BEHAVIOUR OF METALS IN MSW INCINERATOR FLY ASH DURING ROASTING WITH CHLORINATING AGENTS

by

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ABSTRACT

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A process for removal of heavy metals from municipal solid waste (MSW) incinerator fly ash was studied on a laboratory scale. The process is characterized by the formation of volatile chlorides of heavy metals during thermal treatment at temperatures from 600°C to 1050°C. A quartz tube furnace was used for roasting the fly ash sample in an air stream with the presence of a chlorinating agent. Operational parameters, such as roasting temperature, roasting time, and types and quantities of chlorinating agents, were studied. The working conditions for volatilization of Pb, Cu, Zn and Cd, were established. This process not only recovers the valuable heavy metals from the fly ash, but also converts the fly ash from potentially hazardous into non-hazardous material for recycle or its safe disposal in a landfill. Material balances on the fly ash components revealed the metal contaminant distribution between the volatile matter and the ash residue. More acid resistant compounds were formed after the heat treatment. $CaCl_2$

was found to be a more selective chlorinating agent compared to Cl_2 for volatilizing the above heavy metals from a complex matrix such as fly ash. A linear relationship between the efficiencies of volatilization of the partially recovered metals and their standard free-energy changes for the chlorination reactions was indicated. Many of these chlorination reactions were found to be of first order. X-ray powder diffraction was used to identify various chemical compounds to confirm specific reaction mechanisms and to characterize the volatile matter and the heat-treated/untreated fly ash. The reason for the unexpected leachability of Cr and Al from the treated ash residue was investigated and resolved. The applicability of the results to other residues was determined. The techniques developed for the MSW fly ash were applied to a steel dust waste with success for removal of zinc and lead contaminants.

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1. INTRODUCTION

Incineration is a growing option in MSW disposal management. Besides producing energy, the method can reduce the volume of waste (from trash to ash) by about 90% [1]. During incineration, solid, liquid, and gaseous wastes are converted to a residue containing almost no combustible matter and to gases emitted into the air. The hydrocarbon compounds oxidize to form carbon dioxide and water. The residue that settles in the furnace is called bottom ash (comprised of about 95 wt% of the total ash), while the finer particulate matter, entrained by the air stream and captured in the air pollution control devices, is called fly ash (about 5% of total ash) [2]. Fly ash from the MSW incinerators contains heavy metals, such as Pb and Cd [1,3], which can be leached into soil and water bodies if the ash is disposed of in a landfill. Mitchell et al. [1] investigated fly ash samples in the UK and found that the average concentrations of Pb, Cd and Zn in the fly ashes were 108, 113 and 387 times higher respectively than in soil. Graydon and Kirk [3] reported that these metals exist primarily on the surface of larger particles (mostly silicates) in the form of chloride, which is supported by Germani and Zoller's observation [4]. The reported sources of Pb, Cd and Zn in MSW include plastics containing Cd stabilizers and pigments, and discarded Ni-Cd and Pb batteries [5,6].

Leaching of heavy metals from the fly ash in landfill to the environment has received considerable attention and has been addressed in the literature [1,7,8]. According to Mitchell et al. [1], these metals associated with MSW incineration fly ash are likely to be more soluble in landfill than those associated with coal fly ash. Germani and Zoller [4] studied the water solubility of elements in fly ashes, giving solubilities ranging from 63% for Zn to 100% for Cl. This mobility could be greatly enhanced when the ash is co-disposed with organic biodegradable materials found in ordinary domestic refuse [1]. To prevent leaching of heavy metals to the ground water and/or sub soil, one may equip the landfill sites with liners or leachate collection/treatment facilities or remove heavy metals prior to the disposal.

Pb and Cd are the elements commonly detected in the fly ash leachate, concentrations of which often exceed the limits set by legislation [9,10,11], and Zn and Cu are heavy metals which have relatively high concentrations in MSW fly ash. A process which would decontaminate the ash so that it can be safely disposed of in a landfill would be desirable, especially if the process could simultaneously recover the contaminant metals. A wet process of extracting the metals from the fly ash with acids has been used in some places [12,13] for these purposes. The drawbacks of this process are the difficulties of filtering the leachate due to the formation of the gelatinous silicate and aluminum compounds, and in recovering the individual metals from the leachate due to its complex matrix. On the other hand, a dry process, such as thermal treatment, is potentially attractive. In view of the volatile nature of metal chlorides at high temperature, it appears to be possible to separate some heavy metals from the bulk (Si, Al and Ca) of the ash by a thermal process. Furthermore, some metal oxides can be converted to volatile chlorides in the presence of chlorine or chlorine releasing agents at high temperature. This method of chlorination has been described by Alcock and Habashi [14,15] and applied in metallurgy for recovery of metals. The speciation of contaminants in fly ash is complex, so that it is necessary to investigate whether some or all of the species can be recovered and to determine the chemistry involved. One objective of this study was to identify the conditions at which heavy metals would best be removed by chlorination volatilization. The principal parameters investigated in the experiments were heating temperature, heating time, and amount and type of chlorinating agents. Consideration was also given as to whether the chloride content in the fly ash is sufficient for effectively volatilizing the heavy metals.

Jakob et al. [16] studied the evaporation of Zn, Pb, Cd and Cu in a fly ash in various atmospheres at temperatures between 670°

and 1300°C, and found that the evaporation was most effective at temperatures just below the melting range of the ash (1000-1100 °C). Fray [17] reported that Zn, Pb and Cd could be separated from electric arc furnace dust, which was mainly iron oxide, when the dust was heated with chlorine in air. Deng and Li [18] roasted a complex gold ore at 1000-1050°C, using calcium chloride as a chlorinating agent, and were able to recover the precious metals as chlorides. As a common practice, chlorination is an important first step in the extraction of zirconium, vanadium and titanium from their oxides [19]. Temperature is an influential factor in chlorination. When chlorination is conducted in the temperature range 100-600°C, the metal chlorides formed are usually non-volatile, and the metals are recovered by leaching with water. Chlorination can take place in the temperature range 600-1000°C such that the desired metal chlorides are volatilized and can be recovered by condensation, as in the case of titanium recovery.

The criteria of this study was not only confined to Pb, Cd, Zn and Cu, but also extended to many other metals to give a broader scope of their behaviour at high temperature. In order to better understand the distribution of these metals in fly ash and the mechanism by which they are transported in the roasting system, accurate information about the metal content in fly ash and in the volatile matter, as well as knowledge of thermal behaviour of the metal chlorides, are required.

The difficulty of obtaining complete aqueous digestion of MSW fly ash has been noted by several workers [20,21]. Although Cahill et al. [22] claimed that the strong acid digestion ($HF-HClO_4$) caused complete dissolution of the ash particles and provided total metal concentrations, Fernandez et al. [11] admitted the incomplete dissolution by stating 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 often leads to inaccurate analytical results. This report 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. With this background information, the efficiencies of volatilization of metal chlorides from using various solid and gaseous chlorinating agents were compared and discussed.

An X-ray powder diffraction technique was used extensively throughout the study to identify various chemical compounds formed to confirm specific reaction mechanisms and to characterize the volatile matter and the heat-treated and untreated fly ash. The current understanding of fly ash reactions is very limited due to uncertainty of the speciation of metals in the fly ash. Part of this work was designed to develop an understanding of the reactions using thermodynamic and kinetic tools.

2. OBJECTIVES

(1) The main objective was to develop a thermal treatment method for removal of the heavy metals (Pb, Cd, Zn, Cu) from MSW incinerator fly ash, so that the decontaminated fly ash could be recycled or safely disposed of in a landfill. The work involved the investigation of the operational parameters, such as the roasting temperature, roasting time, and types and quantities of the chlorinating agents, so that the working conditions for volatilization and recovery of these metals can be established.

(2) The other objective was to investigate the chlorination mechanism. Although chlorination reactions at high temperatures have been used for extraction of metals from various industrial materials including ores and fly ash, the precise mechanism of the reaction is not entirely understood. One of the difficulties is to understand thoroughly the behaviour of the individual metals at high temperatures. In order to achieve the best effect of the chlorination reaction for a specific application, more detailed knowledge in the area is needed. The following are examples:

i) Characterization of the heat-treated/untreated fly ash and the volatile matter is the first step in understanding their basic chemical nature. Comparison of the chemical content among these samples is needed to trace the pathway of transport of the metals. The identification of the chemical phases (the reaction products) in these samples enables one to disclose some of the chemical reactions involved. The surfaces of the fly ash are the active sites for chemical reactions. Surface analysis can provide information about the major chemical changes from the thermal treatment.

ii) Thermodynamics and kinetics are important tools for studying the reactions. Part of this work was to develop relationship between the efficiencies of volatilization of the metals and the thermodynamic properties, such as the free energy changes of the reactions, and the vapour pressures of the metal chlorides; and to develop reaction rate equations for the chlorination reactions with the metal compounds, thus determining the order of reaction.

(3) In a previous study of thermal treatment of the MSW fly ash in this laboratory, the leaching tests indicated that the concentrations of the metals in the leachate of the heat-treated fly ash were in general lower than those of the untreated fly ash. However, Cr and Al were the exceptions, as there was more leaching from the heat-treated ash. This was not a favourable outcome, since Cr is an element of environmental concern. The reasons for the exceptional behaviour of Cr and Al were not clearly known at the time. An objective was to resolve this enigma, using synthetic chemical samples to study the specific reactions. The results can be pave the way for remedying the problem of leaching Cr and Al.

(4) The roasting process is potentially useful for other applications. This objective was to determine whether the results of this work can be applied to:

i) removal of Zn and Pb from the basic oxygen furnace (BOF) dust so that the dust can be suitable for recycling back to the steelmaking furnaces.

ii) decontamination of dioxins and furans from the MSW fly ash.

3. THEORETICAL

3.1 Genesis of fly ash

MSW is a heterogeneous mixture of different materials. It contains approximately 30% paper, 10% plastics, 5% metals, 10% glass and 40% biological material [3,23]. The elemental composition is subject to considerable variation with time. Upon combustion, some metals and metal compounds in the waste are relatively volatile and vaporize under the conditions encountered in the incinerator [23]. Besides oxidation, other reactions also occur, such as chlorination of alkali metals and heavy metals to form chlorides [3]. These chlorides are also volatile. Together, the vapours are carried away from the waste by the exhaust gas and recondense as the gas cools. The vapours condense both homogeneously to form new particles and heterogeneously on the surfaces of the entrained ash particles [24,25]. Thus, the chloride concentration on the surface of these particles (fly ash) is expected to be much higher than the average chloride concentration of the fly ash, as will be illustrated in a later section (Section 5.5.2, Table 20). In an incineration operation, the fly ash in the incinerator flue gases is trapped by air pollution control devices such as fabric filters or electrostatic precipitators.

3.2 Thermal treatment on fly ash

Thermal treatment can re-vaporize the volatile metal compounds from the fly ash. Massillamany [26] heated the fly ash in air at 1000°C for 3 hours and found that 52-66% of the Cd, 81-97% of the Pb and 30-46% of the Zn were removed by vaporization. Thermal treatment can be carried out either in an oxidizing condition, such as in air, or in a reducing condition, such as in argon atmosphere with the presence of carbon in the sample. Each condition has its own merits and disadvantages. Jakob et al. [16] heat-treated fly ash at 1100°C, and found that the amounts of evaporation were 98-100% of Pb, Cd, and Cu and 50% of Zn in air, and 98-100% of Pb, Cd, and Zn and 10% of Cu in an argon atmosphere, respectively. They explained that given the high chloride content of the fly ash, it was most probable that in air the heavy metals evaporate as chlorides; and in the argon/carbon reducing condition, the heavy metals such as Zn and Cu evaporate as metals. Another reducing condition was employed by Clifford et al. [27] to treat lead-contaminated soil. The sample with the contaminants in the form of $PbSO_4$, $PbCO_3$, PbO and Pb was heated in a Vycor tube furnace at 900°C in a stream of hydrogen. Subsequent analysis of the soil showed that more than 90% of the lead had been removed. In the experiment, they observed an immediate puff of black "smoke" at the outlet end of the Vycor tube when the sample was introduced to the furnace. The black "smoke", which continuously plated out on the outlet end during the heating, was found to be a mixture of carbon, lead and PbS. This deposit was not easily rinsed out or dissolved by acids, and consequently the Pb and other metals in the deposit could not be accurately quantified.

A more effective way to vaporize the heavy metals from fly ash in a thermal treatment is by means of chlorination in an oxidizing condition. Chlorination is a process by which metal chloride is obtained by the reaction of metal oxide with a chlorinating agent. When it takes place at high temperatures, specific metal chlorides are volatilized and recovered from the gaseous phase by condensation. The chlorinating agent can be gaseous, liquid, or solid. For example, chlorine and hydrogen chloride are gaseous agents; carbon tetrachloride and sulphur chloride are liquid agents; and calcium chloride and sodium chloride are solid agents. The overall reaction of a typical chlorination of an oxide, MO, by $M'Cl_2$ can be expressed in the following equation,

$$MO + M'Cl_2 \rightleftharpoons MCl_{2(g)} + M'O \qquad (1)$$

M being the target metal to be volatilized and recovered, and $M'Cl_2$

being a chlorinating agent. There are three main factors that affect the reaction. (i) Stability of $M'Cl_2$. The more stable the $M'Cl_2$, the more difficult it is for the reaction to proceed toward the right, and the yield of MCl_2 less. (ii) The standard free energy change for the reaction. The more negative the ΔG° value for the reaction, the more favourable the reaction. (iii) Volatilization or the vapour pressure of MCl_2. If MCl_2 is volatile, it can be removed readily, and hence the equilibrium of the reaction will shift to the right and the yield will be good.

Holmstrom [28] reported that $CaCl_2$ was found to be a suitable agent in his work since it generates a gas at 600-700°C with a partial pressure of chlorine high enough to chloridize the impurities of Sb, As, and Bi from concentrates containing copper, silver and gold. Morizot et al. [29] worked on a volatilization and chlorination process by roasting antimony sulphide with $CaCl_2$ in the presence of oxygen at 500°C. The overall reaction of the process is

$$Sb_2S_3 + 3\ CaCl_2 + 6\ O_2 \rightarrow 2\ SbCl_3 + 3\ CaSO_4 \qquad (2)$$

They stated that the process is, in fact, separated into a number of stages, including the one which generates the active chlorine,

$$CaCl_2 + 1/2\ O_2 \rightarrow CaO + Cl_2 \qquad (3)$$

which attacks the antimony oxide, an intermediate product, to yield antimony chloride.

$$Sb_2O_3 + 3\ Cl_2 \rightarrow 2\ SbCl_3 + 3/2\ O_2 \qquad (4)$$

The behaviour of a metal in the presence of chlorine and oxygen depends on the relative affinities of chlorine and oxygen for the metal. The reaction

$$MO + Cl_2 \rightarrow MCl_2 + 1/2\ O_2 \qquad (5)$$

is possible only if the chloride is more stable than the oxide. The differences in affinities of the metals for chlorine and oxygen can be expressed by the values of the standard free energy changes for the reactions, ΔG°s. Fig. 1 shows these ΔG° values as a function of temperature. These indicate that at 1000°C, for example, certain oxides, PbO, CdO, and ZnO can be converted directly to chloride by reaction with chlorine under standard condition, i.e., Cl_2 is at 1 atm and produces the volatile chloride and oxygen both at 1 atm; while others such as Al, Ti, and Cr remain substantially as oxides as indicated by the positive sign of ΔG°. The ΔG°, being the difference between the sum of the free energies of formation of the products and the sum of the free energies of formation of the reactants, can be calculated using the available thermodynamic data [30] . The calculated values of the above examples are shown below:

$$PbO + Cl_2 \rightarrow PbCl_2 + 1/2\ O_2 \qquad \Delta G^\circ_{1000C} = -106.2\ kJ \qquad (6)$$

$$CdO + Cl_2 \rightarrow CdCl_2 + 1/2\ O_2 \qquad \Delta G^\circ_{1000C} = -97.7\ kJ \qquad (7)$$

$$ZnO + Cl_2 \rightarrow ZnCl_2 + 1/2\ O_2 \qquad \Delta G^\circ_{1000C} = -55.2\ kJ \qquad (8)$$

$$1/2\ TiO_2 + Cl_2 \rightarrow 1/2\ TiCl_4 + 1/2\ O_2 \qquad \Delta G^\circ_{1000C} = +51.5\ kJ \qquad (9)$$

The requirement for a reaction to be feasible or spontaneous is that the ΔG value, not ΔG°, be negative. However, the ΔG° values have their own usefulness; for one thing, they provide a way for comparing stabilities of similar compounds (chlorides in this case). The more negative the ΔG°, the more stable the compound (chloride) for a given chemical reaction.

It is conceivable that the overall chlorination reaction at 1000°C shown in equation (1) can proceed by several different mechanisms:

(a) The oxide of the target metal dissolves in the melt phase of the fly ash sample and reacts with the chlorinating agent.

$$MO + M'Cl_{2(l)} \rightarrow MCl_{2(g)} + M'O \qquad (1)$$

(b) The overall reaction can be separated into two stages.

$$M'Cl_{2(l)} + 1/2\ O_2 \rightarrow M'O + Cl_2 \qquad (10)$$

$$MO + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2 \qquad (5)$$

The metal oxide dissolves in the melt phase of the fly ash sample and reacts with the dissolved chlorine generated from reaction (10).

(C) The overall reaction is separated into two stages as in (b), but the generated chlorine gas reacts with the solid metal oxide.

(d) The solid metal oxide reacts with the vaporized chlorinating agent.

$$MO_{(s)} + M'Cl_{2(g)} \rightarrow MCl_{2(g)} + M'O_{(s)} \qquad (12)$$

Reaction mechanisms (a), (b) and (c) are all possible. Both (a) and (b) involve reactions in a homogeneous liquid phase, and (c) involves gas-solid phase interactions. Under such conditions, all these reactions can be effective. Mechanism (d) is unlikely to be significant because the vapour pressures of the chlorinating agents are too low to be effective for the reaction.

The chlorination of a metal oxide existing in the fly ash may not be as straightforward as shown in equation (1) or as in

$$MO + CaCl_2 \rightarrow MCl_2 + CaO \qquad (13)$$

and the efficiency of volatilization of the target metal is sometimes difficult to predict, since the fly ash contains many constituents including alumina and silica which affect the reaction. The chlorination reaction using $CaCl_2$ as a chlorinating agent can be greatly enhanced by the addition of an acid oxide such as SiO_2 [15]. The CaO can be converted to silicate and the equilibrium of equation (13) shifted to the right. The overall reaction becomes

$$MO + CaCl_2 + SiO_2 \rightarrow MCl_2 + CaSiO_3 \qquad (14)$$

A similar reaction occurs if NaCl is used as the chlorinating agent.

$$MO + 2\ NaCl + SiO_2 \rightarrow MCl_2 + Na_2SiO_3 \qquad (15)$$

These reactions are used in the recovery of nonferrous metals from pyrite cinder [15]. Deng et al. [18] roasted a gold ore using $CaCl_2$ as chlorinating agent because the latter evolves Cl_2 on reaction with SiO_2 and air as shown in the equation below.

$$CaCl_2 + SiO_2 + 1/2\ O_2 \rightarrow CaSiO_3 + Cl_2 \qquad (16)$$

The atoms on the surface of the elemental gold were able to react with the chlorine to form volatile chloride [31].

As a major component of the fly ash [32], (also see Table 2), silica may enhance the ability of the chlorinating agent in a similar way under oxidising conditions to release chlorine by forming silicates. When the reaction occurs with the $CaCl_2$ in the liquid state, the standard free energy change for the reaction at 1000°C is calculated to be 16 kJ as shown,

$$CaCl_{2(l)} + SiO_{2(s)} + 1/2\ O_2 \rightarrow CaSiO_{3(s)} + Cl_2 \qquad \Delta G^{o}_{1000^{o}C} = 16\ kJ \qquad (16)$$

The available Cl_2 then attacks the metal oxides to form metal chloride as shown in equation (5). Without the aid of SiO_2, the corresponding reaction proceeds with more difficulty, as the standard free energy change is greater compared with reaction (16).

$$CaCl_{2(l)} + 1/2\ O_2 \rightarrow CaO + Cl_2 \qquad \Delta G^{o}_{1000^{o}C} = 107\ kJ \qquad (3)$$

As the chlorides of many heavy metals are easily vaporized at high temperature, a chloride roasting process for the fly ash was investigated. $CaCl_2$ was first chosen for the study as a chlorinating agent because Ca compounds, such as CaO, are generally not volatile at high temperature and because $CaCl_2$ is relatively inexpensive and easy to acquire, and is often a waste product of the chemical industry. Due to the presence of SiO_2 in the fly ash, it is expected that the generation of Cl_2 will be enhanced and as well as its reaction with heavy metal compounds in the fly ash.

4. EXPERIMENTAL

4.1 Apparatus and instrumentation

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 alumina boat and to confine the heating space, (see schematic diagram in Fig. 2); an absorber containing 5% HNO_3 to absorb the volatile metal chlorides; air and nitrogen supplies from cylinders; chlorine supply from lecture bottle; Teflon beakers, 30 mL, for digestion of samples with HF and other acids; graphite crucibles, 8 mL, for fusion of acid resistant residues; a muffle furnace, Hotpack Model 4601, for heating pure chemicals for the study of chemical reactions.

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 ion chromatograph, Dionex Model 2000i/SP; a gas chromatograph, Hewlett-Packard Model HP5890 Series II, and a mass spectrometer, VG Model AutoSpec; a Du Pont Instruments Model 951 Thermogravimetric Analyzer interfaced with a VG Model EGA 300 MM mass spectrometer. For identification of chemical compounds and elemental species, two X-ray powder diffractometers, Philips Model PW 1120-60 and Siemens Model D 5000, and an X-ray photoelectron spectrometer, Leybold Model MAX 200 were employed.

