCl_2$), to form metal chloride, silica, and oxygen, was also used to calculate the $\Delta G°$'s for the alkali and alkaline earth elements (Na, K, Ca, Mg, Sr, and Ba), such as,

$$Na_2SiO_{3(s)} + Cl_2 \rightarrow 2NaCl_{(g)} + SiO_{2(s)} + \frac{1}{2}O_2$$

$$\Delta G°_{1273\ K} = -35.8\ kJ/mol\ Cl_2$$

Both $\Delta G°$ values (calculated from metal oxides and from metal silicates) for these six elements are shown in Table 5. It is understood that the value of $\Delta G°$ for a certain

Table 5

Volatilization efficiencies and standard free energy changes for reactions for 18 elements using $CaCl_2$ as chlorinating agent and heating at 1000°C for 3 h

Element (1)	E (%) (2)	$\Delta G°$ (kJ/mol Cl$_2$) (3)[a]	$\Delta G°$ (kJ/mol Cl$_2$) (4)[b]
Pb	94.7	−106.2	
Cu	90.5	−75.4	
Zn	96.4	−55.2	
Cd	98.5	−97.7	
Cr	6.5	53.7	
Mn	38.9	13.2	
Fe	0.4	45.5	
Al	<.1	78.0	
Ti	0	51.5	
V	1.7	66.0	
Co	38.7	−6.3	
Ni	28.0	−4.0	
Na	75.4	−262.0	−35.8
K	93.1	−366.4	−88.2
Mg	<.1	41.7	74.7
Ca	<.1	−0.2	90.2
Sr	0.2	−51.1	79.2
Ba	0.3	−107.0	49.7

[a] Based on $MO_{(s)} + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2$.
[b] Based on $MSiO_{3(s)} + Cl_2 \rightarrow MCl_{2(g)} + SiO_{2(s)} + 1/2\ O_2$.

reaction depends on the physical states of the reactants and products. For chlorides, the gaseous state was used in the calculation, since the metals removed were in gaseous form. There was an exception. For $CdCl_2$, the liquid state was used, since no data was available for its gaseous state. For the rest of the compounds the most stable state under the roasting condition was used. The E values (volatile/total, in %) of 18 metals, calculated from the data in Table 1, and their corresponding $\Delta G°$ values are tabulated in Table 5.

There is no overall relationship between the E values and the $\Delta G°$ values (column 3) calculated from using metal oxides. However, if the $\Delta G°$ values for the alkali and alkaline earth metals are replaced with the $\Delta G°$ values in column 4, calculated from using metal silicates, a plot of the E values vs. $\Delta G°$'s produces a linear trend for the partially recovered elements, as shown in Fig. 3. It appears that near complete volatilization occurs for a reaction with a $\Delta G°$ value lower than -50 kJ/mol Cl_2 for 3 h of roasting, and little volatilization takes place for a reaction with a $\Delta G°$ value greater than 40 kJ/mol Cl_2. The linear trend between these limits indicates that the degree of volatilization of a metal is approximately proportional to the $-\Delta G°$ value of the corresponding chlorination reaction. The metals with large E, such as Zn and Cu, have large negative $\Delta G°$ and likely form stable chlorides. On the other hand, metals with very small E, such as Ba and Ti, have large positive $\Delta G°$ and likely form stable oxides. Between these two extreme groups, Mn, Co, and Ni have about the same tendency to form oxides and chlorides.
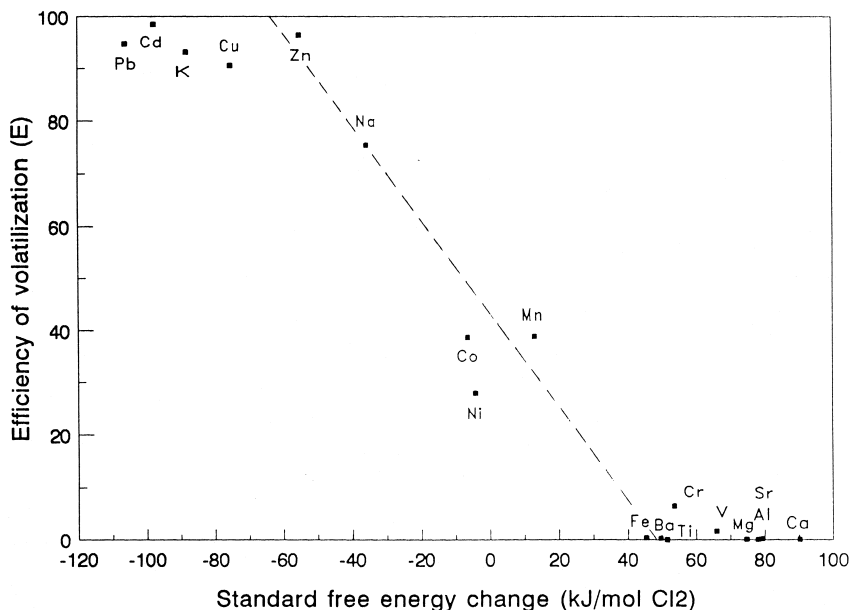