4.2 Materials and reagents

The fly ash used in this study came from an incineration plant in New York State in 1991. The flue gas from the combustor was passed through electrostatic precipitators prior to discharge. Grab samples of the ash were collected from each of the four precipitators. Each sample was passed through a 20 mesh sieve and was mixed with a tumbling mixer for several days in this laboratory to ensure that the samples became homogeneous. They were distinguished by coding A, B, C and D. In the following experiments, mainly sample D was used.

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), perchloric acid (60%, w/w), and hydrochloric acid (38%, 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, and Cr for preparation of working standard solutions for analytical calibration. The chlorinating agents were $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$, $AlCl_3 \cdot 6H_2O$, and NaCl. Cr_2O_3, CrO_3, Al_2O_3, CaO, and $ZnO \cdot Fe_2O_3$ were used for study of chemical reactions.

4.3 General procedure for roasting samples

A sample and a chlorinating agent which was in powder form, were weighed out. They were thoroughly mixed in a weighing dish with a plastic rod before being transferred to an alumina boat. The sample in the boat was then pushed with a steel rod into the mid section of the quartz tube. The arrangement of the roasting system is shown in Fig. 2.

The furnace was turned on. The heating parameters were selected by using the controller. The typical values of parameters and the programmed heating sequence are shown as follows:

1st ramp speed (Rate of change of temperature)	20°C/min
1st level of temperature (T_1)	500°C
1st dwell at T_1 (Holding time)	10 min
2nd ramp speed	13°C/min
2nd level of temperature (T_2)	1000°C
2nd dwell at T_2 (Holding time)	1-3 h
Heating off	

The parameter, "1st holding time", was selected as 10 min to provide sufficient time to burn off the carbon in the sample at 500°C, to ensure that the roasting was carried out under oxidizing condition. About 30 min was required for the furnace to reach 500°C from room temperature, and about 40 min from 500 to 1000°C. After heating was turned off, about 4 h was needed for the furnace to cool down from 1000 to 500°C.

During heating, dry air was supplied at $\approx$ 150 mL/min to entrain the volatile matter. On leaving the furnace, the volatile matter first condensed partially on the wall of the quartz tube outside the heating zone (area 1) and then on the condensation tube (area 2); the rest of the volatile matter was absorbed in 5% (v/v) HNO_3 solution in a scrubber (area 3). After heating, the condensed volatile matter in area 1 and 2 were dissolved in 5% (v/v) HNO_3. They were 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.

4.4 **Procedure for determination of total elemental content in fly ash**

A 0.5 g of fly ash sample 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. 1 mL 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.

5. RESULTS AND DISCUSSION

5.1 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, so that the degree of change or removal of the metals due to the thermal treatment could be quantified by comparing with their original amounts.

Following the procedure of determination of total content of chemical elements, a fly ash sample (sample D) 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.

Table 1
Chemical contents of 32 elements in fly ash (sample D), µg/g. Elements were determined by ICP following sample dissolution.

	Direct digestion	Fusion residue	Total
Pb	3870	< 1	3870
Cu	1028	2	1030
Zn	9454	14	9468
Cd	142	< 1	142
Cr	230	135	365
Mn	1900	14	1914
Na	49400	66	49460
K	24400	< 1	24400
Mg	12200	100	12300
Ca	105800	114	105900
Fe	18540	126	18660
Al	69580	1538	71120
Ti	17670	940	18610
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

All the results shown in the Tables throughout the work are the mean values of duplicate analysis, unless specified as single analysis. Whenever duplicate analysis differed by more than 10%, additional samples were run until the combined error was within ±10%. The precision of analysis will be described in Section 5.2.5.

The accuracy for determining the analytes in the sample solutions was demonstrated by the close agreement of the analytical results with the certified values of two standard reference samples (NIST 3171a and NIST 3172a), as shown in the quality control data in Appendix A.

Besides the refractory elements, most of the elements, such as Pb, Cu, Zn, and Cd, were small in quantity in the acid resistant residue (the fusion residue in Table 1). Those small quantities can be ignored when referring to 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.

For a typical fly ash sample, a bulk chemical analysis was done by Graydon and Kirk [3], and the results were 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. The ranges of concentration of inorganic constituents in MSW incinerator fly ash [33] are given in Appendix B. The fly ash studied has concentrations which fall within the range of the reported values.

Table 2 *
Typical chemical analysis of fly ash (in weight percent)

Major elements		Other elements **	
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		

* This Table is quoted from Ref. [3]
** P_2O_5, C, and MnO are not included.

5.2 Establishment of working conditions for roasting fly ash

The first goal of the study was to establish the roasting conditions which will remove most effectively the concerned heavy metals, Pb, Zn, Cu, and Cd from the fly ash. The roasting parameters under investigation included (i) temperature, (ii) roasting time, (iii) type and amount of chlorinating agents, and (iv) type of carrier gas.

5.2.1 Effect of temperature on roasting fly ash samples

5.2.1.1 Effect of roasting temperature

The roasting parameter that was investigated first was temperature. The immediate questions were how high should the temperature be in order to effectively volatilize the heavy metals and what would be the minimum temperature that would allow effective volatilization. To answer these questions, experiments were designed. A 3 g sample (sample D) was heated in the tube furnace at various temperatures (500, 600, 700, 800, 900, 1000, and 1050°C) for a 3 h period of time. The volatile matter was collected. It was very soluble in dilute acid. A 5% HNO_3 was used for its dissolution. Five heavy metals, Pb, Cd, Zn, Cu, and Cr in the solution were analyzed by atomic absorption spectroscopy (AAS). These metals were chosen as indicators because they are either of environmental concern or are relatively abundant in the fly ash. Table 3 shows the quantities volatilized and Fig. 3, shows the efficiencies of volatilization. The results point out that the higher the temperature, the higher the amount of all these elements volatilized (except Cr which was not volatile). The results indicate that at temperatures below 900°C, poorer yields are obtained; and no reaction occurs below 500°C. The minimum temperature that produces maximum yields for all five elements was achieved at 1000°C. A temperature higher than 1050°C is undesirable for several reasons: the quartz tube of the furnace deteriorates more rapidly and thus shortens the tube life; some compounds in the fly ash may start to sinter and the sample becomes fused, making the transfer of the sample difficult; and the cost of operation and maintenance of such a heating system in a commercial scale increases drastically. Therefore, only the temperature range of 1000-1050°C was chosen for further studies, in particular, 1000°C. To quantify the degree of volatilization of the metals, the efficiency represented by E is used, which is defined as the percentage of a metal that is removed from the fly ash.

Table 3
Temperature effect on volatilization of heavy metals, µg/g sample, based on heating sample D for 3 h.

Element	Temperature, °C						
	500	600	700	800	900	1000	1050
Pb	26	169	2614	2875	3268	3557	3522
Cu	0	0	40	282	666	735	725
Zn	15	13	117	1000	3666	3766	3766
Cd	1	4	57	108	112	117	121
Cr	< 10	< 10	< 10	< 10	< 10	< 10	< 10

The yield of the volatilized Pb and Cd at 1000°C is quite high with an E value above 80% (see Fig. 3), suggesting that they are mostly in a chloride form in the fly ash and are ready to be volatilized at that temperature. Cu and particularly Zn, have lower efficiencies at the temperature range 1000-1050°C, with E values of 70% and 40% respectively. Jacob et al. [16] reported that, after thermal treatment of a fly ash for 3 h at 1030°C, the fractions of metal evaporated were ≈ 90% for both Pb and Cd, 80% for Cu and 40% for Zn. This agrees well with our observations. Unlike the current work involving complete recovery of condensable materials, they used a water-cooled cold finger to collect a portion of the volatile compounds. The low yields of Cu and Zn in both studies may be due to the fact that these metals are not in a chloride form. Many studies report that heavy metals exist as chlorides, oxides and other salts in the fly ash. McKinley et al. [12] and Jakob et al. [16] suggested that a large portion of the Zn was in an oxide form.

To convert a metal oxide into a volatile metal chloride, chlorine is required. The source of chlorine can be a solid chlorinating agent such as calcium chloride or can be directly chlorine gas. It was reasonable to expect that if a chlorinating agent is used in roasting a fly ash sample, the yield would be higher.

5.2.1.2 **Effect of roasting temperature with the presence of a chlorinating agent**

As in the study of the temperature effect (the above section), 3 g of sample D was heated at various temperatures for 3 h, but with 10 wt% of Cl as calcium chloride (equivalent to 0.3 g Cl). Temperatures of 500, 600, 700, 800, 900, 1000, and 1050°C were chosen for the testing as before. The volatile matter was collected and dissolved in 5% HNO_3. Pb, Cd, Zn, Cu, and Cr in the solution were analyzed by AAS. Table 4 shows the amounts volatilized and Fig. 4 shows the efficiencies of volatilization. With a chlorinating agent, the trend of temperature dependence of E was similar to that without a chlorinating agent. However, the E value for Zn increased significantly throughout the entire temperature range when calcium chloride was added. At 1000°C, the E value increased from 40% to above 95%. This means that if this most abundant heavy metal in fly ash is to be recovered, the use of a chlorinating agent is essential. The results suggest that a significant portion of the zinc in fly ash is not as chloride, but as an oxide. The yields of Cu, Pb, and Cd at 1000°C were all improved. As for Cr, the quantities recovered were too small to be accurately quantified and compared, whether a chlorinating agent was used or not. Details of the effects of chlorinating agents will be discussed in Section 5.2.3. From Fig. 4, it can be observed that at about 750°C (below the melting point of $CaCl_2$, 775°C), significant conversion of ZnO to $ZnCl_2$ had already taken place with a E value of about 60%. This suggests that the chlorination reaction could follow mechanism (c), a gas-solid phase reaction as described in Section 3.2, p. 10.

Table 4
Temperature effect on volatilization of heavy metals, µg/g sample, based on heating sample D for 3 h with 0.3 g Cl added.

Element	Temperature, °C						
	500	600	700	800	900	1000	1050
Pb	150	1056	3018	3170	3590	3653	3710
Cu	2	4	44	272	669	853	960
Zn	21	800	2933	7533	8796	9166	9266
Cd	4	13	58	131	134	135	137
Cr	< 10	< 10	< 10	< 10	< 10	17	19

5.2.1.3 **Effect of roasting temperature on volatilization of Na and K**

Another reason for choosing 1000°C instead of 1050°C as the working temperature for volatilizing heavy metals is that the matrix of the volatile matter is simpler. This is explained as follows. Na and K are major constituents in fly ash as can be seen from Tables 1 and 2. Unlike the other major constituents, i.e., Ca, Mg, Si, Al, Fe, Ti, and Si, which remain in the ash, Na and K undergo volatilization as chlorides at 1000°C. More details regarding the efficiencies of volatilization of the metals will be discussed in the later sections (Sections 5.5.1 and 5.7.1.2). Furthermore, the degree of volatilization increases significantly at higher temperatures. Table 5 shows the yields at both temperatures 1000 and 1050°C with and without the addition of a chlorinating agent.

Table 5
Temperature effect on volatilization of Na and K, µg / g sample, based on heating 3 g sample for 3 h with and without $CaCl_2$.

Element	No $CaCl_2$ added		$CaCl_2$ added, equivalent to 0.3 g Cl	
	1000°C	1050°C	1000°C	1050°C
Na	8000	8330	43300	51300
K	8000	8660	17700	22600

A mere 50°C increase at this temperature significantly increases the recovery of Na and K when a chlorinating agent is used. If the metal contaminant recoveries are only concerned with heavy metals, and if lower salt content in the recovery solution is desired for further processing to separate the heavy metals from the solution more easily, 1000°C for roasting would be an adequate temperature. On the other hand, if the removal of Na and K from the ash is important, then the choice of 1050°C is preferable. The recoveries of Na and K are very much dependent upon whether a chlorinating agent is used. Without the addition of a chlorinating agent, there is not enough Cl from the fly ash to chlorinate all the Na and K compounds. Note the values in Table 5, that 43300 µg Na to be volatilized as NaCl requires 66700 µg Cl (6.67% Cl in sample). Since sodium and potassium oxides are too reactive to exist in the fly ash, the enhanced recovery using chloride additions would suggest that these metals exist as silicate salts which are susceptible to chlorination. The form in which Na and K volatilize is not only NaCl and KCl, but also double salts. This will be described in a later section (Section 5.4.2)

5.2.2 Effect of roasting time

Reaction time is an important parameter to be considered in process development. It directly relates to the operating cost.

To study the effect of roasting time, 3 g of sample D with 0.622 g of $CaCl_2 \cdot 2H_2O$ (0.3 g Cl) was gradually heated up in the furnace from room temperature to 1000°C following the programmed sequence. It was then put on hold at 1000°C. Various holding times, up to 3 hours, were tested for their effects on volatilization of the heavy metals. Table 6 shows the amounts volatilized and Fig. 5 shows the efficiencies of volatilization. It should be noted that at holding time zero ($t = 0$), the evaporation of metals had already begun, as some volatilization took place during the heating period from 500°C to 1000°C, which lasted about 40 min.

Table 6
Effect of heating time on volatilization of heavy metals, µg/g sample. (0.622 g of $CaCl_2 \cdot 2H_2O$ was added to sample D)

Metal	Holding time, min (at 1000°C)					
	0	15	30	60	120	180
Pb	3387	3497	3606	3661	3606	3661
Cu	186	493	666	790	900	883
Zn	7000	8433	9166	9170	8933	9170
Cd	119	134	140	140	137	137
Cr	< 10	< 10	< 10	< 10	22	26

From Table 6, it becomes apparent that the holding time of 30 min at 1000°C is sufficient for volatilizing a maximum amount of Pb, Zn, and Cd. However, more time is required for Cu, a minimum of 2 hours. Verhulst et al. [34] studied the behaviour of metal chlorides using the computer program ChemSage. They reported that $CuCl_2$ is stable up to 200°C, and at temperatures above 900°C, CuCl is the predominant species. $CuCl_2$ decomposes at 630°C [36]. The boiling point of CuCl is 1400°C (see Appendix C), which is much higher than those of $ZnCl_2$, $CdCl_2$, and $PbCl_2$ (732°C, 960°C and 951°C). The low volatility of CuCl at 1000°C is obviously one of the reasons for the different behaviour of Cu. Formation of the double oxides $CuO \cdot Fe_2O_3$ and $CuO \cdot Al_2O_3$, or silicates [34], could also slow down the chlorination reaction. From the practical perspective, the recovery of Cu may not be important due to its insignificant quantity in fly ash. Thus, the heating time can just be 30 min. The reduction of hours of heating time could substantially reduce the cost for a large scale heating operation.

5.2.3 Effect of solid chlorinating agents

5.2.3.1 Effects of type and amount of solid chlorinating agents

The effects of each type of solid chlorinating agent on metal removal was studied. Different amounts of equivalent Cl of each chlorinating agent were used to compare the effects at each addition level. To be useful as a chlorinating agent, it ($M'Cl_2$) must be able to release a chlorine-containing gas (Cl_2 or HCl) when it reacts with oxygen or water according to the following general reactions.

$$M'Cl_2 + 1/2\ O_2 \rightarrow M'O + Cl_2 \qquad (10)$$
$$M'Cl_2 + H_2O \rightarrow M'O + 2\ HCl \qquad (17)$$

The oxide (M'O) should be stable chemically and have low vapour pressure, so that the metal initially associated with the chlorinating agent will remain in the fly ash and will not cause any environmental harm when the treated fly ash is disposed of in a landfill. Chlorides, such as $CaCl_2$, $MgCl_2$, $FeCl_2$ and $AlCl_3$ meet these requirements. Hence, they were used in this test. NaCl was also included because it is a common chlorinating agent in some metallurgical processes for recovery of metals.

The fly ash contains 0.5 % moisture (see sec. 5.3.1), which is readily removed when the temperature is over 100°C. Some of the chlorinating agents contain water of crystallization; calcium chloride may have two H_2O units per molecule, and magnesium chloride may have six. Upon heating, however, calcium chloride loses all water at 200°C [35]. From the previous section, temperatures higher than 600°C were shown to be necessary to initiate volatilization of the metal chlorides. At these temperatures no residual water would be present. Hence, the chlorination through HCl, as shown in equation (17), is unlikely to occur in this system where dry air is used.

A 3 g sample (sample D) with the addition of various amounts of equivalent Cl of each of the above chlorides was heated at 1000°C for 1 hour. The volatile matter obtained was dissolved and the heavy metals, i.e., Pb, Cu, Zn, Cd, and Cr were determined by AAS. The amounts of metals volatilized are shown in Tables 7-11 and the volatilization efficiencies graphically summarized in Fig. 6.

Table 7
$CaCl_2$ effect on volatilization of heavy metals, µg / g sample.
(Sample D was heated at 1000°C for 1 h)

Element	Cl added, g				
	0	0.1	0.2	0.3	0.4
Pb	3355	3567	3525	3660	3660
Cu	696	742	757	707	727
Zn	3722	7525	8666	9000	9000
Cd	114	125	130	130	130
Cr	< 20	< 20	< 20	< 20	< 20

Table 8
$FeCl_2$ effect on volatilization of heavy metals, µg / g sample.
(Sample D was heated at 1000°C for 1 h)

Element	Cl added, g			
	0	0.1	0.2	0.3
Pb	3355	3600	3666	3666
Cu	696	777	861	858
Zn	3722	7000	9000	9000
Cd	114	127	134	134
Cr	< 20	< 20	< 20	< 20

Table 9
$MgCl_2$ effect on volatilization of heavy metals, µg / g sample.
(Sample D was heated at 1000°C for 1 h)

Element	Cl added, g			
	0	0.1	0.2	0.3
Pb	3355	3605	3605	3537
Cu	696	767	828	787
Zn	3722	7833	8566	8500
Cd	114	130	130	130
Cr	< 20	< 20	< 20	< 20

Table 10
NaCl effect on volatilization of heavy metals, µg / g sample.
(Sample D was heated at 1000°C for 1 h)

Element	Cl added, g				
	0	0.1	0.2	0.3	0.4
Pb	3355	3649	3649	3649	3649
Cu	696	810	799	757	704
Zn	3722	6200	6666	6666	6624
Cd	114	125	127	127	127
Cr	< 20	< 20	< 20	< 20	< 20

Table 11
$AlCl_3$ effect on volatilization of heavy metals, µg / g sample, shown in duplicate. (Sample D was heated at 1000°C for 1 h)

Element	Cl added, g				
	0	0.1	0.2	0.3	0.4
Pb	3355	3647 3402	3459 3611	3522 3514	3647 3472
Cu	696	777 777	833 828	898 838	833 878
Zn	3722	6500 6266	6666 5933	6666 6466	7340 6833
Cd	114	136 124	137 132	130 134	133 131
Cr	< 20	< 20	< 20	< 20	< 20

Fig. 6 shows the effect of the type as well as the amount of chlorinating agent on the removal of Pb, Cu, Zn, and Cd. Regardless of the type of chlorinating agent, the E values of these metals increased clearly with the first 0.1 g Cl added into the 3 g of ash. There was no significant change for Pb, Cd and Cu when more chlorinating agent was added. The minimum amount of equivalent Cl required for Zn appears to be 0.2 g. To ensure a sufficient amount of Cl in the sample at all times during roasting, 0.3 g Cl (10 wt% of Cl), equivalent to 0.622 g of $CaCl_2 \cdot 2H_2O$, was chosen for the experiment. Amounts of $CaCl_2$ equivalent to 0.5 and 0.6 g Cl were also run, and similar results to 0.3 g Cl were obtained. There is no need to use more than 0.3 g Cl, because the excessive chloride does not further affect the volatilization of the metals.

The addition of a chlorinating agent is hardly needed for vaporization of the existing metal chlorides. Thus, evidence from the high recovery of Pb, Cd and Cu with no additional chlorinating agent, and from the small increase in recovery with addition of a chlorinating agent, suggests that very large portions of Pb, Cd and Cu are already in the form of chlorides in fly ash. On the other hand, the strong dependence of Zn removal on the addition of chlorinating agents indicates that a significant fraction of Zn is in the form of ZnO or in forms other than chloride.

The tendency to release Cl_2 from different chlorinating agents varies depending on their stability in air. This tendency can be demonstrated by the equilibrium partial pressure of chlorine over the chlorinating agent under a constant partial pressure of oxygen (0.21 atm). For the reaction of

$$M'Cl_{2(s)} + 1/2\ O_2 \rightarrow M'O_{(s)} + Cl_2 \qquad (10)$$

the standard free energy change is

$$\Delta G^\circ = -RT \ln (p_{Cl_2} / p^{1/2}_{O_2}) \qquad (18)$$

Since ΔG° is a constant at a given temperature, the equilibrium partial pressure of Cl_2 (p_{Cl_2}) at the same temperature can be calculated. The relationship between temperature and p_{Cl_2} from different chlorinating agents is shown in Fig. 7. The equilibrium partial pressures of Cl_2 decrease according to the sequence $AlCl_3$, $MgCl_2$, $FeCl_2$, $CaCl_2$, and NaCl at a given temperature within the range of 600-1200°C. When chlorination is a necessary step for removal of metal, such as Zn in this case, there should be some dependence of E on the type of chlorinating agent. It seems then, $AlCl_3$ should have the greatest tendency to release Cl_2 at 1000°C and thus it should have the best effect on volatilization of Zn. However, the experimental results indicate otherwise (see Fig. 6). The order of effectiveness of the chlorinating agents for Zn removal was found to be $MgCl_2 = FeCl_2 \approx CaCl_2 > NaCl = AlCl_3$. The low effectiveness of $AlCl_3$ is thought to be due to its high tendency to release Cl_2 at relatively low temperatures at which the rate of chlorination of Zn is not significant. In fact, $AlCl_3$

sublimes at 190°C, and decomposes at 262°C [36]. To remove Zn via chlorination, the temperature has to be higher than 600°C (see Fig. 4). Thus, $AlCl_3$ may have partially evaporated or released Cl_2 prematurely before the reaction with zinc oxide can occur. The suggestion is supported by the result of a thermal gravimetric analysis (TGA) which was carried out by heating a sample of anhydrous $AlCl_3$ in air at the rate of 25°/min. The thermogram shown in Fig. 8 reveals that the $AlCl_3$ lost about one third of its weight as the temperature rose from 100-600°C.

The low effectiveness of NaCl can further be demonstrated by heating 0.100 g of ZnO with NaCl (0.3 g Cl) as against $CaCl_2$ (0.3 g Cl) in the tube furnace at 1000°C for 2 hours. The recovery of Zn was found to be 2.1% and 80% respectively. Similar results were obtained by heating zinc ferrite ($ZnO \cdot Fe_2O_3$), a common form of Zn compound in fly ash [34], with NaCl vs. $CaCl_2$. The recovery of Zn was 6.5% and 93% respectively. The low tendency to release Cl_2 from NaCl indicated in Fig. 7 agrees with the experimental results that the efficiency of volatilization of Zn was low. Furthermore, the vapour pressure of NaCl at 1000°C is three orders of magnitude higher than that of $CaCl_2$ (see Table 29, p. 69). As a result, it is easier for NaCl to evaporate without reacting with oxygen or metal oxides, and to end up with the volatile matter. In other words, less NaCl will be available as a chlorinating agent. A TGA experiment confirmed that synthetic NaCl evaporates at above 800°C. The thermogram, Fig. 8, shows that at 1000°C, about 68% of the NaCl remained (a 32% loss of weight). For the fly ash, analysis of the sodium content of the condensed matter revealed that more than 70% of the sodium salt (see Table 27) ended up with the volatile matter after 3 hours of heating at 1000°C, compared with less than 1% of Ca, Mg, and Fe salts.

NaCl is more stable than $CaCl_2$ in the presence of SiO_2 as indicated by a large positive $\Delta G°$ value for the chlorination reaction of

$$2\ NaCl_{(l)} + SiO_2 + 1/2\ O_2 \rightarrow Na_2SiO_{3(s)} + Cl_2 \qquad \Delta G°_{1000C} = 130\ kJ \qquad (19)$$

compared with a small ΔG^{o} for the reaction of

$$CaCl_{2(l)} + SiO_2 + 1/2\ O_2 \rightarrow CaSiO_{3(s)} + Cl_2 \qquad \Delta G^{o}_{1000C} = 16\ kJ \qquad (16)$$

Hence, it is more difficult for NaCl to release Cl_2 and more likely for NaCl to undergo evaporation. This is also consistent with the experimental results that Zn was poorly recovered when NaCl was used as a chlorinating agent as shown in Fig. 6.

According to Fig. 6, there was no significant difference between $MgCl_2$, $CaCl_2$, and $FeCl_2$ in the volatilization of Zn. When these chlorides are used, the partial pressure of chlorine in the system may be about the same. The reaction between the chlorinating agent and oxygen may be controlled by the oxygen partial pressure in the air, which is close to constant in an open system such as the one used in this study.

There are some other factors that might affect the volatilization. The addition of a chlorinating agent may enhance the metal removal by some mechanisms other than just supplying chlorine. Added chloride may lower the melting point of some species in the ash so that the contact pattern is changed and the reactions are accelerated. For example, NaCl and $CdCl_2$ can form an eutectic phase with a melting point of 397°C [37]. Adding chloride can also lower the viscosity of a molten phase so that the rate of diffusion increases. KCl can lower the viscosity of $CdCl_2$ from around 200 poise to about 150 poise at 650°C [38]. The significance of these factors was not directly determined.

5.2.3.2 Effect of better contact between the chlorinating agent and fly ash

So far, the results presented were based on mixing the dry powder of a chlorinating agent with fly ash. Since the contact of the added chloride salt with the ash phase which contains the extractable metal, may have a role in affecting the reaction rate, a more intimate mixing was performed to determine the magnitude of the effect. To achieve a better contact, the chlorinating agent ($CaCl_2$ or $MgCl_2$) and the ash were thoroughly mixed and wetted with water to form a slurry. After being dried in an oven at 105°C, the sample was heated at 1000°C for 1 hour with up to 0.2 g Cl added. Table 12 shows the amounts volatilized and Fig. 9 shows the volatilization efficiencies. The metal removal from the pre-wetted samples was somewhat improved, particularly for Cu at all chloride additions. The increase in E was up to about 10% for Cu with 0.1 g Cl added as $CaCl_2$. As mentioned before, Cu removal was a relatively slow process. After the wet treatment, the distribution of both added chloride salt and heavy metal chloride was likely more uniform. Thus, the contact of the added chloride salt and the targeted metal-containing phase was more intimate. Again, there was no significant difference found between $CaCl_2$ and $MgCl_2$. Although the wet treatment resulted in some gain in the efficiency of volatilization, the time consumed and the cost for drying the mass will offset the gain in a large scale operation.

Table 12
Recovery of heavy metals from pre-wetted sample with chlorinating agents, µg / g sample.
(Sample D was heated at 1000°C for 1 h)

Element	Cl added, g			
	$CaCl_2$		$MgCl_2$	
	0.1	0.2	0.1	0.2
Pb	3666	3733	3733	3666
Cu	851	851	842	879
Zn	8100	8533	8100	8833
Cd	131	131	130	133
Cr	< 20	< 20	< 20	< 20

5.2.4 Effect of type of carrier gas

Both air and nitrogen were used as carrier gases to study the effect on volatilization of heavy metals. With air, the roasting was under oxidizing conditions; and with nitrogen, it was under reducing conditions because the carbon in the sample acted as a reducing agent. A 3 g sample (sample D) was heated at 1000°C for 3 h with the carrier flow rate at 150 mL/min under the following three conditions: (i) air as carrier, (ii) nitrogen as carrier, (iii) air as carrier at temperature below 480°C and during the holding period at the same temperature for 15 min to burn off the carbonaceous matter, followed by nitrogen as carrier at 480-1000°C. The volatile heavy metals recovered are shown in Table 13.

Table 13
Heavy metals recovered using different carriers, µg / g sample

Heavy metal	(1) Air	(2) N_2	(3) N_2 Pre-heated under air
Pb	3557	2810	3191
Cu	735	85	445
Zn	3766	1866	2000
Cd	117	111	120

Under reducing condition using N_2 as the carrier, the recovery of metals was poor, especially that of Cu, because there was little chance for Cu to form the volatile $CuCl_2$ but CuCl (b.p. 1400°C) during the entire period of heating (see also Section 5.2.2.). Heating the sample under this condition (ii) caused massive dark coloured deposit in the combustion tube. Note the similarity to literature [27] reported earlier (Section 3.2). This deposit was not completely dissolved in acids, and its chemical nature is not known. Therefore, the results in Table 13 under N_2 are inaccurate and underrated, and can only be treated as a qualitative interpretation. When the sample was heated in air first before being subjected to N_2 in an inert condition at higher temperatures as in condition (iii), the recovery was not as poor as in condition (ii), especially for Cu, because there was some chance for Cu to form $CuCl_2$. Moreover, the black deposit was less apparent, which suggests that the deposit contained carbon which could be burned off. By burning off the carbon first, the reducing condition under which the recovery of these metals is unfavourable can be avoided. There was no significant difference for the recovery of Cd, whether the treatment was under oxidizing or reducing condition. For this work, oxidizing conditions were seen as more effective in volatilizing heavy metal contaminants when chlorinating agents were used.

5.2.5 Precision of the method

The best conditions, thus far, for roasting a 3 g fly ash sample, under which maximum volatilization of Pb, Zn, Cu and Cd can be obtained with minimum temperature, time, and amount of the most effective chlorinating agent, are summarized as follows:

Roasting temperature: 1000°C
Roasting time: 3 h; ½ h (Cu not required)
Wt. of $CaCl_2 \cdot 2H_2O$ added: 0.622 g (0.3 g Cl)
Air (carrier) flow rate: 150 mL/min.

Once the roasting conditions had been established, the reproducibility of the process could be assessed. The precision of the method, including volatilization of the heavy metals from the fly ash sample and the determination of the metals (Pb, Cu, Zn, and Cd) using AAS, is expressed as a relative standard deviation (r.s.d.) which is calculated from the results of replicate runs. The volatilization conditions were: a 3 g sample (sample D) with the addition of 0.622 g $CaCl_2 \cdot 2H_2O$ (0.3 g Cl) was heated at 1000°C for 3 h. The results are shown in Table 14. Precision of < 3% r.s.d. for all the elements was achieved.

Table 14
Precision of the volatilization of the heavy metals which were determined by AAS. (3 g sample D with 0.3 g Cl was heated at 1000°C for 3 h.)

	Pb	Cu	Zn	Cd
	µg / g sample			
n = 5	3645	909	8866	130
	3645	858	8666	130
	3888	858	9166	136
	3715	878	9000	133
	3750	888	9166	136
Mean	3728	878	8973	133
s.d. (σ)	101	22	216	3
r.s.d. (%)	2.7	2.5	2.4	2.3

5.2.6 Variation of chemical content in fly ash samples from different ash collectors

5.2.6.1 Variation of elemental content in fly ash samples

Although the four fly ash samples, A, B, C, D were taken from the same incinerator at the same time, due to being collected in different electrostatic precipitators, slight variation of the chemical composition among the samples was expected. Consider sample A. The total content of Pb, Cu, Zn, and Cd were obtained by the following procedure: a 3 g of sample was roasted with 0.3 g Cl at 1000°C for 3 h, and the volatile matter was collected and dissolved in 5% HNO_3 (solution 1); and the fly ash residue was digested with the acid mixture and diluted with 5% HNO_3 (solution 2). The elemental concentrations in both solutions were determined by AAS. The sum of an elemental content from both solutions represents the total content of the element in the fly ash. The results are shown in Table 15. The elemental content of sample A is somewhat different than that of sample D (shown in the last column of Table 15, quoted from Table 1, page 16).

Table 15
Heavy metal contents in sample A, µg / g sample

Element	Volatile matter (1)	Digestion ash residue (2)	Total in sample A (1) + (2)	Total in sample D (From Table 1)
Pb	3422	179	3601	3870
Cu	1062	157	1219	1030
Zn	8634	374	9008	9468
Cd	126	3	129	142

The small difference in chemical composition among sample A, B, C, and D can also be seen from the amounts of the heavy metals volatilized, as will be demonstrated in the following section.

5.2.6.2 Variation of volatilization of heavy metals from the four fly ash samples, A, B, C, and D

Chemical analysis of the heavy metals, Pb, Cu, Zn, Cd, and Cr, volatilized from roasting each of the four samples, also confirmed the variation of elemental content among the samples, as can be seen from Table 16. The results were obtained by heating 3 g of each sample with the addition of 0.622 g of $CaCl_2 \cdot 2H_2O$ (0.3 g of Cl) at 1000°C for 3 h, and analyzing the heavy metals in the captured volatile matter by AAS.

Table 16
Heavy metals volatilized from four fly ash samples, µg/g sample. Samples were heated at 1000°C for 3 h with 0.3 g Cl.

Heavy metal	Sample			
	A	B	C	D
Pb	3422	4104	2708	3728
Cu	1062	777	621	878
Zn	8634	9500	7083	8972
Cd	126	148	110	133
Cr	< 10	27	22	< 10

Samples A and D contain the most similar quantities of these heavy metals. Due to limited quantities of the fly ash samples (sample D as well as the others) available in this laboratory, sample A was chosen as a supplement of sample D for some experiments. In addition, sample C was also used in one experiment, i.e., in the determination of dioxins (Section 5.9.2).

5.2.7 Air flow as carrier during roasting

The function of air flow is to carry the volatile matter which contains the metal chlorides, from the furnace to the condensation assembly. Too fast a flow rate may not allow enough time for the volatile chlorides to be absorbed in the absorber and could cause particulate matter to be entrained in the gas; too slow a flow rate would cause difficulty in maintaining a steady gas flow due to the pressure drop created in the fritted gas disperser. A flow rate between 50 to 300 mL/min was found practicable. The effect of flow rate was tested at 100 and 200 mL/min. The flow rates were measured and calibrated by a soap-film flowmeter connected to the exit of the gas absorber. The amounts of Pb, Cu, Zn, and Cr volatilized from heating a 3 g of sample (sample A) with the presence of $CaCl_2$ at 1000°C for 3 hours at both flow rates are shown in Table 17. No appreciable difference was found on the effect of flow rate. Excluding Cr due to its low values, the differences are within ± 2%, less than the analytical uncertainty. The results are comparable with those shown in Table 15, column (1).

Table 17
Effect of air flow rate on volatilization of metal chlorides.

Air flow rate	Element collected, μg / g sample			
	Pb	Cu	Zn	Cr
100 mL/min	3174	1018	8258	10
200 mL/min	3206	1008	8133	14

The fact that there was no significant difference in amount of the captured volatile suggests that either all of the volatilization has taken place before the end of the experiment, or the rate of volatilization is independent of the gas composition (μgM / mL air / min) in the quartz tube. In the latter case, it implies that the reaction:

$$MCl_{2(s)} \rightarrow MCl_{2(g)}$$

was not in equilibrium for the roasting, since doubling the air flow rate did not produce twice as much metal chloride. Fig. 5 showing the effect of roasting time demonstrates that the volatilization is essentially complete after 90 min. Thus, the results cannot distinguish these two possibilities.

5.3 Moisture, carbon content, and mass loss on roasting

In order to better understand the nature of the fly ash, determinations of its moisture, carbon content, and mass loss on roasting, were done.

5.3.1 Moisture

An amount of the fly ash sample A (8 g in this case) was spread on a watch glass and dried in an oven at 105°C for a period of two hours. After cooling in a desiccator, the sample was re-weighed. The weight lost due to evaporation of moisture (unbound water) in the sample was recorded. Further drying of the sample in the oven did not result in further loss of weight, which indicated that the moisture had been completely driven off. The moisture content of the sample was calculated to be 0.50%. This low content would not appreciably affect the chemical analytical results, even if not accounted for in the total sample weight.

The dry fly ash sample tends to absorb moisture strongly. To see how much and how quickly it will absorb moisture from the air, the same sample was exposed to ambient air, and was weighed consecutively at short intervals until its weight became constant. At that stage absorption and desorption were in equilibrium. Fig. 10 (a) depicts how the sample weight was regained as time progressed. The weight rose rapidly during the first few minutes and then gradually levelled off. About 80% of the original weight of moisture was regained in 18 min. Fig. 10 (b) shows that the weight of moisture absorbed is proportional to the square root of exposure time.

5.3.2 Carbon content

An amount of the dried sample A (3 g in this case) was placed in an alumina boat and heated in the tube furnace at 500°C for a period of 15 minutes. Air flowing through the sample was maintained during heating. The sample was then removed from the furnace and allowed to cool in a desiccator. The sample was weighed. The weight loss, mainly due to the conversion of the carbon in the sample into carbon dioxide, was recorded. Further heating of the sample for a period of 45 minutes resulted in only a slight decrease in sample weight; no further loss of weight was noticed if the heating was prolonged. The carbon content of the sample, based on the weight loss at 500°C, was calculated to be 1.37%.

5.3.3 Mass loss on roasting

After the sample was roasted, it appeared whiter in colour and had lost weight. Weight loss on roasting is the percentage of sample-weight loss, other than the losses of moisture and carbon, after roasting. The weight loss from roasting a 3 g of sample A with the addition of 0.6261 g of $CaCl_2$ at 1000°C for 3 h is calculated from the following:

Wt. of sample A		3.0000 g
Wt. of $CaCl_2$		0.6261 g
Wt. of CaO	0.6261 x 56/111 =	0.3159 g
(assuming $CaCl_2$ completely converted to CaO after roasting)		
Total wt. after roasting		2.8385 g
Sample wt. after roasting	2.8385 - 0.3159 =	2.5226 g
Sample wt. loss	3.0000 - 2.5226 =	0.4774 g
% Sample wt loss	0.4774/3.000 x 100 =	15.91%
(including % losses of moisture and carbon)		
Loss on roasting	15.91% - 0.50% - 1.37% =	14.04%

The loss on roasting was mainly due to the vaporization of the metal chlorides.

5.4 Characterization of the volatile matter

5.4.1 Anions in the volatile matter

One way to confirm that the metals in the volatile matter were mainly in chloride form was to analyze the dissolved volatile matter for Cl^- using an analytical technique such as ion chromatography (IC). 3 g of sample D was roasted at 1000°C for 1 h with and without the addition of $CaCl_2$. The volatile matter was collected in areas (1) and (2) of the condensation assembly and the rest was dissolved in 5% HNO_3 in the absorber (area 3, see Section 4.3). In addition, an impinger containing NaOH solution was connected to the exit of the gas absorber. It served to absorb any chlorine gas generated, which was not combined with the metals. The volatile matter from areas (1) and (2) was dissolved with 5% HNO_3 and combined with the solution in the absorber. The Cl^- in this combined solution was determined, and is referred to as the Cl^- from metal chlorides in Table 18. Although hydrogen chloride would also be measured if present, this experiment did not have water vapour in the gas phase and hence the chloride values should represent metal chloride. There is one other possible source of chloride, considering that Cl_2 reacts with water to form HCl according to the following equation,

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

However, with the presence of a strong acid solution (HNO_3), Cl_2 is unable to react with water freely. Hence, the formation of HCl is greatly suppressed if not eliminated. The NaOH solution in the impinger was diluted and was analyzed for Cl^-. AAS analysis showed that this solution did not contain metals such as Pb, Cu, Zn, Cd, and Cr. It is understood that the metal chlorides are soluble and will remain in the 5% HNO_3 in the absorber, while Cl_2 will not dissolve and remain in the acidic solution. The Cl^- in the NaOH solution was determined and is referred to as the Cl^- from chlorine in Table 18. According to the following equation,

$$Cl_2 + 2\ NaOH \rightarrow NaCl + NaClO + H_2O \qquad (20)$$

one weight of chlorine gas produces only a half weight of chlorine as Cl^-. To convert Cl^- to Cl_2 or vice versa in calculation, a factor of 2 should be applied. For example, if 1.6 mg of Cl^- is detected by IC in the NaOH trapping solution, it would represent 3.2 mg of chlorine gas captured in the solution. In terms of percentage of Cl, the volatile chloride in the fly ash sample (3 g) was calculated (see Table 18) to be:

(79.8 mg + 3.2 mg) / 3000 mg = 2.7% Cl

Along with Cl^-, $SO_4^=$ and Br^- were also analyzed in the same run by IC. The results are shown in Table 18. A separate experiment was done using water as absorbent and for rinsing. No appreciable amount of NO_3^- was found.

Table 18
Analysis of anions in the volatile matter from a 3 g sample D roasting at 1000°C for 1 h with and without $CaCl_2$.

Anion	Source	No Cl added	0.3 g Cl added
		mg detected	
Cl^-	Metallic chlorides	79.8	119.7
	Chlorine	1.6	13.6
$SO_4^=$	Metallic sulphate	11.2	14.3
	Non-metallic sulphate	n.d.	0.8
Br^-		n.d	n.d

n.d. means not detected, < 0.1 mg.

Table 18 shows that a substantial amount of Cl^- was found, suggesting that the volatile metals are mainly in the form of chloride with some in the sulphate form, and a negligible amount of bromide or nitrate. The results may have underestimated the chlorine generation since the efficiency of the impinger for absorbing Cl_2 was not determined and expected to be less than 100%, and some Cl_2 might have escaped. With the addition of $CaCl_2$, the quantity of Cl^- was more than sufficient for combining all the heavy metals of interest. A significant portion of the Cl^-, however, was associated with Na and K.

5.4.2 Chemical phases in the volatile matter

The volatile matter accumulated in the condensation tube is a yellowy and greenish colour. The sample was examined by X-ray powder diffraction (XRPD), using copper K_α radiation (34 kV, 20 mA). Because of its highly hygroscopic nature, the volatile matter was collected in a dry-air environment, and was immediately sealed by an organic cement to prevent absorption of moisture. 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. 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. An XRD spectrum is shown in Fig. 11. It confirms that the heavy metals, such as Pb and Zn, were in the form of chloride. The suggestion by Jakob et al. [16] that in air the heavy metals are probably evaporated as chlorides is supported by this work. It also shows that the metal chlorides tend to form double salts when they are condensed at a lower temperature. These results are consistent with the finding of potassium-zinc-lead chloride and the K_2ZnCl_4 phase by Graydon and Kirk [3] in raw fly ash. Thus indirectly this work suggests that the source of heavy metals in fly ash is from a chloride volatilization reaction.

5.4.3 Distribution of volatile matter during collection

During roasting of the fly ash sample, the volatile matter was carried by air and collected in three areas (see description in Section 4.3) of the condensation assembly. It was not known how the volatile matter was distributed along the collection route or whether a particular area contained more volatile matter. Therefore, the volatile matter was analyzed separately for each of the collection areas to determine how the metals were distributed in those three areas. A second absorber was added to determine whether any residual volatile metal escapes from the first absorber. The solutions of the volatile matter in each area were prepared for elemental analyses. The total amount of each element in the volatile matter is the sum of the analytical results from these three separate solutions.

Duplicate samples of 3 g of fly ash (sample A) were thermally treated on separate days at 1000°C for 3 h with addition of 0.4 g of Cl. The volatile matter was analyzed for the elemental content by ICP after sample dissolution by using dilute HNO_3. Some elements were also analyzed by AAS for comparison with ICP. The results are presented in Appendix D. Both analytical techniques, ICP and AA, render comparable results, and the duplicate values show that the products from the roasting process are quite reproducible. No metal was detected in the solution in the second absorber, indicating that the use of one absorber is sufficient. As can be seen, the distribution of the elements in three areas did not have a specific pattern. Each area picked up a substantial amount of the metals. K and Na were not retained significantly in the quartz tube (area 1) once vaporized, and tended to condense quickly (area 2), leaving not as much vapour to be carried into the absorbing solution (area 3).