Fig. 3. Dependence of E on $\Delta G°$ for reactions between metal oxides and chlorine to form metal chlorides and oxygen.

4. Conclusions

(1) A total elemental analysis on a MSW fly ash sample, before and after it was treated at 1000°C, revealed the metal distribution between the volatile matter and the ash residue.

(2) More refractory compounds which contain Mg, Ca, Fe, Al and Ti are formed in the fly ash after roasting. All 32 elements, except Cr and Sn, in the fly ash under study, form more acid-resistant compounds after heat treatment which require fusion for dissolution. Two chemical phases $Ca(Mg,Al)(Si,Al)_2O_6$ (pyroxene) and $CaAl_2Si_2O_8$ (anorthite) have been identified in the heat-treated fly ash, but not found in the untreated fly ash.

(3) The metal chlorides in the volatile matter tend to form double salts. Three chemical phases, $Na_2ZnCl_4 \cdot 3H_2O$, K_2ZnCl_4 and KPb_2Cl_5, have been identified. A significant portion of the volatile chloride is associated with Na and K.

(4) The efficiencies of volatilization of the metals, using Cl_2 as a chlorinating agent, are generally higher compared with using $CaCl_2$. However, $CaCl_2$ is a more selective chlorinating agent for volatilizing the heavy metals of concern, i.e., Pb, Cd, Zn and Cu.

(5) The volatilization efficiencies of the recovered metals are approximately proportional to their $-\Delta G°$ values for the corresponding chlorination reactions.

Acknowledgements

References

[1] J.W. Graydon, D.W. Kirk, in: J.P. Hager (Ed.), Proceedings of EPD Congress, 1992, pp. 327–350.
[2] D.J. Mitchell, S.R. Wild, K.C. Jones, Environmental Pollution 76 (1992) 79.
[3] C. Chan, C.Q. Jia, J.W. Graydon, D.W. Kirk, J. Hazardous Materials 50 (1996) 1.
[4] T.T. Eighmy, J.D. Eusden, J.E. Krzanowski, D.S. Domingo, D. Stämpfli, J.R. Martin, P.M. Erickson, Environ. Sci. Technol. 29 (1995) 629.
[5] E. Massillamany, MS Thesis, Department of Chemical Engineering and Applied Chemistry, University of Toronto, 1993.
[6] B. Griepink, H. Mintau, Z. Fresenius, Anal. Chem. 326 (1987) 414.
[7] K.H. Karstensen, W.J. Lund, Anal. At. Spectrom. 4 (1989) 357.
[8] C.A. Cahill, L.W. Newland, Int. J. Environ. Anal. Chem. 11 (1982) 227.
[9] M.A. Fernandez, L. Matinez, M. Segara, J.C. Garcia, F. Espiell, Environ. Sci. Technol. 26 (1992) 1040.
[10] O. Kubaschewski, C.B. Alcock, Metallurgical Thermochemistry, 5th edn., Pergamon, Oxford, 1979, pp. 214–215.
[11] A. Jakob, S. Stucki, P. Kuhn, Environ. Sci. Technol. 29 (1995) 2429.
[12] I. Barin, Thermochemical Data of Pure Substances, 2nd edn., VCH, New York, 1993.
[13] F. Habaschi, Principles of Extractive Metallurgy, Vol. 3, Gordon and Breach, New York, 1986, p. 229.
[14] C.S. Kirby, J.D. Rimstidt, Environ. Sci. Technol. 27 (1993) 652.
[15] H. Deng, X. Li, Trans. Min. Metall. (Sect. C: Mineral Process Extr. Metall.) 96 (1987) 44–46.