5.5 Characterization of the ash residue

5.5.1 Effect of thermal treatment on the refractory elements in fly ash

After the fly ash was roasted, 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 leads to the conclusion 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 required. This was done in the following manner.

A 3 g fly ash sample D 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 an 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 dissolved (solution 3) by a fusion method as described in the Experimental Section (Section 4.4) The solutions (1-3) were used for determination of the chemical elements by ICP. The results for 32 elements are shown in Table 19, column (1-3), respectively. The sum of the content of an element in each solution represents the total content of the elements in the fly ash. The results obtained by direct digestion of the fly ash shown in Table 1 are also included here, (see last three columns), so that comparison of data can be made more easily.

Table 19
Chemical contents of 32 elements in fly ash sample D, µg/g.
Elements were determined by ICP following sample dissolution.

	Volatile (1)	Ash digest (2)	Fusion residue (3)	Sum (1+2+3)	Direct digest (4)	Fusion residue (5)	Total (4+5)
Pb	3666	136	9	3811	3870	< 1	3870
Cu	933	138	11	1082	1028	2	1030
Zn	9133	392	24	9549	9454	14	9468
Cd	140	4	< 1	144	142	< 1	142
Cr	24	284	41	347	230	135	365
Mn	746	1108	88	1942	1900	14	1914
Na	37330	12120	513	49960	49400	66	49460
K	22730	1650	103	24480	24400	< 1	24400
Mg	4	9383	2666	12050	12200	100	12300
Ca	152	147700	6185	*154000 **(101400)	105800	114	105900
Fe	83	15930	1765	17770	18540	126	18660
Al	1	59780	9164	68950	69580	1538	71120
Ti	< 1	16730	1350	18080	17670	940	18610
Be	< 1	4	< 1	4	2	< 1	2
P	8	6521	125	6654	6800	30	6830
Sc	< 1	4	< 1	4	5	< 1	5
V	1	49	6	56	58	< 1	58
Co	12	21	< 1	33	31	< 1	31
Ni	58	137	3	198	207	< 1	207
As	< 1	58	< 1	58	60	< 1	60
Sr	1	415	14	430	444	1	445
Y	< 1	8	1	9	8	< 1	8
Zr	< 1	131	46	177	167	4	171
Mo	2	31	5	38	43	< 1	43
Ag	7	5	1	13	27	< 1	27
Sn	< 1	346	22	368	259	71	330
Sb	< 1	526	8	534	526	< 1	526
Ba	3	542	172	717	918	16	934
La	< 1	18	< 1	18	18	< 1	18
W	< 1	18	< 1	18	21	< 1	21
Bi	11	< 1	< 1	11	8	4	12
Hg***	0.3	< 0.1	< 0.1	0.3	0.4	< 0.1	0.4

* The 0.622 g $CaCl_2 \cdot 2H_2O$ added to the 3 g sample D contained 0.158 g of Ca, moisture being excluded. Therefore, the Ca added / g sample = 158000 µg x 1/3 = 52600 µg. This amount should be excluded for mass balance calculation,
** that is, 154000 - 52600 = 101400 µg Ca / g sample.

***Hg was analyzed by cold vapour AAS.

The total content (1+2+3), thus obtained, agrees well with the sum (4+5). Columns (3) and (5) indicate that the acid resistant matter contained some amounts of Mg, Ca, Fe, Al, and Ti. Moreover, the undigested ash residue from the heat-treated fly ash sample (column 3) contained more of these elements than did the undigested fly ash sample (column 5). This suggests that after heat treatment, more refractory compounds containing these elements were formed. The X-ray powder diffraction (XRPD) analysis confirmed that more crystalline compounds existed in the heat-treated fly ash sample than in the untreated one. Figs. 12 and 13 are the powder X-ray diffraction spectra. 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. In general, the elements shown in Table 19 formed more acid-resistant compounds after heat treatment. Cr and Sn were exceptional. They formed more acid-soluble compounds.

It is also interesting to note that the Hg content is very low in this fly ash sample. Hg is an element of environmental concern. When the MSW is incinerated, Hg remains in 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. The vapour pressures of Hg and $HgCl_2$ at which temperature are 0.57 and 2.09 atm respectively [19]. As expected, there is little chance for Hg to stay in the fly ash, which is consistent with our finding.

5.5.2 Effect of thermal treatment on the surface of the fly ash

The X-ray photoelectron spectroscopy (XPS) in the Centre for Biomaterials, University of Toronto, was used for determination of a number of elements on the surface of both the heat-treated and untreated fly ash samples (sample D). Unmonochromatized Mg K_α X-ray radiation was used as the excitation source. The source was run at 15 kV and 20 mA. The XPS spectra were obtained on a Leybold

MAX 200 XPS system and are shown in Fig. 14. The results of the elemental composition of the surface, 10 nm deep, for both samples are shown in Tables 20 and 21 as the relative atomic percentages.

Table 20
XPS analysis on a single sample of fly ash (sample D)

Element	Binding energy	Area	Relative atomic %	As oxide	%
Na	-1072.58	3.68e+004	3.0	Na_2O	9.73
Zn	-1022.48	6.02e+004	2.4	ZnO	7.20
O	-531.83	2.25e+005	43.7		
Ca	-348.86	5.69e+004	4.3	CaO	14.50
K	-294.18	1.64e+004	1.5	K_2O	4.34
C	-284.54	6.31e+004	28.7		
Cl	-199.46	2.37e+004	3.4	Cl	8.19
S	-169.12	1.59e+004	3.0	S	7.22
Pb	-140.61	2.60e+004	0.4	PbO	1.04
Si	-101.94	1.68e+004	6.8	SiO_2	35.04
Al	-73.43	4.36e+003	2.8	Al_2O_3	12.74

Table 21
XPS analysis on a single sample of heat-treated fly ash (sample D). 3 g sample was heated at 1000°C for 3 h with 0.622 g of $CaCl_2 \cdot 2H_2O$.

Element	Binding energy	Area	Relative atomic %	As oxide	%
Na	-1071.83	1.88e+004	1.5	Na_2O	4.14
Zn	-1021.75	2.29e+003	0.1	ZnO	0.25
O	-530.89	2.42e+005	46.4		
Ca	-347.90	1.13e+005	8.5	CaO	24.40
K	-291.15	3.80e+002	0	K_2O	0
C	-284.52	5.63e+004	25.2		
Cl	-200.45	9.42e+002	0.1	Cl	0.21
S	-168.54	1.23e+004	2.3	S	4.72
Pb	-142.01	5.36e+003	0.1	PbO	0.22
Si	-100.66	2.56e+oo4	10.2	SiO_2	44.76
Al	-73.19	8.78e+003	5.5	Al_2O_3	21.30

The large carbon peaks, shown as relative atomic %, were due to surface contamination which is common to XPS analysis. This contamination can be picked up merely during atmosphere exposure, and from sample containers (especially from those made of organic materials containing plasticizers), [39]; the carbon can sometimes be observed to build-up during actual examination in the spectrometer. The large oxygen peaks were mainly contributed by the metal oxides. Clearly some of the oxygen is from the silicates where Si:O ranges from 1:2 for quartz to 1:4 in anorthite. Excluding carbon and treating all metals as oxides, the relative abundances of the compounds in the samples were recalculated as shown in the last two columns of Tables 20 and 21.

These results of the surface analysis provide the following information:

(1) Cl was quite concentrated on the surface of the fly ash, about 8% (the average concentration of Cl in the fly ash was about 2.7%, as shown in Section 5.4.1, p. 41). Upon heat treatment, it volatilized almost totally as metal chlorides. The finding of high concentration of Cl on the surface of the fly ash confirms the fact that the vapour of metal chlorides in the incinerator recondenses on the surfaces of the entrained ash particles as the exhaust gas cools (see Section 3.1).

(2) Na reduced to about one half of its amount after the heat treatment.

(3) Zn, K, and Pb almost completely volatilized after the heat treatment.

(4) Al almost doubled its concentration on the surface of the heat-treated sample, while Si increased about 30%. This means that after the volatile compounds were vaporized from the fly ash particles, these remaining elements, Al, and Si became more concentrated and exposed.

5.5.3 Effect of thermal treatment on leachability of Cr and Al compounds

Massillamany [26] thermally treated the fly ash samples at various temperatures and lengths of time. In a subsequent leaching test using 0.5N acetic acid solution, he found that smaller amounts of metals leached out from the heat treated ash than from the ash without heat treatment (see Appendix E). However, there were exceptions. Cr and Al leached out more from the ash that had been heat treated.

5.5.3.1 Leaching of Cr

Massillamany reported in his thesis [26] that the untreated ashes had leachable Cr concentrations of 0.1, 0.2 and 0.1 ppm for Canadian, French and American ashes respectively. After treatment at 1000°C for 3 hours, the concentrations of the leachates increased to 2.8, 5.0 and 1.7 ppm for the three ashes. This was not a desirable outcome of the thermal treatment process. Fortunately, the concentrations of Cr in the leachates from all three heat-treated ash samples did not exceed the regulatory limit of 5 ppm [9]. He speculated that the Cr in the fly ash was in Cr^{+3} insoluble form which was converted to the soluble Cr^{+6} form during heat treatment. A possible reaction was suggested as

$$Cr_2O_3 + 3/2\ O_2 \rightarrow 2\ CrO_3 \qquad (21)$$

This subject area, including why Cr becomes more soluble, is part of the current work. Further investigation has been carried out to identify possible reactions using synthetic samples. An initial experiment by heating Cr_2O_3 in a muffle furnace at 1000°C for an hour proved that no appreciable amount of Cr was in the leachate. Thus, the formation of CrO_3 which is soluble does not appear to take place. This finding led to a new direction in planning of further experiments. Since the fly ash contains alkaline-earth metal oxides, they may react with the Cr compounds to form soluble compounds during heat treatment. A possible reaction is

$$Cr_2O_3 + 2\ CaO + 3/2\ O_2 \rightarrow 2\ CaCrO_4 \qquad (22)$$

In the study of solidification of chromium-containing sludge, Shoto et al. [40] attempted to fix chromium oxide in a Na_2O-CaO-SiO_2 glass matrix by heating this mixture at elevated temperatures (800-1000°C) for 2 hr. Subsequent leach test on the solidified mass indicated that the Cr concentration in the leachates was substantial. They also viewed that the Cr extraction was probably caused by the formation of the soluble chromate. To prevent the leaching of Cr, they modified the composition of the glass matrix by increasing the amount of SiO_2.

When roasting the fly ash sample with a chlorinating agent, such as $CaCl_2$, one may think that $CrCl_3$, a soluble compound, may form according to the following reaction

$$Cr_2O_3 + 3\ CaCl_2 \rightarrow 2\ CrCl_3 + 3\ CaO \qquad (23)$$

The other possibility would be a reaction, similar to (22),

$$Cr_2O_3 + 2\ CaCl_2 + 5/2\ O_2 \rightarrow 2\ CaCrO_4 + 2\ Cl_2 \qquad (24)$$

In both equations (22) and (24), calcium chromate, $CaCrO_4$, is the product which is soluble with solubility of 16.3 g / 100 c.c. [36].

To investigate these reactions, experiments were carried out by first heating Cr_2O_3 with and without the presence of $CaCl_2$ at 1000°C followed by dissolution of the products. The same experiments were repeated with CaO replacing $CaCl_2$. Since both $CrCl_3$ and $CaCrO_4$ are soluble, any quantity of Cr detected in the solutions should represent their existence in the products. Some parameters of the experiments are shown as follows:

Cr_2O_3 - 0.050 g sample (equivalent to 34,210 µg Cr) was used in each test. The compound is bright green in color.

$CaCl_2$ - 0.100 g was used in each test.

CaO - 0.100 g in each test.

Heating - ½ h at 1000°C.

Dissolution sequence - After heating, the sample in a porcelain crucible was leached in water overnight. The supernatant solution was decanted out for Cr analysis. The water insoluble mass was then leached in 5% HNO_3 for 1 h, and the solution was analyzed for Cr by AAS. The Cr content obtained under different heating conditions are shown in Table 22.

Table 22
Cr content in leachates under different heating conditions

Condition	Cr in leachate, µg	
	H_2O	5% HNO_3
(1) Cr_2O_3 (34,210 µg Cr), no heating	2	4
(2) Heating Cr_2O_3 at 1000°C, ½ h	10	1
(3) Heating Cr_2O_3 at 1000°C, ½ h with 0.1 g $CaCl_2$	764	8,470
(4) Heating Cr_2O_3 at 1000°C, ½ h with 0.1 g CaO	4,400	14,000

In condition (2), practically no conversion of Cr_2O_3 to a soluble compound, such as CrO_3, took place, contrary to what Massillamany suggested. In condition (3), the conversion to a soluble compound became obvious. In (4), the conversion was significant, 4400 / 34210 = 12.8% of Cr_2O_3 alone being converted to a water soluble compound. That is why the Cr content in the leachate of the heat-treated fly ash (in the presence of CaO or $CaCl_2$) is higher than that of the untreated fly ash.

A similar experiment was also carried out using CrO_3 instead of Cr_2O_3. This hygroscopic dark purple brown coloured compound is readily soluble in water and forms chromic acid, H_2CrO_4, an orange-brown coloured solution. It is not likely that this compound exists in the fly ash. However, it is worthwhile to understand the behaviour of CrO_3 at high temperatures. Under similar heating conditions as before, the Cr content of the leachates were obtained. The results are shown in Table 23.

Table 23
Cr contents in leachates under different heating conditions

Condition	Cr in leachate, µg	
	H_2O	5% HNO_3
(1) CrO_3, 0.050g (26,000 µg Cr), (dark purple brown colour) no heating	(Completely dissolved)	
(2) Heating CrO_3 at 1000°C, ½ h, (turned bright green)	10	1
(3) Heating CrO_3 at 1000°C, ½ h, with 0.1 g $CaCl_2$, (turned bright green)	788	6,029

The condition (2) showed practically all the CrO_3 had converted to an insoluble compound, presumably Cr_2O_3, according to the following equation

$$2\ CrO_3 \rightarrow Cr_2O_3 + 3/2\ O_2 \qquad (25)$$

The reaction proceeds from left to right, not right to left. Both the appearance of the characteristic bright green colour and the similar leaching behaviour of the product lead to this conclusion. In condition (3), some CrO_3 reacted with $CaCl_2$ to form $CaCrO_4$ according to the equation

$$CrO_3 + CaCl_2 + 1/2\ O_2 \rightarrow CaCrO_4 + Cl_2 \qquad (26)$$

and the rest of the CrO_3 converted to Cr_2O_3.

The next step of the experiment was to examine the products (the solid masses) left after heating under conditions (3) and (4) in Table 22, using powder XRD technique. In both cases, $CaCrO_4$ and Cr_2O_3 were identified as the main phases, Cr_2O_3 being the excess reactant. Just as important, no $CrCl_3$ was found in the product from condition (3), Table 22. Fig. 15 is the powder X-ray diffraction spectra. This experiment confirms that reactions (22) and (24) are correct, and that the soluble product, $CaCrO_4$, is the cause of more Cr leached out from the heat-treated fly ash.

5.5.3.2 **Leaching of Al**

Scanning electron microscope analysis of the heat-treated ash showed that many of the silicate spheres in the ash were broken and shattered due to the heat. Massillamany [26] explained in his thesis that the heat treatment may result in more aluminum from the aluminum silicate within the sphere being exposed to the leachate solution and thus resulting in an increase in aluminum extraction. The explanation seemed partially satisfactory. Further investigation into this matter, particularly the possible reactions involved, was desired.

Al_2O_3 is insoluble in water and dilute acids. When it reacts with CaO or $CaCl_2$ at 1000°C, calcium aluminate, $Ca(AlO_2)_2$ (or $CaO\cdot Al_2O_3$), may form according to the following equations:

$$Al_2O_{3(s)} + CaO_{(s)} \rightarrow Ca(AlO_2)_{2(s)} \qquad \Delta G^\circ_{1000^\circ C} = -45.1\ kJ \quad (27)$$

$$Al_2O_{3(s)} + CaCl_{2(l)} + 1/2\ O_2 \rightarrow Ca(AlO_2)_{2(s)} + Cl_2 \qquad \Delta G^\circ_{1000^\circ C} = 60.9\ kJ \quad (28)$$

$AlCl_3$ cannot be the solid product at 1000°C, since it sublimes readily at 190°C. If these equations hold, Al should be able to be detected in the aqueous solutions of the products, since $Ca(AlO_2)_2$ is soluble in water [36]. The fact that Al was leached from the heat-treated fly ash does not necessarily reveal the soluble salt phase nor confirms the presence of $Ca(AlO_2)_2$, since the leachable fraction is much less than 1% of the sample and XRD could not be used to identify the new phase in the residue. Therefore, synthetic samples had to be tested to uncover the chemical reactions.

To verify these reactions, experiments were carried out by heating Al_2O_3 with equimolar of each of $CaCl_2$ and CaO at 1000°C in a muffle furnace followed by dissolution of the products first in water and then in 5% HNO_3, and the concentrations of Al in the solutions were determined. Some parameters of the experiment are as follows:

Al_2O_3 - 204.0 mg was used in each test, equivalent to 108.0 mg of Al.
$CaCl_2$ - 222.2 mg was used in each test.
CaO - 112.0 mg was used in each test.
Heating - 1 h at 1000°C.

Dissolution sequence - After heating , the sample in a porcelain crucible was leached with water overnight. The supernatant solution was decanted out for Al analysis by AAS. The water insoluble mass was then leached by 5% HNO_3 for 1 h, and the solution was also analyzed for Al. The Al content obtained under different heating conditions are shown in Table 24.

Table 24
Al content in leachates from different heating conditions

Condition	Al in leachate, mg	
	H_2O	5% HNO_3
(1) Al_2O_3, (108 mg Al), no heating	< 0.01	0.09
(2) Al_2O_3, heating	< 0.01	0.09
(3) Al_2O_3, $CaCl_2$, pre-wet, heating	0.40	14.12
(4) Al_2O_3, $CaCl_2$, dry mix, heating	0.39	10.32
(5) Al_2O_3, CaO, pre-wet, heating	0.66	19.82

Conditions (1) and (2) show that heating Al_2O_3 alone would not alter its insoluble nature; conditions (3) to (5) show that about 10 to 20% of the Al_2O_3 converted to acid soluble aluminum compound; and conditions (3) and (4) show that the pre-wetted reactants had a better yield compared with that from dry mixed reactants, since pre-wetting resulted in better contact between the reactants.

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. 16 and 17 are the powder X-ray diffraction spectra. In case (i) two chemical phases were identified, $Ca(AlO_2)_2$ and $12CaO\cdot 7Al_2O_3$. In case (ii) only $12CaO\cdot 7Al_2O_3$ was found. Both compounds are soluble in water and in acidic solution [41]. The XRD results demonstrate that reaction (27) can occur, but do not support reaction (28). This is in consistent with the thermodynamic data which indicate that reaction (27) with a ΔG° value of -45.1 kJ is more favourable than reaction (28) with a ΔG° of +60.9 kJ. The XRD results also suggest two more possible reactions:

$$12\ CaCl_{2(l)} + 7\ Al_2O_{3(s)} + 6\ O_2 \rightarrow 12CaO \cdot 7Al_2O_{3(s)} + 12\ Cl_2 \qquad (29)$$

$$\Delta G^{o}_{1000^{o}C} = -2140\ kJ$$

$$12\ CaO_{(s)} + 7\ Al_2O_{3(s)} \rightarrow 12CaO \cdot 7Al_2O_{3(s)} \qquad (30)$$

$$\Delta G^{o}_{1000^{o}C} = -3413\ kJ$$

Given the low yield of soluble Al in the fly ash sample, the relative dominance of reactions (27), (29) and (30) can not be resolved, but the cause of solubilization is explained. The finding from Massillamany that the heat treated fly ash produces more leachable Al, can also be explained by the fact that soluble Al compounds, as mentioned above, are formed after heat treatment.

5.6 Fate of $CaCl_2$ during roasting

A preliminary test for the behaviour of $CaCl_2$ at high temperatures by thermogravimetric analysis and evolved gas analysis using a mass spectrometer (TGA-MS) was carried out by heating $CaCl_2$ in air at the rate of 5°C/min. The thermogram is shown in Fig. 18. All the moisture and hydrated water evaporated before reaching 200°C, which is in consistency with the data in the Chemistry Handbook [35] (Section 5.2.3.1). The test revealed:

(1) The anhydrous $CaCl_2$ began to lose weight at about 725°C in air, melted at 772°C, and the evaporation accelerated at the range of 772-1100°C.

(2) Cl_2 was detected starting at about 900°C and the amount increased as the temperature further increased.

(3) No Ca compound was detected by MS, indicating that it condensed along the exit end of the heating chamber before reaching the mass spectrometer.

(4) After heating, some residue was left on the inside and outside walls of the platinum sample holder. It did not completely dissolve in water in a short period of time. This suggests that some $CaCl_2$ was converted to CaO by reacting with O_2 and releasing Cl_2.

There could be a number of ways in which $CaCl_2$ could react when roasted in air. (i) It may remain as a liquid all along, since its boiling point is very high, 1935°C. (ii) It may vaporize partially. (iii) It may react with oxygen in the vapour or liquid phases (melting point is 775°C) to produce chlorine, such as:

$$CaCl_{2(g,l)} + 1/2\ O_2 \rightarrow CaO + Cl_2 \qquad (3)$$

To clarify the situation, an experiment was carried out to identify the distribution of the reaction products at 1000°C. A 0.622 g sample of $CaCl_2 \cdot 2H_2O$, contained in an alumina boat, was heated in the quartz tube furnace at 1000°C for 3 h using air as carrier. In addition to the absorber which contained 5% HNO_3 solution, an impinger containing NaOH solution was added to trap the chlorine from the exit of the absorber. It was noticed that the efficiency of the impinger was not high enough to capture all the chlorine, since the smell of the escaped chlorine gas was quite distinct. After roasting, the boat was retrieved. A slick film covered the entire inside and outside surface of the boat was observed. This surface was rinsed with water. The rinsing is referred to as solution (1). The quartz tube was rinsed with 5% HNO_3, as solution (2). The connecting tube between the quartz tube and the absorbing solution was rinsed with 5% HNO_3, solution (3). The 5% HNO_3 in the absorber was solution (4), and the NaOH solution in the impinger was solution (5). These solutions, (1) to (5), were analyzed for Ca and Cl^-, and the contents in each solution are shown in Table 25

Table 25
Ca and Cl^- contents in rinsing and absorbing solutions, from roasting 0.622 g $CaCl_2 \cdot 2H_2O$ (3500 µmol $CaCl_2$)

Solution	Location	Ca		Cl^-	
		µg	µmol	µg	µmol Cl_2
(1)	Boat	32360	809	47200	665
(2)	Quartz tube	81300	2032	48800	687
(3)	Connecting tube	2	-	560	8
(4)	Absorber	< 2	-	39200	552
(5)	Impinger	8	-	52480	740
	Total		2841		2652

Solutions (1) and (2) reveal that the $CaCl_2$ melted and crept over the boat during roasting at 1000°C. 665 µmol, about 20% of the original, survived the ordeal and remained intact sticking on the surface of the boat. 809 - 665 = 144 µmol $CaCl_2$ in liquid phase reacted with O_2 to form CaO which remained on board. At the same time 144 µmol of Cl_2 were generated. 687 µmol of $CaCl_2$ vaporized from the boat and condensed in the quartz tube outside the heating zone; the other 2032 - 687 = 1345 µmol $CaCl_2$ also vaporized, but reacted with O_2 to form 1345 µmol CaO which deposited on the quartz tube, generating another 1345 µmol of Cl_2. (Total Cl_2 generated was 144 + 1345 = 1489 µmol). None of the $CaCl_2$ or CaO was able to travel beyond the quartz tube. Solution (3) shows that the connecting tube contained little of either Ca or Cl_2, since not only the Ca could not reach that area, but also there was little chance for Cl_2 to stay there without being swept away by the air stream. Solutions (3), (4) and (5) indicate that they captured 8 + 552 + 740 = 1300 µmol of Cl_2 , allowing 1489 - 1300 = 189 µmol to escape.

The mass balance of Ca and Cl was not exact. There are some reasons for it. (i) The $CaCl_2$ used in this test may contain more moisture, and therefore the equivalent weight could well be less than 3500 µmol. (ii) Some CaO formed may not be completely dissolved by the 5% HNO_3 rinsing solution, and, therefore, those amounts of Ca and the associated Cl_2 have not been accounted for. (iii) The Cl_2 evolved was not completely captured, and the true amount of Cl_2 could be higher. Nevertheless, the analysis can be considered semi-quantitative, and the results reflect the fate of $CaCl_2$ during roasting.

As shown above, there was about 20% of $CaCl_2$, 665 µmol, left in the sample boat after roasting. To see whether the same amount of $CaCl_2$ would be left if roasted with the fly ash sample, a duplicate of 3 g samples was run under the same conditions. After roasting, the samples were leached with water overnight. (These leachates were equivalent to solution (1) in Table 25). The leachates were analyzed for Cl^- and Ca along with the detectable metals. The contents of these elements are shown in Table 26.

Table 26
Elemental content (µmol) in water leachates.
Duplicate of 3 g sample D were roasted with
0.622 g $CaCl\cdot 2H_2O$, (3500 µmol $CaCl_2$)

Element	µ mol (Duplicate run)	
Cl_2 (Cl^- x 2)	297	270
Ca	328	311
Na	19	19
K	3	3
Sr	1	1

The duplicate results are close, indicating that the roasting process is quite reproducible. There were only about 290 µmol of $CaCl_2$ left, about 8% of the original, after it was roasted with the sample. This occurred because the other metals in the fly ash also consumed the $CaCl_2$ to form volatile metal chlorides. Also from Table 26, there is strong evidence that Ca forms refractory compounds (about 3500 - 328 = 3172 µmol) during roasting, which cannot be dissolved in acids, let alone water. The results demonstrate that the reactions involved in roasting $CaCl_2$ alone are quite different compared with roasting $CaCl_2$ with the sample.

Although $CaCl_2$ has a very low vapour pressure at 1000°C, 4.8×10^{-5} atm. (see Table 29, p. 69), it can still vaporize. The escape of molecules from a liquid phase into a vapour phase in an open system is affected by many factors. Vaporization takes place faster when there is a large surface. A current of air across the surface of the evaporating liquid also increases the rate of evaporation, since the volatilized molecules are swept away from the liquid surface. In addition, prolonging the evaporation time is bound to produce more vapour in an open system, since equilibrium cannot be established. All these factors exist under the roasting conditions and explain the evaporation of $CaCl_2$.

5.7 Gaseous chlorinating agents

5.7.1 Chlorine as chlorinating agent

5.7.1.1 Effect on volatilization using chlorine as chlorinating agent

The effect on volatilization of metals from the fly ash depends on many factors as reported in our study [42]. Among them are the types of chlorinating agents and 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. From the mechanism given earlier, the generation of chlorine gas from the chloride salt under oxidizing condition is possible. Thus, the investigation of the importance of chlorine gas in volatilization was carried out. Chlorine from a lecture bottle was introduced into the pre-heated furnace with sample (sample D) at 900°C. The air carrier flow rate was kept at 150 mL/min. Within the next 10 minutes, the temperature of the quartz tube reached 1000°C. The chlorine flow rate was controlled by a non-corrodible regulator. The effect on volatilization of six elements (Pb, Cu, Zn, Cd, Cr, and Mn) 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), was examined. Chemical analysis on the captured volatile matter was done by AAS. The quantities of the elements volatilized are plotted as a function of time in Figs. 19 and 20. 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 the effect on volatilization whether the Cl_2 flow rate is 3 or 6 mL/min, once the Cl_2 is in excess.

5.7.1.2 **Comparison of volatilization using $CaCl_2$ vs. Cl_2**

In order to better understand the chlorination mechanism, it might be important to know the difference made, by using a solid chlorinating agent such as $CaCl_2$ as 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 for 3 h. The rest of the heating parameters remained the same, namely, 3 g of sample D were heated at 1000°C with the air flow rate of 150 mL/min. The ICP analytical results of the volatile matter for 32 elements, using Cl_2 as chlorinating agent, are shown in Table 27, column 3. The parallel results obtained from using $CaCl_2 \cdot 2H_2O$, and the total, as quoted in Table 19 (p. 45), are also tabulated here for comparison purposes. E is the efficiency of volatilization.

Table 27
Effect of chlorinating agents (Cl_2 vs. $CaCl_2 \cdot 2H_2O$) on volatilization of 32 elements in sample D, heating at 1000°C for 3 h.
Values are in µg/g sample.

Element	Volatile matter		Total	E, %	
	$CaCl_2$	Cl_2		$CaCl_2$	Cl_2
Pb	3666	3723	3870	94.7	96.2
Cu	933	1010	1030	90.5	98.0
Zn	9133	9500	9468	96.4	100
Cd	140	145	142	98.5	100
Cr	24	133	365	6.5	36.4
Mn	746	2016	1914	38.9	100
Na	37330	37360	49460	75.4	75.5
K	22730	22000	24400	93.1	90.1
Mg	4	1200	12300	< .1	9.7
Ca	152	1000	105900	< .1	0.9
Fe	83	11000	18660	0.4	58.9
Al	1	60	71120	< .1	< .1
Ti	< 1	< 1	18610	0	0
Be	< 1	< 1	2	< .1	< .1
P	8	86	6830	0.1	1.2
Sc	< 1	< 1	5	< .1	< .1
V	1	40	58	1.7	68.9
Co	12	33	31	38.7	100
Ni	58	210	207	28.0	100
As	< 1	10	60	< .1	16.6
Sr	1	3	445	0.2	0.6
Y	< 1	< 1	8	< .1	< .1
Zr	< 1	< 1	171	0	0
Mo	2	40	43	4.6	93.0
Ag	7	10	27	25.9	37.0
Sn	< 1	320	330	< .1	96.9
Sb	< 1	480	526	< .1	91.2
Ba	3	10	934	0.3	1.0
La	< 1	< 1	18	< .1	< .1
W	< 1	< 1	21	< .1	< .1
Bi	< 1	24	12	< .1	100
Hg	0.3	0.4	0.4	75.0	100

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 of environmental concern, the 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) The Cl_2 is as effective for Na and K.

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

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

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 [1,43]. These compounds have very different thermal behaviour. In general, chlorides have lower melting and boiling points than oxides and sulphates (see Appendix C). Upon heating, sulphates usually decompose to form oxides. Consequently, the metals in chloride form are likely easier to be removed than the metals in oxide or sulphate form. To be effectively volatilized, the metals have to be in or converted to chloride form. It is the whole purpose of using a chlorinating agent, so that chlorine can be generated for reacting and converting the oxide or sulphate into chloride.

One of the possible reactions of chlorination using $CaCl_2$ are as follows:

$$CaCl_{2(l)} + 1/2\ O_2 \rightarrow CaO + Cl_2 \qquad (3)$$

$$MO + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2 \qquad (5)$$

The first stage is the generation of chlorine, and the second stage is the 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 effective or slow. It is, therefore, expected that by using Cl_2 directly, the chlorination of a metal chloride should be more effective. The higher E values in the last column in Table 27 indicate that that is the case. The results support the said reaction mechanism.

The other reasons for Cl_2 to be more effective than $CaCl_2$ include:

(i) The ΔG^o value for the chlorination reaction is smaller. Take ZnO for example.

$$ZnO_{(s)} + Cl_2 \rightarrow ZnCl_{2(g)} + 1/2\ O_2 \qquad \Delta G^o = -55.2\ kJ/mol$$

$$\underset{(-604.7)}{ZnO_{(s)} + CaCl_{2(l)}} \rightarrow \underset{(-498.7)}{ZnCl_{2(g)} + CaO_{(s)}} \qquad \Delta G^o = +50.8\ kJ/mol$$

The ΔG^o_f for $CaCl_{2(l)}$ and $CaO_{(s)}$ are -604.7 and -498.7 kJ/mol respectively. There is always 604.7 - 498.7 = 106 kJ/mol higher for the ΔG^o if $CaCl_2$ is used instead of Cl_2.

(ii) 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 this 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 desired for certain heavy metals, such as Pb, Cu, Zn, and Cd, which impose a potential environmental problem or 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. Besides, $CaCl_2$ is much safer to use in the roasting operation, while Cl_2, basically a poisonous gas, will pose a health hazard if leakage occurs.

5.7.1.3 **Fe behaviour during chlorine roasting**

When Cl_2 was used as a chlorinating agent in the experiment instead of $CaCl_2$, a black layer accumulated at the exit end of the quartz tube after many roastings of samples. This black deposit was not soluble in the 5% HNO_3 rinsing solution. Pieces were broken loose when shaken with the solution. They were collected, dried, and subjected to various tests. The results were:

(1) The pieces were not soluble in HNO_3, HCl, and aqua regia, nor were they with the aid of HF and $HClO_4$. They were only slightly soluble in boiling HCl.

(2) When held in a flame, the pieces glowed but did not combust. Thus, the possibility of their being carbon is ruled out.

(3) They were fused with $LiBO_2$ and were completely dissolved in dilute acid. The elements in the solution were analyzed by ICP. The main constituents of the black deposit, in terms of elements, were found to be Fe, 50%; Na, 1.4%; Ca, 0.5%; and Cr, 0.5%.

(4) They were examined by powder XRD. The main mineral phase was identified as Fe_2O_3 (hematite).

The result in (4) explains the result in (1), since hematite, a dark coloured compound, is virtually insoluble in acids. The fact that a large quantity of Fe volatilized, as shown in Table 27, should lead us to believe that accumulation of some dark coloured deposit (Fe compound) in the quartz tube would be inevitable after many roastings of samples. Fe^0 is not volatile, nor are Fe_2O_3 and FeO with melting points of 1565°C and 1337°C respectively. Fernandez et al. [11] reported that iron presented a complex situation in the combustion gases of MSW incinerators. $FeCl_3$ is not stable at temperatures above its boiling point, 316°C [11]. The only way for iron to form a volatile compound is by forming the chloride of Fe^{+2} [11]. They explained that the possibility of iron occurring at its lower valence depends on the composition of the combustion gas stream. An excess amount of air will prevent Fe distillation, while a reducing atmosphere will favour the formation of Fe^{+2}. It is possible that in the Cl_2 atmosphere, both $FeCl_3$ and $FeCl_2$ are formed. These compounds can react with oxygen to form solid Fe_2O_3 via an oxychloride (FeOCl) even at lower temperatures (400°C) as suggested by Pechkovskii and Vorob'ev [44]. The black deposit at the exit end of the quartz tube was probably the product of this reaction.

5.7.2 HCl as chlorinating agent

Besides $CaCl_2$ and Cl_2, HCl is also a common chlorinating agent used in many industrial processes [45]. The reaction is expressed in the form,

$$MO + 2\ HCl_{(g)} \rightarrow MCl_{2(g)} + H_2O \qquad (31)$$

The study of the effect of using HCl on volatilization of the heavy metals in fly ash was included. A glass boat containing concentrated hydrochloric acid was inserted in the inlet end of the quartz tube when the temperature of the furnace reached about 900°C. Within the next 10 minutes, the temperature of the quartz tube reached 1000°C. The HCl vapour was swept by the air stream into the heating zone where it reacted with the fly ash (sample D).

One to two hours were normally required for the HCl to completely evaporate from the boat depending on the amount of HCl used. Various amounts, 1, 2 and 3 mL, of HCl were placed in the glass boat in the experiment, and the volatile metals (Pb, Cu, Zn, Cd and Cr) obtained in each run were analyzed by AAS. The results are shown in Table 28. The E values, calculated based on using 3 mL HCl, are shown in the last column. Apparently, HCl is also a very effective chlorinating agent if used sufficiently. As a chlorinating agent for the above heavy metals, HCl is comparable with $CaCl_2$ and Cl_2. All three agents achieve >90% efficiency of volatilization for Pb, Cu, Zn and Cd (see Table 27, p. 62, for the E values from $CaCl_2$ and Cl_2). Considering the factors of safety and easiness of handling, $CaCl_2$ is clearly the best choice among the other two, particularly for a large scale operation.

Table 28
HCl effect on volatilization of heavy metals, μg / g sample.
(Sample D was heated at 1000°C until HCl was completely evaporated)

Element	HCl used, mL				
	0	1	2	3	E, %
Pb	3355	3545	3611	3758	97.1
Cu	696	909	909	1021	99.1
Zn	3722	7666	8333	8666	91.5
Cd	114	130	130	130	91.5
Cr	< 20	< 20	< 20	< 20	< 6

5.8 Thermodynamics and kinetics of volatilization

5.8.1 Thermodynamics of volatilization

5.8.1.1 Volatilization efficiencies vs. vapour pressures of metal chlorides

The degree of volatilization of a metal chloride at a given temperature is very much dependent on its vapour pressure (v.p.). The higher the v.p. of a chloride, the easier its vaporization. The efficiency of volatilization (E) of a metal compound in a fly ash sample, however, depends not only on the v.p. of the metal chloride, but also the convertibility of the metal compound into chloride. If the metal compound contains a large portion of unconvertible metal, then the E could not be high, even if the v.p. of its chloride is high. Zn is known to exist in fly ash in large portion as an oxide, but because it can be converted to chloride, its E can still be very high. The v.p. of a number of the metal chlorides at 1000°C were calculated from thermodynamic data [36,46]. They are shown in Table 29 along with the E values. From the Table, there is observed a correspondence of vapour pressure with recovery. In general, high v.p., above 1 atm, results in high E, greater than 90%, for elements such as Zn and Pb; medium v.p., 0.1 to 1 atm, results in medium E, 20-40%, for elements such as Mn and Co; and for low v.p., below 0.1 atm, leads to low E, less than 7%, for elements such as Cr and Mg.

Table 29
Volatilization efficiencies vs. vapour pressures of metal chlorides at 1000°C

Chloride	v.p., atm	E, %
$ZnCl_2$	17.8	96.4
$PbCl_2$	1.85	94.7
$CdCl_2$	1.54	98.5
CuCl	1.12	90.5
$NiCl_2$	1.13	28.0
$MnCl_2$	0.12	38.9
$CoCl_2$	0.81	38.7
$FeCl_2$	0.79	0.4
$CrCl_2$	5.5×10^{-3}	6.5
$MgCl_2$	2.1×10^{-2}	< .1
$CaCl_2$	4.78×10^{-5}	< .1
$BaCl_2$	9.28×10^{-3}	0.3
NaCl	1.07×10^{-2}	75.4
KCl	2.03×10^{-2}	93.1

There are exceptions to this general trend. $FeCl_2$ has a v.p. almost the same as that of $CoCl_2$ and yet only volatilized 0.4%. $FeCl_2$ is not stable at 1000°C [47], and for the conditions of oxygen and Cl used, Fe_2O_3 rather than $FeCl_2$ is the stable Fe phase. The same is true for the stability of NiO with respect to $NiCl_2$. $NiCl_2$ has a high v.p. similar to CuCl and yet is only 28% vaporized. Verhulst et al. [34] reported that $NiCl_2$ is stable only at low temperature, and is converted to NiO above about 250°C in air. They found that only small quantities of $NiCl_{2(g)}$, and $NiCl_{(g)}$ can exist in the higher temperature range. Their findings support our results. It is reasonable that if the formation of a compound is difficult, the recovery of that compound has to be low. NaCl and KCl have a low v.p., but are substantially vaporized. The reason is that the formation of NaCl and KCl is thermodynamically favourable with reference to oxides, as can be seen from the following equations:

$$Na_2O + Cl_2 \rightarrow 2\ NaCl_{(g)} + 1/2\ O_2 \qquad \Delta G^\circ_{1000°C} = -262\ kJ$$

$$K_2O + Cl_2 \rightarrow 2\ KCl_{(g)} + 1/2\ O_2 \qquad \Delta G^\circ_{1000°C} = -366\ kJ$$

Substantial amounts of Na and K can be recovered because the NaCl and KCl are stable in the tube furnace and their vapour will be removed by the gas carrier over a long period of time.

5.8.1.2 **Relationship between E and ΔG°**

The reaction of a metal chloride with oxygen is reversible:

$$MCl_2 + 1/2\ O_2 \rightleftharpoons MO + Cl_2$$

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 (ΔG°) 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 ΔG° values for a number of reactions were calculated using the available thermochemical data [30]. For example, ΔG° for Co was calculated based on the following equation.

$$CoO_{(s)} + Cl_2 \rightarrow CoCl_{2(g)} + 1/2\ O_2 \qquad \Delta G^\circ_{1000°C} = -6.3\ kJ/mol\ Cl_2 \qquad (32)$$

Only those metals which have sufficient amount 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 silicate and the chlorine (released from $CaCl_2$), to form chloride, silica, and oxygen, was also used to calculate the ΔG°s for the elements of Na, K, Ca, Mg, Sr, and Ba, such as,

$$Na_2SiO_{3(s)} + Cl_2 \rightarrow 2\ NaCl_{(g)} + SiO_{2(s)} + 1/2\ O_2 \qquad (33)$$
$$\Delta G^\circ_{1000^\circ C} = -35.8\ kJ/mol\ Cl_2$$

Both ΔG° values (calculated from metal oxides and from metal silicates) for these six elements are shown in Table 30. It is understood that the ΔG° for a certain 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 is available for its gaseous state. For the rest of the compounds the most stable state under the roasting condition was used. The equations for the reactions and the calculation of their ΔG° values at 1000°C are shown in Appendix F. The E values (volatile / total, in %) of 18 metals, calculated from Table 19, and their corresponding ΔG° values are tabulated in Table 30.

Table 30
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)	* ΔG°, kJ/mol Cl_2 (3)	** ΔG°, kJ/mol Cl_2 (4)
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

* Based on $MO_{(s)} + Cl_2 \rightarrow MCl_{2(g)} + \frac{1}{2} O_2$

** Based on $MSiO_{3(s)} + Cl_2 \rightarrow MCl_{2(g)} + SiO_{2(s)} + \frac{1}{2} O_2$

There is no overall relationship between the E values and the ΔG° values (column 3) calculated from metal oxides. However, if the ΔG° values for the alkali and alkaline earth metals are replaced with the ΔG° values in column 4, calculated from metal silicates, a plot of the E values vs. ΔG°s produces a linear trend for the partially recovered elements, as shown in Fig. 21. It appears that near complete volatilization occurs for a reaction with a ΔG° value lower than -50 kJ/mol Cl_2, and little volatilization takes place for a reaction with a ΔG° 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 $-\Delta G^\circ$ value of the corresponding chlorination reaction. The metals with large E, such as Zn and Cu, have large negative ΔG° and likely form stable chlorides. On the other hand, metals with very small E, such as Ba and Ti, have large positive ΔG° and likely form stable oxides. Between these two extreme groups, Mn, Co, and Ni have about the same tendency to form oxides and chlorides.

5.8.1.3 Comparison of ΔG for chlorination using $CaCl_2$ vs. Cl_2

The free energy change for a chlorination reaction, such as

$$MO_{(s)} + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2 \qquad (5)$$

can be calculated by the equation

$$\Delta G = \Delta G^\circ + RT \ln (p^{1/2}_{O_2} \cdot p_{MCl_2} / p_{Cl_2}) \qquad (34)$$

if all the unknowns on the right side of the equation can be accounted for. Since

ΔG° can be calculated from the thermochemical data;
T is 1000°C (1273°K);
the partial pressure of O_2 is 0.21 atm;
the roasting time is 3 h (180 min);
the air flow rate is 150 mL/min;
the partial pressure (p.p.) of Cl_2 is:

i) using $CaCl_2$ (0.3 g Cl_2), assuming 92% of the Cl_2 evolved (see Section 5.6, p. 59),
   - at 25°C and 1 atm, 300 mg x 0.92 = 276 mg of Cl_2 occupies (276 / 71) x 24.47 mL = 95.1 mL,
   - its average flow rate is 95.1 mL/180 min = 0.528 mL/min (the rate of release of Cl_2 may not be constant),
   - the average p.p. of Cl_2 during the 3 hours period of roasting is 0.528/150 = 0.0035 atm,

ii) using Cl_2 at the flow rate of 3 mL/min,

- the p.p. of Cl_2 is 3/150 = 0.02 atm;
  and the partial pressure of MCl_2 is calculated in a similar way, knowing the total amount of M volatilized (see calculation in Appendix G),

Therefore, ΔG can be calculated. For example, the free energy change for the chlorination of lead oxide

$$PbO_{(s)} + Cl_2 \rightarrow PbCl_{2(g)} + 1/2\ O_2 \qquad (6)$$

using $CaCl_2$ as chlorinating agent at 1000°C is

$$\Delta G = \Delta G^{\circ} + RT \ln\ (\ p^{1/2}_{O_2} \cdot p_{PbCl_2}\ /\ p_{Cl_2}\ ) \qquad (35)$$
$$= -106 + 0.008314 \times 1273 \ln\ (\ 0.21^{1/2} \times 4.8 \times 10^{-5}\ /\ 0.0035\ )$$
$$= -160 \text{ kJ/mol } Cl_2$$

A detailed calculation is shown in Appendix G. Similar calculations were applied to a number of chlorination reactions, and the ΔG values are shown in Table 31. When Cl_2 is used as chlorinating agent, p_{Cl_2} = 0.02 atm is substituted for 0.0035 atm in equation (35) for calculation of ΔG. The ΔG values thus calculated for the same chlorination reactions are also shown in Table 31.

Table 31
ΔG values for chlorination reactions, using $CaCl_2$ vs. Cl_2

Reaction	ΔG, kJ/mol Cl_2	
	$CaCl_2$	Cl_2
$PbO_{(s)} + Cl_2 \rightarrow PbCl_{2(g)} + 1/2\ O_2$	-160	-178
$ZnO_{(s)} + Cl_2 \rightarrow ZnCl_{2(g)} + 1/2\ O_2$	-88	-105
$6\ CuO_{(s)} + 3\ Cl_2 \rightarrow 2\ Cu_3Cl_{3(g)} + 3\ O_2$	-112	-129
$CdO_{(s)} + Cl_2 \rightarrow CdCl_{2(g)} + 1/2\ O_2$	-180	-197
$Mn_2O_{3(s)} + 2\ Cl_2 \rightarrow 2\ MnCl_{2(g)} + 3/2\ O_2$	-48	-55
$Fe_2O_{3(s)} + 2\ Cl_2 \rightarrow 2\ FeCl_{2(g)} + 3/2\ O_2$	-38	-5

As can be seen from the last two columns of Table 31, the ΔG values from using Cl_2 are smaller (more negative) for Pb, Zn, Cu, Cd and Mn. This is consistent with the fact that more of these elements were volatilized when Cl_2 was used. However, the interpretation of the ΔG values for Fe contradict the experimental finding. This disagreement implies that the true reactions of Fe may not be the one shown in Table 31. $FeCl_2$ is not stable at 1000°C as mentioned in 5.8.1.1. [47]. Fe very often exists in the form of double oxides, such as $MgO \cdot Fe_2O_3$ and $CaO \cdot Fe_2O_3$ [34]. Not many thermodynamic values describing the mixing properties of different types of phases are available. In the present study, Fe_2O_3 and $FeCl_2$ have been assumed to be present as single phases. Consequently, the interpretation of the presumed reaction with the basic thermodynamic data could be inaccurate.

5.8.2 Kinetics of chlorination of selected metals in fly ash

The effect of roasting time on volatilization of Pb, Zn, Cd, and Cu using $CaCl_2$ as a chlorinating agent can be observed from Fig. 5. The reaction of Cu was clearly the slowest of all. Two hours were needed for Cu to complete volatilization, while only half an hour was needed for Pb, Zn, and Cd.

In a reaction involving two reactants, such as

$$A + B \rightarrow \text{product(s)}$$

the rate equation is $-dC_A/dt = kC_A \cdot C_B$

where C is the concentration of a reactant, t is the time, $-dC_A/dt$ is the rate at which the concentration of reactant A decreases, and k is the rate constant. If one of the reactants, B, is in great excess so that its concentration, C_B, is essentially constant, the rate equation becomes

$$-dC_A/dt = k'C_A \qquad \text{where } k' = kC_B$$

The reaction is called a pseudo-first-order reaction [48]. It has the characteristic of a first-order reaction. A plot of ln C_A against t will be linear. In the chlorination of a metal species (M) or metal oxide (MO) in a well mixed fly ash sample using excess chlorinating agent, $CaCl_2$,

$$MO + CaCl_{2(l)} \rightarrow MCl_{2(g)} + CaO \qquad (13)$$

or $$MO + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2 \qquad (5)$$

the reaction may fall into the same category, an essential first-order reaction. The rate equation is

$$-dC_M/dt = kC_M$$

where C_M, is the concentration of the metal species in the homogeneous melt phase of the fly ash sample, in µg M / g sample. Equation (13) represents reaction mechanism (a) described in Section 3.2., p. 9; and equation (5) represents reaction mechanism (b) in the same Section, p. 10.

The rate of reaction can be determined experimentally by measuring the amounts of the reactant left in the ash sample after suitable time intervals; and a rate equation can be developed. Recently, Jakob et al. [49] performed experiments with fly ash from a MSW incineration plant as well as synthetic powder mixtures in the temperature range of 670-1000°C. They described the rates of Cd, Cu, Pb, and Zn evaporation by a simple first-order rate law. In their experiments, they did not use $CaCl_2$ as a chlorinating agent for roasting samples, instead, they relied mainly on the NaCl available in the fly ash samples. Consequently, the efficiency as well as the rates of evaporation of the heavy metals may vary from sample to sample depending on the amounts of NaCl present in the samples. In some fly ashes, the chloride concentrations are less than 1% (see Appendix B) and are insufficient for reacting with all the heavy metals. For example, the average Cl concentration of the fly ash over a period of 16 months in Alexandria (Va.) Municipal Incinerator in the Washington, D.C., area was 0.8% [50]. In those cases, the efficiency of volatilization of the metals will suffer. Moreover, the results from Jakob et al. indicate that the recovery of Zn at 1000°C in air was far from complete, about 50%. Zn is the most abundant heavy metal in MSW fly ash, and its good yield in recovery is vitally important. Zinc is present mainly in the form of oxide and is common to associate with ferric oxide to form zinc ferrite ($ZnO \cdot Fe_2O_3$). As we have described previously (see page 29 and Fig. 6), that NaCl is not an effective chlorinating agent for volatilizing Zn from fly ash or from zinc oxide and ferrite. To be effective, $CaCl_2$ must be used. Our study of reaction rates of the selected metals (Cu, Cr, Mn, Ni, Na, K, Zn. Cd and Pb) in fly ash was based on the roasting conditions - using $CaCl_2$ (10 wt% of Cl) as a chlorinating agent at 1000°C.

5.8.2.1 **The reaction rate of Cu in fly ash**

The fly ash used for the study had been well mixed as described in Section 4.2. The uniformity of the sample is reflected by the reproducibility of the analytical results in general. The concentration of a metal species in the fly ash can be represented by μg M / g sample. The rate of disappearance of Cu in the heated fly ash sample is -dC/dt, where C is the concentration of the remaining volatile Cu in the sample (μg Cu / g sample) at time t (minutes); let C_0 be the initial concentration of the volatile Cu, at time t = 0. If the reaction is of first-order, as shown in the following equation,

$$-dC/dt = kC \qquad (36)$$

which upon integration gives

$$\ln C = \ln C_0 - kt \qquad (37)$$

where k is the rate constant with the unit of min^{-1}, a plot of ln C against t will be linear with a slope of -k and an intercept of ln C_0.

Experimental data of the Cu concentrations, obtained by heating 3 g of ash samples (sample D) with $CaCl_2$ (0.3 g Cl) at 1000°C for various periods of time, are given in Table 32. The concentration, C, values were calculated by subtracting each volatile Cu content from its total volatile. Since temperature is a critical factor affecting reaction rate, the samples were placed in and removed from the furnace at the same temperature, 1000°C.

Table 32
Cu concentrations in fly ash after heating sample D for various periods of time.

Time, minutes	C, µgCu/g sample	ln C
0	1030	6.94
1	1019	6.92
3	942	6.85
5	880	6.78
10	663	6.50
20	398	6.00
30	278	5.63
60	56	4.00

The relationship between C and t is shown in Fig. 22 (a). A plot of ln C vs. t produces a straight line as shown in Fig. 22 (b), indicating that the reaction of Cu compound in fly ash with excess of $CaCl_2$ is a first-order one. An excellent correlation was found ($r^2 = 0.997$). The slope of the straight line, -k, can be calculated as

$$(6.94 - 4.00) / -60 \text{ min} = -0.049 \text{ min}^{-1}.$$

The reaction-rate constant becomes, k = 0.049 min^{-1}.

Equation (37) can also be written as

$$\ln C = 6.94 - 0.049\,t$$

or $$C = 1030\, e^{-0.049t}$$

5.8.2.2 **The reaction rates of selected metals in fly ash**

The reaction rates for a number of metals were also studied. They are Cr, Mn, Ni, Na, K, Zn, Cd and Pb. The experimental data of the metal concentrations, obtained by heating the samples with $CaCl_2$ at 1000°C for various periods of time, are shown in Tables (1)-(8) in Appendix H. The total volatile concentrations were used as their initial concentrations in the fly ash , since only those volatile metals participated the chlorination reactions.

The relationships between the concentration of the metal, C, and t are shown in Figs. 23(a)-30(a). All the plots of ln C vs. t produce straight lines as shown in Figs. 23(b)-30(b), indicating that the reactions of these metal compounds in fly ash with excess of $CaCl_2$ are of first order. Good linear relationships were observed with correlation coefficients (r^2) ranging from 0.940 to 0.997.

The k values were calculated using equation (37).

$$\ln C = \ln C_0 - kt \qquad (37)$$

$$k = (\ln C_0 - \ln C)\,/\,t$$

for Cr, $$k = (3.40 - 1.99)\,/\,120\ \text{min}$$

$$= 0.012\ \text{min}^{-1}$$

The other k values were calculated in a similar way, and they are grouped in Table 33.

Table 33
k values for the chlorination reactions

Element	k, min^{-1}
Cu	0.049
Cr	0.012
Mn	0.0044
Ni	0.0053
Na	0.012
K	0.017
Zn	0.13
Cd	0.20
Pb	0.33

The k values for Zn, Cd and Pb are larger, indicating that the chlorination of these metal compounds are faster reactions compared with the others. This is consistent with the experimental observation (see Fig. 5).

5.8.2.3 **The chlorination reaction mechanisms**

Rate study and knowing the reaction order can be used to analyze and propose possible reaction mechanisms, and eliminate impossible ones. The rate of the overall reaction is determined by the slowest reaction in the sequence. The finding suggests that the rate determining step of the chlorination reaction mechanism (a), described in Section 3.2., p. 9, is

$$MO + CaCl_{2(l)} \rightarrow MCl_{2(g)} + CaO \qquad (13)$$

where MO and $CaCl_2$ are dissolved in the melt phase of the fly ash sample; and the rate determining step of the reaction mechanism (b) is

$$MO + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2 \qquad (5)$$

where MO and chlorine are dissolved in the melt phase of the fly ash sample. Both reaction mechanisms (a) and (b) are consistent with and supported by the kinetic data. In this study, no attempt was made to distinguish which of them is more prevailing. Mechanism (c) cannot be supported because the reaction took place in a heterogeneous phase, and its rate equation cannot be derived from the present data.

A physical change could also be a rate determining step. Consider the process of volatilization. Let r be the rate of evaporation of MCl_2 in mass per unit area (top surface area of the pile of the ash sample), per unit time, at a fixed temperature. This rate depends on the difference between the concentration and the saturation concentration of MCl_2 in the sample. The situation is described mathematically as follows:

$$\begin{aligned} r &= k(C_s - C) \\ &= -k(C - C_s) \end{aligned}$$

where C is expressed in mass per unit volume of the ash sample. If the top surface area is A and the depth of the pile is h, then the rate of loss to evaporation is $r \cdot A$ or

$$-A \cdot k(C - C_s) \qquad \text{(Rate 1)}$$

From another point of view, the rate of change of concentration of MCl_2 in the sample at the same temperature is dC/dt; and the rate of change of mass of MCl_2 in the sample is

$$A \cdot h \cdot dC/dt \qquad \text{(Rate 2)}$$

Rate 1 and rate 2 are equal, that is

$$A \cdot h \cdot dC/dt = -A \cdot k(C - C_s)$$

or

$$dC/dt = -k/h(C - C_s)$$

integrating, we have $(C - C_s)/(C_0 - C_s) = e^{-kt/h}$

or $$C = C_s + (C_0 - C_s)e^{-kt/h} \qquad (38)$$

This has the same linearity as the rate limiting chemical step of ln C vs. t. Also, if the species has a high vapour pressure and thus high saturation concentration, $C_s >> C_0$, equation (38) becomes

$$C = C_s(1 - e^{-kt/h}) \qquad (39)$$

Thus, the first order plot might also imply a physical evaporation rate limiting step.

5.9 Application of the roasting process

5.9.1 Treatment of the iron oxide dusts from a steel works

In the steelmaking process, various kinds of dusts are generated in different areas of the facilities. These dusts contain high concentrations of iron. The basic oxygen furnace (BOF) iron oxide dust is captured from the fumes generated by the hot metal above the BOF vessels and collected by means of an electrostatic precipitator; It is predominantly magnetite (Fe_3O_4) and lime (CaO and $CaCO_3$) with minor phases of hematite (Fe_2O_3), quartz (SiO_2) and periclase (MgO). The O.G. sludge is the solid concentrate from the wet scrubber system; it is primarily composed of iron in magnetite form (Fe_3O_4). Both the BOF oxide and the O.G. sludge contain more than 50% Fe. The high content of iron induce an incentive to recycle these materials back to the steelmaking furnaces. However, these dusts usually contain zinc and lead at concentration levels too high to be reused as an iron-bearing feed. The zinc is combined with iron as zinc ferrite and the lead is in oxide form. The zinc, particularly, could promote refractory attack. The zinc should be removed from the dusts to as low a level as possible before recycling of the dusts is considered.

In view of the effectiveness of removal of zinc and other heavy metals from fly ash by the roasting process, the same success might be met if the process is applied to the iron dusts. There was awareness about the effectiveness of the application because the zinc in the iron dusts is in the form of ferrite ($ZnO \cdot Fe_2O_3$) and the Zn may not be released easily. However, the promising results from a previous experiment in which 93% of the Zn was recovered from heating $ZnO \cdot Fe_2O_3$ with $CaCl_2$ (see Section 5.2.3.1, p. 29) prompted the investigation of the two dust samples, BOF Oxide and O.G. Sludge. These two samples were obtained from Stelco Inc., Hamilton, Ontario. Given what we know about Fe and Zn in fly ash, we would expect that (i) $ZnCl_2$ would be produced if the iron dusts are to be chlorinated with $CaCl_2$, (ii) the efficiencies of volatilization for Zn and Pb should be high, and (iii) time for roasting does not need to exceed two hours if the volatilization of Zn and Pb is the main concern. Due to the difference of the matrices of the samples (fly ash vs. iron dusts), the volatilization efficiencies for some metal species may differ. For example, in the presence of Fe_2O_3, Cu may form the stable $CuO \cdot Fe_2O_3$ [34] and may not be readily released by $CaCl_2$ (see Section 5.2.2, p. 24), and hence will have a lower E value; on the other hand, Pb does not form a double oxide with Fe_2O_3, and therefore, its full recovery is expected. Study of the parameters of roasting was needed before the conditions of the roasting process can be determined. The parameters include the amount of chlorinating agent, $CaCl_2$ (and/or HCl), and the time of roasting. The samples were dried first before being used in the experiments. The water contents were found to be 11.5 and 60.7% for the BOF Oxide and the O.G. Sludge respectively.

A 3 g sample of dried BOF Oxide was heated at 1000°C for 1.5 h with addition of various amounts of $CaCl_2$, i.e., equivalent to 0 - 0.4 g of Cl. The volatile matter obtained was dissolved and Zn, Pb, Cu, Cd and Cr were determined by AAS. The results are shown in Table 34. The minimum amount of Cl added to achieve the best yields for Zn and Pb appears to be 0.2 g.

Table 34
$CaCl_2$ effect on volatilization of heavy metals, µg/g sample.
BOF Oxide sample was heated at 1000°C for 1.5 h (single analysis).

Metal	Equivalent Cl added, g					
	0	0.05	0.1	0.2	0.3	0.4
Zn	38	4466	8333	10000	10000	9733
Pb	111	375	486	430	375	333
Cu	9	18	28	22	16	16
Cd	< 2	< 2	< 2	< 2	< 2	< 2
Cr	< 2	< 2	< 2	< 2	< 2	< 2

The total amounts of the above heavy metals in the dried BOF oxide sample were determined by digestion of the sample directly with aqua regia followed by AAS. The results are shown in Table 35 along with the efficiencies of volatilization of the metals.

Table 35
Metal contents in BOF Oxide sample, and E values

Metal	µg/g sample	E, %
Zn	12000	83
Pb	364	100
Cu	430	5
Cd	< 5	-
Cr	307	< 1

A general view was noted from the results. More than 80% of the Zn and Pb were removed. Cu and Cr were not affected under the above heating conditions. In the presence of Fe_2O_3 as in this case, formation of $CuO \cdot Fe_2O_3$ could explain why Cu volatilization remains very limited.

An experiment was also carried out on roasting 3 g of dried O.G. Sludge sample at 1000°C under various conditions: (i) using 0.3 g Cl ($CaCl_2$) for 2 h, (ii) using 0.3 g Cl ($CaCl_2$) for 3 h, and (iii) using 0.3 g Cl ($CaCl_2$) in addition with 3 mL HCl for 3 h. The volatile metals are shown on the left hand side of Table 36. Duplicate sludge samples, using 0.2 and 0.5 g, were digested with aqua regia followed by ICP analysis to obtain the total content of the metals. The E values were calculated and are also shown in Table 36.

The roasting condition (3), namely using HCl as well as $CaCl_2$ is most effective for volatilizing metals, particularly for Zn. More than 90% of Zn and Pb can be removed. By comparison, the E values for many metals other than Zn and Pb are lower than those in the fly ash, notably Cr, Mn and Cu. This indicates that these metal compounds in the sludge are not easily converted to chloride form under the roasting conditions. Nevertheless, the roasting process proves to be useful for removal of Zn and Pb from the steelmaking dusts.

Table 36

O.G. Sludge sample was heated at 1000°C
(single analysis for each condition)

Volatile: From 3 g sample	Total digestion:
(1) 2 h, 0.3 g Cl	(1) 0.2 g
(2) 3 h, 0.3 g Cl	(2) 0.5 g
(3) 3 h, 0.3 g Cl + 3 mL HCl	

	Volatile µg/g sample	Total content µg/g sample	E, %
	(1) (2) (3)	(1) (2)	
Be	--	--	
Na	326; 413; 586	1450*; 680	
Mg	--; --; --	18350; 17680	0
Al	--; --; --	400; 440	0
P	--; --; --	460	0
K	520*; 200; 133	100; 120	100
Ca	233; 340; 466	49000; 47800	0.8
Sc	--; --; --	--	
Ti	--; --; --	--	
V	--; --; --	135; 130	0
Cr	1; 1; 1	485; 528	< 1
Mn	10; 11; 54	10100; 10120	0.5
Fe	--; --; --	575000; 582000	0
Co	--; --; --	15	0
Ni	--; --; --	40; 50	0
Cu	77; 68; 123	265	46
Zn	33400; 31860; 49600	49000; 50200	> 90
As	--	--	
Sr	--	--	
Y	--	--	
Zr	--	--	
Mo	--	--	
Ag	3; 3; 35	35; 25	10
Cd	44; 45; 44	120	37
Sn	--	--	
Sb	--	--	
Ba	--	--	
La	--	--	
W	--	--	
Pb	7400; 7466; 7533	7300; 7460	> 90
Bi	6; 5; 6	--	

* Possible outlier.

Before the steelmaking dusts can be recycled to the furnaces, they have to be sintered in order to obtain the required physical properties and chemical composition. Many steel companies experiment with the sinter making process. Stelco has investigated the process using a sinter pot to heat the raw sinter mix with the addition of calcium chloride. They have succeeded in reducing the alkali content, but failed in eliminating zinc. Because the flame front temperature during sintering was 1300°C, there was a concern that at this temperature, chloridization of Zn may not be effective, although it works well at 1000°C as was demonstrated by our experiment. According to the thermodynamic data for the reaction,

$$ZnO + Cl_2 \rightarrow ZnCl_2 + 1/2\ O_2 \qquad \Delta G^{\circ}_{1000C} = -55\ kJ \qquad (8)$$

$$\Delta G^{\circ}_{1300C} = -82\ kJ$$

the conversion of the zinc compound at 1300°C should be even more favourable than at 1000°C, assuming the above reaction is the predominant one.

To test the effect of temperature at 1300°C, an O.G. Sludge sample was roasted in a high temperature tube furnace, and the Zn remaining in the residue was determined. The analytical procedure was as follows:

(a) Heating of the O.G. Sludge sample.
    (1) 1.000 g of the dried sludge sample was thoroughly mixed with 0.2 g of $CaCl_2$.
    (2) the sample was transferred to a alumina boat using a piece of platinum foil as a liner.
    (3) When the tube (alumina) furnace reached 1300°C, the sample boat was pushed into the centre section of the tube by means of a metal rod.
    (4) After 45 min of heating, the sample was retrieved from the furnace.

(b) Analysis of the residue.

(1) The sample residue which remained on the platinum foil was boiled with aqua regia for about 20 min. Not all of the residue can be dissolved. The solution was collected.

(2) Some spilt deposit on the alumina boat was also rinsed with boiling aqua regia. The solution was collected and combined with the previous one.

(3) The Zn concentration of the combined solution was determined by AAS.

(c) Calculation.

The Zn content was calculated as 154 μg which accounts for the Zn remaining in the residue after heating 1 g of the sludge sample. The Zn content in the original sludge sample was 49600 μg/g as previously determined. Therefore, in terms of percentage, the Zn remained in the residue was only

$(154 / 49600) \times 100\% = 0.31\%$

This experiment confirms that the Zn can be removed effectively by the roasting process even at 1300°C.

5.9.2 Decontamination of dioxins and furans from the MSW fly ash

In the environment, dioxins and furans are almost always found adsorbed onto particles such as soil, sediment and ash [51]. In addition to the heavy metals, these highly toxic compounds have been detected in MSW incinerator fly ash samples. The term dioxins refers to chlorinated dibenzo-p-dioxins (CDDs) which are a series of 75 different compounds as illustrated in Fig. 31(a) [51]. The same applies to furans which are chlorinated dibenzofurans (CDFs) and are comprised of 135 compounds (also see Fig. 31(a)). Out of this total of 210 compounds, 17 receive more attention due to their potential human toxicity. These are the chlorinated dioxins and furans that contain 4 or more chlorines per molecule with the chlorine atoms in the 2,3,7 and 8 positions. These 17 are listed in Fig. 31 (b).

The dioxins and furans are very insoluble in water and are only sparingly soluble in most organic solvents. They are highly inert and difficult to eliminate. They can be destroyed only by using very harsh methods such as photolysis with high power UV lamps, catalytic hydro-dehalogenation, and high temperature incineration [51]. In view of the availability of the roasting process, there should be a good chance that the process might be able to remove these organic compounds, if there are any, from the fly ash. To test this possibility, a 3 g of fly ash (sample C) was roasted at 1000°C for an hour without the addition of a chlorinating agent. The heat-treated fly ash along with an untreated fly ash sample, were analyzed for dioxins and furans. The analyses were performed in the laboratory of Ontario Ministry of Environment and Energy. The analytical procedure is outlined as follows: (see the detailed procedure in Appendix I).

The toxins in the sample were extracted in refluxing toluene for 16 hours using a Soxhlet extractor. The toxins in the toluene were purified. The interfering organic compounds were removed from the sample extract by use of open-column liquid-solid chromatography. The toxins in the extract were then analyzed by gas chromatography/mass spectrometry.

The results shown in Table 37 demonstrate that dioxins and furans do exist in the fly ash. They were reduced to negligible amounts in the fly ash after the thermal treatment. However, the fate of these toxins, whether they volatilize, break down or are more created during roasting, has not yet been determined.

Table 37
Dioxins and furans in MSW fly ash samples, pg/g sample (single analysis)

Toxin	Untreated ash	Heat treated ash
Tetrachlorofuran, total (18 i*)	16,000	< 1
Tetrachlorodioxin, total (15 i)	8,100	< 1
Pentachlorofuran, total (15 i)	31,000	< 1
Pentachlorodioxin, total (12 i)	30,000	< 3
Hexachlorofuran, total (12 i)	43,000	< 2
Hexachlorodioxin, total (7 i)	79,000	< 3
Heptachlorofuran, total (4 i)	50,000	< 2
Heptachlorodioxin, total (2 i)	120,000	< 4
Octachlorofuran	16,000	< 2
Octachlorodioxin	170,000	< 20
2378-tetrachlorofuran	3,000	< 1
2378-tetrachlorodioxin	450	< 1
12378-pentachlorofuran	1,700	< 1
23478-pentachlorofuran	2,800	< 1
12378-pentachlorodioxin	2,800	< 1
123478-hexachlorofuran	7,700	< 2
123678-hexachlorofuran	5,100	< 1
234678-hexachlorofuran	5,700	< 2
123789-hexachlorofuran	370	< 2
123478-hexachlorodioxin	5,300	< 3
123678-hexachlorodioxin	6,300	< 3
123789-hexachlorodioxin	11,000	< 3
1234678-heptachlorofuran	33,000	< 2
1234789-heptachlorofuran	2,500	< 2
1234678-heptachlorodioxin	65,000	< 4

* i = isomers

6. SUMMARY

A thermal treatment method using $CaCl_2$ as a chlorinating agent for removal of the heavy metals (Pb, Zn, Cd, Cu) from MSW incinerator fly ash has been developed.

Two possible chlorination reactions are:

(a) $MO + CaCl_{2(l)} \rightarrow MCl_{2(g)} + CaO$

The metal oxide dissolves in the melt phase of the fly ash sample and reacts with the $CaCl_2$.

(b) $CaCl_{2(l)} + 1/2\ O_2 \rightarrow CaO + Cl_2$ (I)

$MO + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2$ (II)

The chlorine generated from (I) dissolves in the melt and reacts with the dissolved metal oxide. In the presence of SiO_2, equation (I) could proceed as:

$$CaCl_{2(l)} + SiO_2 + 1/2\ O_2 \rightarrow CaSiO_3 + Cl_2$$

The chlorination reaction with Cu is the slowest among those with Pb, Zn an Cd. The slow volatilization is due to the high boiling point (1400°C) of CuCl, the stable species at 1000°C. Another possibility could be the formation of the double oxides, $CuO \cdot Fe_2O_3$ and $CuO \cdot Al_2O_3$, or silicates, which hinder the chlorination reaction.

Volatilization of a total of 32 elements were studied. The complete elemental analysis revealed the elemental distribution among the heat-treated and untreated fly ash, and the volatile matter. More refractory compounds containing Mg, Ca, Fe, Al and Ti, were formed after heat treatment. Two chemical phases, $Ca(Mg,Al)(Si,Al)_2O_6$ (pyroxene), and $CaAl_2Si_2O_8$ (anorthite), were identified in the heat treated fly ash.

Cl was quite concentrated, about 8 wt%, on the surface of the fly ash before the heat treatment. Upon heat treatment, the Cl volatilized almost totally as metal chlorides. A significant portion of the Cl was associated with Na and K in the volatile matter. Moreover, the metal chlorides tend to form double salts. Three chemical phases, $Na_2ZnCl_4 \cdot 3H_2O$, K_2ZnCl_4 and KPb_2Cl_5, were identified in the volatile matter, the former being the most dominant one.

More than 70% of the Na salt and 90% of K salt ended up in the volatile matter after the heat treatment on a fly ash sample. This is one of the reasons that NaCl is not a good chlorinating agent. The recovery of Zn from pure ZnO was only 2.1% when NaCl was used as a chlorinating agent, compared with 80% when $CaCl_2$ was used; and the recovery of Zn from $ZnO \cdot Fe_2O_3$ was 6.5% when NaCl was used as against 93% when $CaCl_2$ was used.

The volatilization efficiency (E) of most metal chlorides was proportional to the vapour pressure of the chlorides at 1000°C. There was a linear relationship between the E of the partially recovered metals and their ΔG^o values for the corresponding chlorination reactions. The chlorination reactions with the metals (Cu, Cr, Mn, Ni, Na, K, Zn, Cd and Pb), using $CaCl_2$ as a chlorinating agent, followed the first-order rate law.

Cl_2 is a more effective chlorinating agent compared with $CaCl_2$ for volatilizing Mn, Ni, and particularly for Fe.

The exceptional leaching behaviour of Cr and Al, more leaching out from the ash that has been heat-treated, is due to the formation of the soluble $CaCrO_4$, $Ca(AlO_2)_2$, and $12CaO \cdot 7Al_2O_3$.

The roasting process is useful for (i) removal of Zn and Pb from the steelmaking dust, so that the dust can be suitable for recycling back to the ironmaking furnaces and (ii) decontamination of dioxins and furans from the MSW fly ash.

7. CONCLUSIONS

(1) A thermal treatment method in a laboratory scale for removal of the heavy metals (Pb, Zn, Cd, Cu) from MSW incinerator fly ash has been developed. The satisfactory operating conditions for a 3 g sample are as follows:

$CaCl_2 \cdot 2H_2O$ added,	0.622 g (0.3 g Cl)
Roasting temperature,	1000°C
Roasting time (for recovering Pb, Zn, Cd, Cu),	3 h
(for recovering Pb, Zn, Cd),	½ h
Air (carrier) flow rate,	150 mL/min

(2) The heavy metals, such as Pb, Zn, Cu and Cd, are volatilized under the roasting conditions as chloride. For those metals not in chloride form, the reactions of chlorination follow two possible mechanisms:

(a) $MO + CaCl_{2(l)} \rightarrow MCl_{2(g)} + CaO$

where the metal oxide and $CaCl_2$ are dissolved in the melt phase of the fly ash sample.

(b) $CaCl_{2(l)} + 1/2\ O_2 \rightarrow CaO + Cl_2$ (I)

$MO + Cl_2 \rightarrow MCl_{2(g)} + 1/2\ O_2$ (II)

The chlorine generated from (I) dissolves in the melt and reacts with the dissolved metal oxide. In the presence of SiO_2, equation (I) could proceed as,

$$CaCl_{2(l)} + SiO_2 + 1/2\ O_2 \rightarrow CaSiO_3 + Cl_2$$

NaCl is not an effective chlorinating agent for volatilizing Zn because NaCl is not reactive to the dominant Zn compounds, such as ZnO and $ZnO \cdot Fe_2O_3$, hence, $CaCl_2$ must be used in order to achieve high efficiency of volatilization.

(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.

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.

Cl is highly concentrated on the surface of the fly ash; upon heat treatment, Cl volatilizes almost totally as metal chlorides, and Ca, Al and Si become more concentrated and exposed on the surface of the fly ash.

(4) The volatilization efficiency (E) of most metal chlorides is proportional to the vapour pressure of the chlorides. There is a linear relationship between the E of the partially volatilized metals and their ΔG^0 values for the corresponding chlorination reactions. The chlorination reactions with the metals (Cu, Cr, Mn, Ni, Na, K, Zn, Cd and Pb), using $CaCl_2$ as a chlorinating agent, follow the first-order rate law.

(5) The exceptional leaching behaviour of Cr and Al, (more leaching out from the fly ash that has been heat-treated), is due to the formation of soluble $CaCrO_4$, $Ca(AlO_2)_2$ and $12CaO \cdot 7Al_2O_3$.

(6) The roasting process developed for the MSW fly ash can be applied to a steel dust waste to remove zinc and lead impurities so that the dust becomes suitable for recycling back to the steelmaking furnaces. The process can also decontaminate dioxins and furans from the MSW fly ash.

(7) This work opens up many subject areas in MSW fly ash for further in-depth studies, such as (i) thermal behaviour and reaction rate of Fe, (ii) remedy for the leachability of Cr, (iii) behaviour of metals during roasting under reducing conditions, (iv) the fate of dioxins under thermal treatment, and (v) use of a rotary kiln instead of a tube furnace for thermal treatment.

8. NOMENCLATURE

MSW	Municipal solid waste
AAS	Atomic absorption spectroscopy
ICP	Inductively coupled plasma spectroscopy
IC	Ion chromatography
TGA	Thermogravimetric analysis
XRD	X-ray diffraction spectroscopy (powder diffraction)
XPS	X-ray photoelectron spectroscopy
GC	Gas chromatography
MS	Mass spectroscopy
E	Volatilization efficiency (% of a metal volatilized)
s.d.	Standard deviation
r.s.d.	Relative standard deviation
p	Pressure, atm.
v.p.	Vapour pressure, atm.
T	Temperature, °C or °K
R	Gas constant (0.008314 kJ deg^{-1} mol^{-1})
ΔG^o	Standard free energy change for a reaction
ΔG	Free energy change for a reaction
C	Concentration of a volatile metal in fly ash sample
t	Time, min
k	Reaction-rate constant, min^{-1}
BOF	Basic oxygen furnace
CDDs	Chlorinated dibenzo-p-dioxins
CDFs	Chlorinated dibenzofurans

9. REFERENCES

1. Mitchell, D.J.; Wild, S.R.; Jones, K.C. Environ. Pollution. 1992, 76, 79-84.

2. Tauscher, D.M. W.I.S.E. research report, J. Environmental Sciences, March/April, 1989, pp. 18-20.

3. Graydon, J.W.; Kirk, D.W., Proceedings of EPD Congress, ed. J.P. Hager. 1992, 327-350.

4. Germani, M.S. and Zoller, W.H. Atmos. Environ., Vol. 16, 8, 1994, 1393.

5. Hutton, M. and Symon, C. Sci. Total Environ., 57, 1986, 129.

6. Korzun, E.A. and Heck, H.H.J. Air Waste Manage. Assoc., Vol. 40, 1990, 1220.

7. Francis, C.W. and White, G.H.J. Water Pollut. Control Fed., Vol. 59, 1987, 979.

8. Cernuschi, S., Giugliano, M. and de Paoli, I. Waste Manage. Res., Vol. 8, 1990, 419.

9. General - Waste Management Regulation, under the Environmental Protection Act, Regulation 347 of the Revised Regulations of Ontario, 1990. Printed by the Queen's Printer for Ontario.

10. Gong, Y. and Kirk, D.W. J. Hazard. Mater., Vol. 36, 1994, 249.

11. Fernandez, M.A., Martinez, L., Seggara, M., Garcia, J.C. and Espiell, F. Environ. Sci. Technol., Vol. 26, 1992,1040.

12. McKinley, M.D., Warren, G.W., Lahoti, S.M. and Sreenivasaroa, K. J. Hazard. Mater., 29 (1992) 255-273.

13. Vehlow, J., Braun, H., Horch, K. Merz, A. Schneider, J. Stieglitz, L. and Vogg, H. Waste Management & Research, Vol. 8, 1990, 461-472.

14. Alcock, C.B. Principles of Pyrometallurgy, Academic Press Inc. (London) Ltd., 1976, pp. 28-35.

15. Habashi, F. Principles of Extractive Metallurgy, Vol.3: Pyrometallurgy, Gordon and Breach Science Publishers, New York, 1986, pp. 217-239.

16. Jakob, A., Stucki, S. and Kuhn, P. Environ. Sci. Technol. 29, 1995, 2429-2436.

17. Fray, D.J. in: Hager, J. et al. (Ed.), Extraction and Processing for the Treatment and Minimization of Wastes, The Minerals, Metals & Materials Society of Canada, 1993.

18. Deng, H. and Li, X. Trans. Instn. Min. Metall. Section C, March, 1987, p. 96.

19. Kubaschewski, O. and Alcock, C.B. Metallurgical Thermochemistry, 5th edn., Pergamon Press, Oxford, 1979, pp. 214-215.

20. Griepink, B.; Mintau, H. Fresenius Z. Anal. Chem. 1987, 326, 414-418.

21. Karstensen, K.H. and Lund, W.J. Anal. At. Spectrom. 1989, 4, 357-359.

22. Cahill. C.A. and Newland, L.W. Intern. J. Environ. Anal. Chem. 11, 1982, pp. 227-239.

23. Vogg, H. International Chemical Engineering, Vol. 27, No. 2, 1987, pp. 177-182.

24. Senior, C.L. and Flagan, R.C. Aerosol Science and Technology, 1, 1982, p. 371.

25. Clapp, T.C., Magee II, J.F., Ahlert, R.C. and Kosson, D.S. Environmental Progress, Vol. 7, No. 1, 1988, pp. 22-29.

26. Massillamany, E. Thesis for M.A.Sc., Department of Chemical Engineering and Applied Chemistry, University of Toronto, 1993.

27. Clifford, D.A., Chen, S. and Reznik, C. Waste Management, 13, 1993, pp. 467-479.

28. Holmstrom, A. Scandinavian J. Metallurgy 17, 1988, 272-280.

29. Morizot, G., Winter, J.M. and Barbery, G. Complex Sulphide Ores, Pap. Conf., Edited by Jones,M.J. Inst. Min. Metall.: London, 1980, 151-158.

30. Barin, I. Thermochemical Data of Pure Substances, 2nd. ed.; VCH, New York, 1993.

31. Zyryanov, M.N. and Gakhlebnikova, G.A. Tsvetnye Metally, Mosk., 45, No. 6, 1972, 22.

32. Kirby, C.S. and Rimstidt, J.D. Environ. Sci. Technol. 27, 1993, 652-660.

33. NUS Corporation, "Characterization of Municipal Waste Combustion residue and their Leachate, A Literature Review", U.S. Department of Commerce, National Technical Information Services, 1987.

34. Verhulst, D., Buekens, A., Spencer, P.J. and Eriksson, G. Environ. Sci. Technol., 30, 1996, 50-56.

35. Sax, N.I. and Lewis Sr, R.J. (Revised), Hawley's Condensed Chemical Dictionary, 11th edn., 1987, Van Nostrand Reinhold, New York.

36. D.R. Lide, Editor-in-Chief, Handbook of Chemistry and Physics, 77th Edition, 1996 -1997, CRC Press, Inc. Boca Raton, Florida, USA.

37. Deadmore, D.L. and Machin, J.S. J. Am. Ceram. Soc. 43 (1960) 11, p. 593.

38. Harrap, B.S. and Heymann, E. Chem. Rev. 48 (1951) p. 45.

39. Briggs, D. Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy, Heyden & Son Ltd., London, 1977.

40. Shoto, E. and Hattori, M. Toxic and Hazardous Waste Disposal, Vol. 3, edited by R.B. Pojasek, 1980, pp. 125-140.

41. Taylor, H.F.W. Cement Chemistry, Academic Press, New York, 1990, pp. 35-38.

42. Chan, C., Jia, C.Q., Graydon, J.W., Kirk, D.W. J. Hazardous Materials. 50, 1996, 1-13.

43. Eighmy, T.T., Eusden Jr., J.D., Krzanowski, J.E., Domingo, D.S., Stämpfli, D., Martin, J.R. and Erickson, P.M. Environ. Sci. Technol. 29, 1995, pp. 629-646.

44. Pechkovskii, V.V. and Vorob'ev, N.I. Russian Journal of Inorganic Chemistry, 9 (1) 1964, p. 6.

45. Coudurier, L., Hopkins, D.W. and Wilkomirsky, I., Fundamentals of Metallurgical Processes, 2nd. Edition, Pergamon Press, 1978, pp. 179-183.

46. Thompson, W.T.; Pelton, A.D.; Bale, C.W., Guide to Operations FACT (Facility for the Analysis of Chemical Thermodynamics), May, 1985, Thermfact Ltd., Mount-Royal, Quebec, Canada.

47. Hupa, M., Backman, P., Backman, R., and Tran, H.N., Engineering Foundation Conference on Fireside Problems While Incinerating Municipal and Industrial Solid waste, Florida, Oct. 1989.

48. Keenan, C.W., Kleinfelter, D.C. and Wood, J.H., General College Chemistry, Sixth Edition, Harper & Row Publishers, 1980, p. 424.

49. Jakob, A., Stucki, S. and Struis, R.P.W.J. Environ. Sci. Technol. 30, 1996, 3275-3283.

50. Greenberg, R.R., Zoller, W.H. and Gordon, G.E. Environ. Sci. Technol. 12, No. 5, 1978, pp. 566-573.

51. Chittim, B.G. Environ. Sci. & Engineering, 8, No. 3, 1995, pp. 68-70.

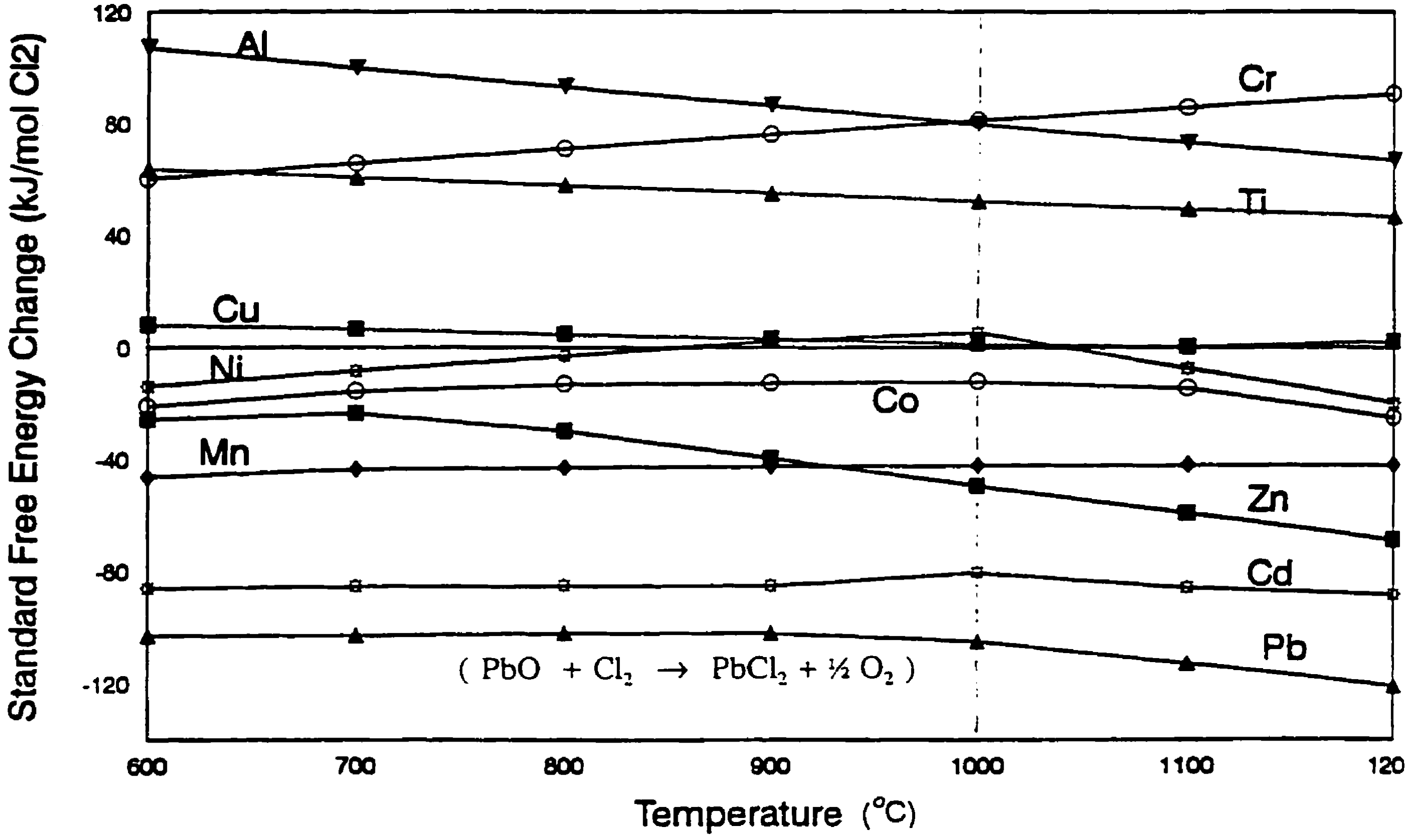


Fig. 1. Temperature dependence of standard free energy change of reactions between metal oxide and 1 mol chlorine forming chloride and ½ mol oxygen (Data was calculated via Ref. [30])

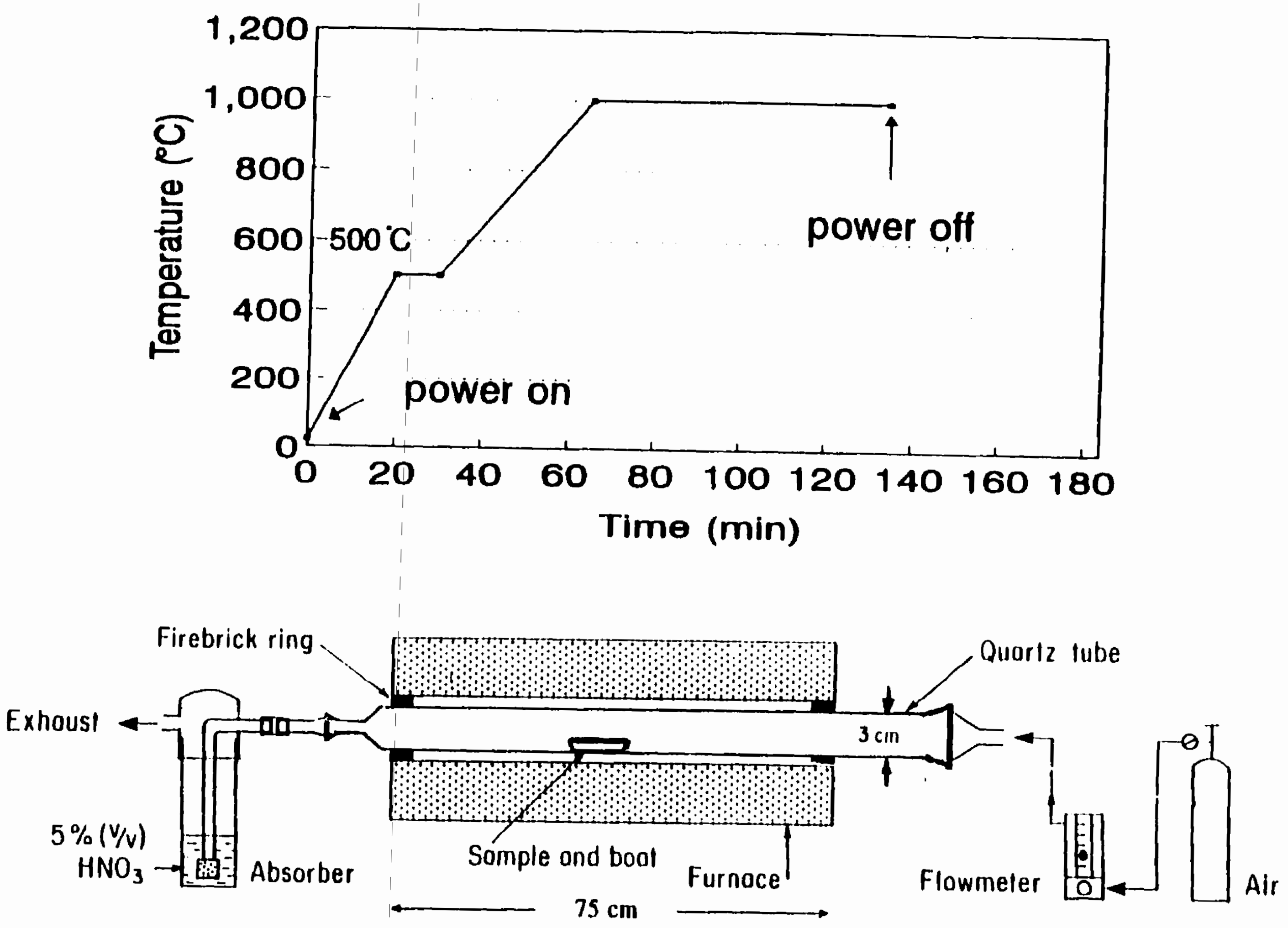


Fig. 2. Experimental apparatus and the heating sequence

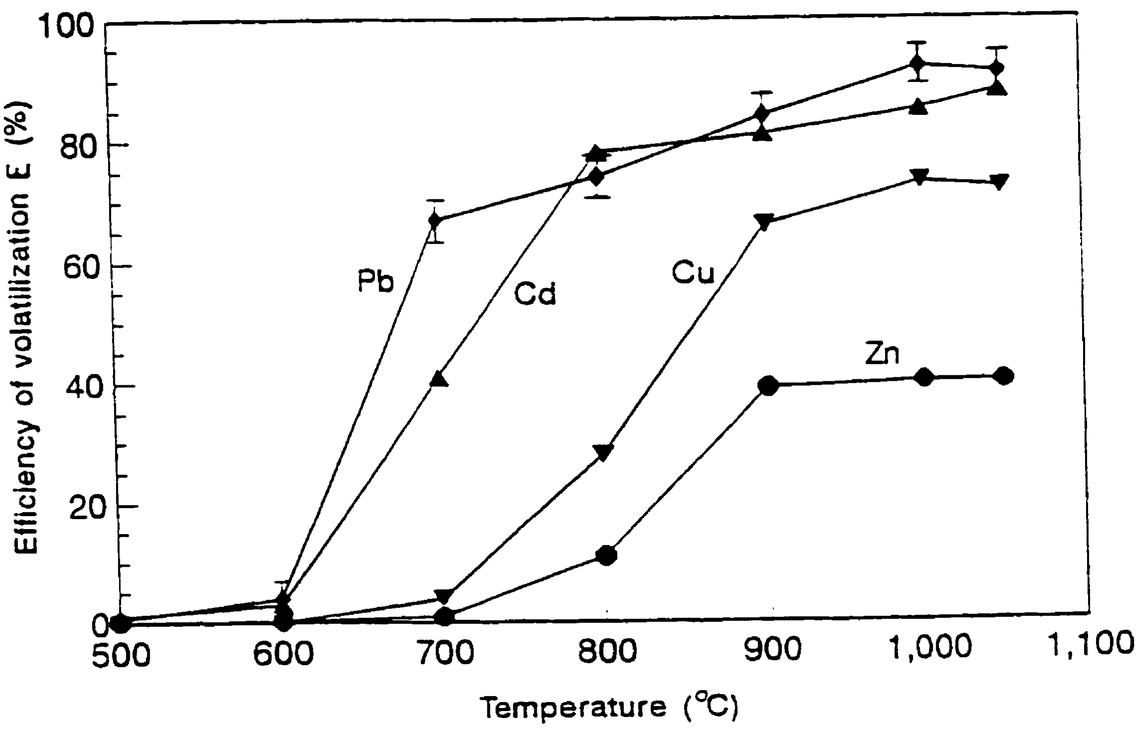


Fig. 3. Temperature dependence of heavy metal removal without chlorination agent (holding at target temperature for 180 minutes)

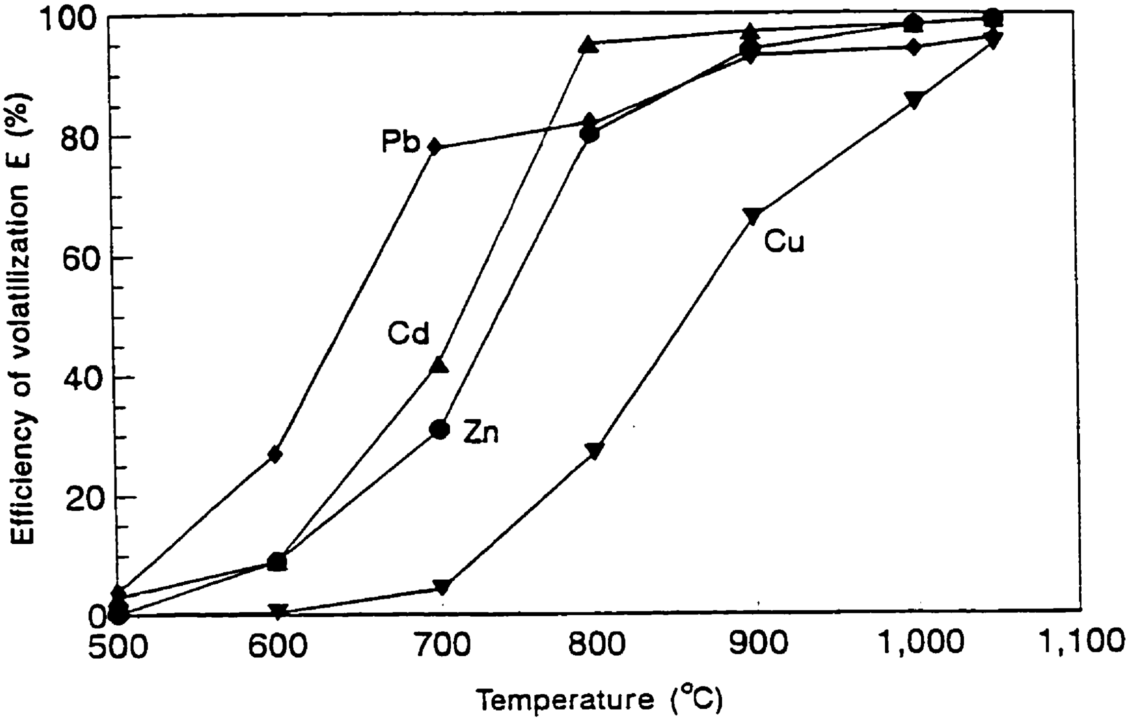
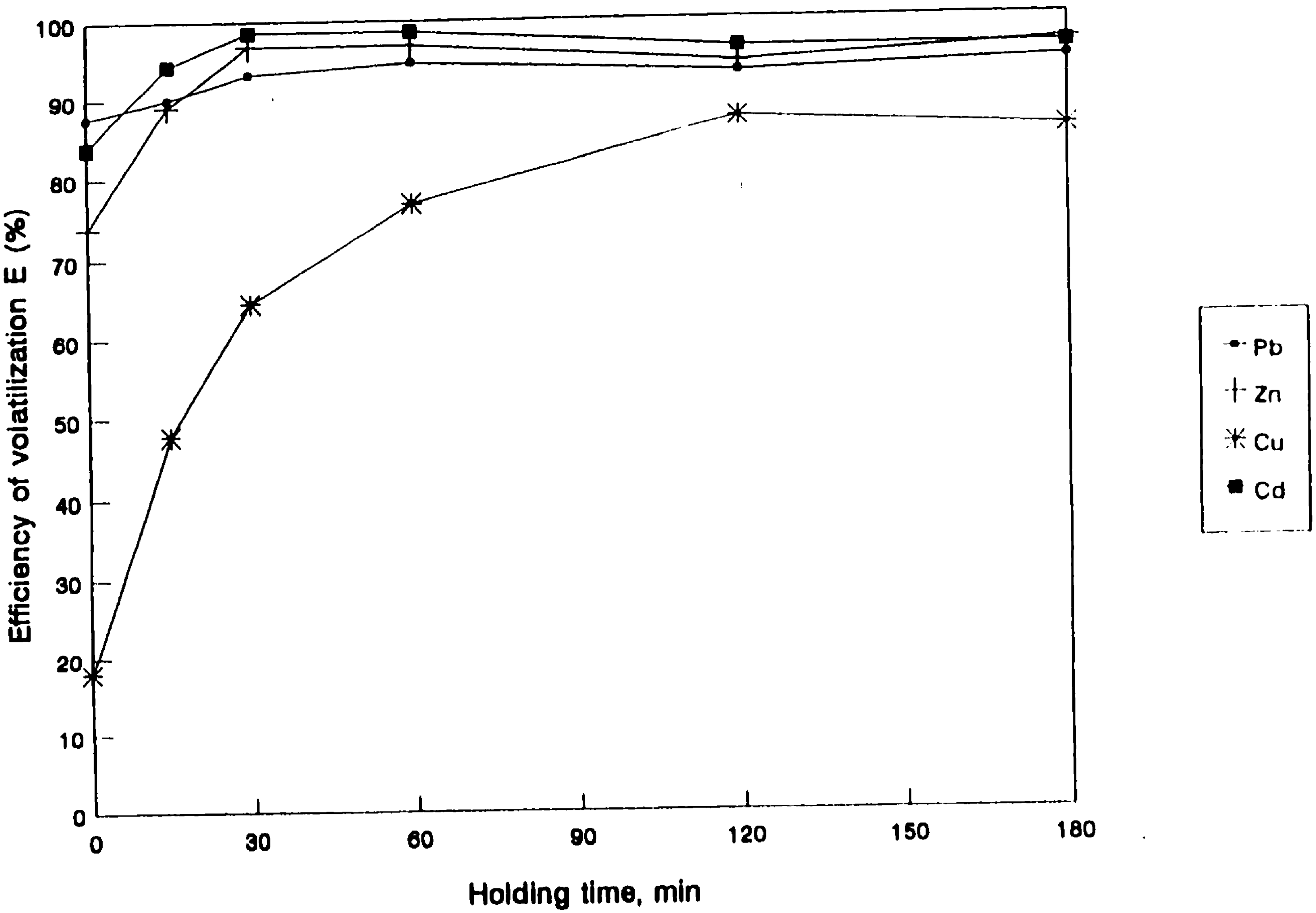


Fig. 4. Temperature dependence of heavy metal removal with 0.3 g Cl added (holding at target temperature for 180 minutes)

Fig. 5. Time dependence of heavy metal removal at 1000°C with 0.3 g Cl added



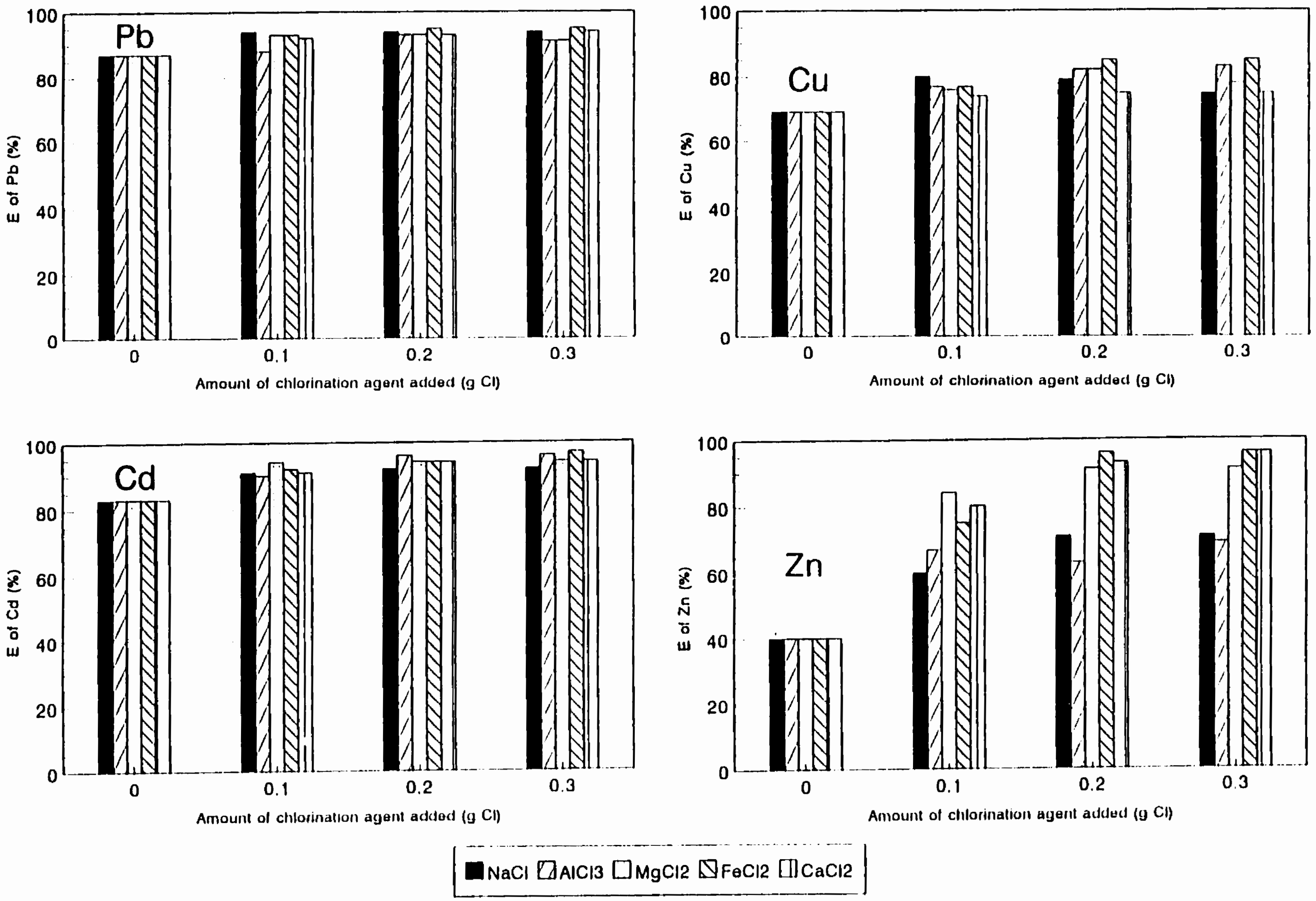


Fig. 6. Effect of amount and type of chlorination agents on heavy metal removal (holding at 1000 °C for 60 minutes)

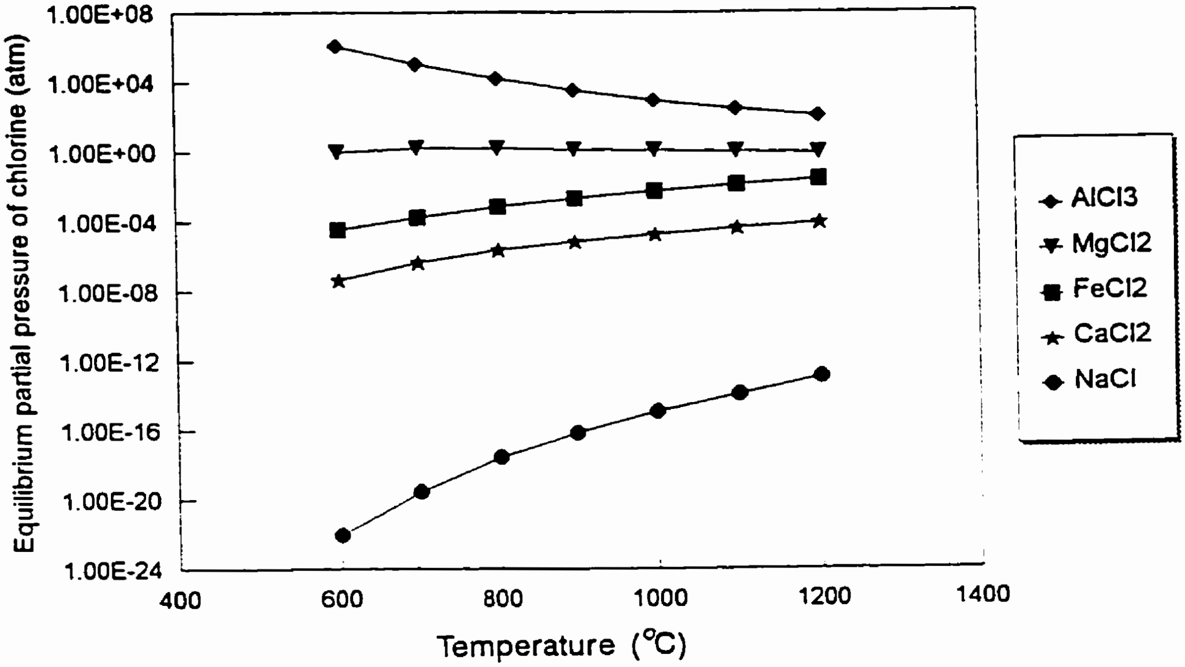
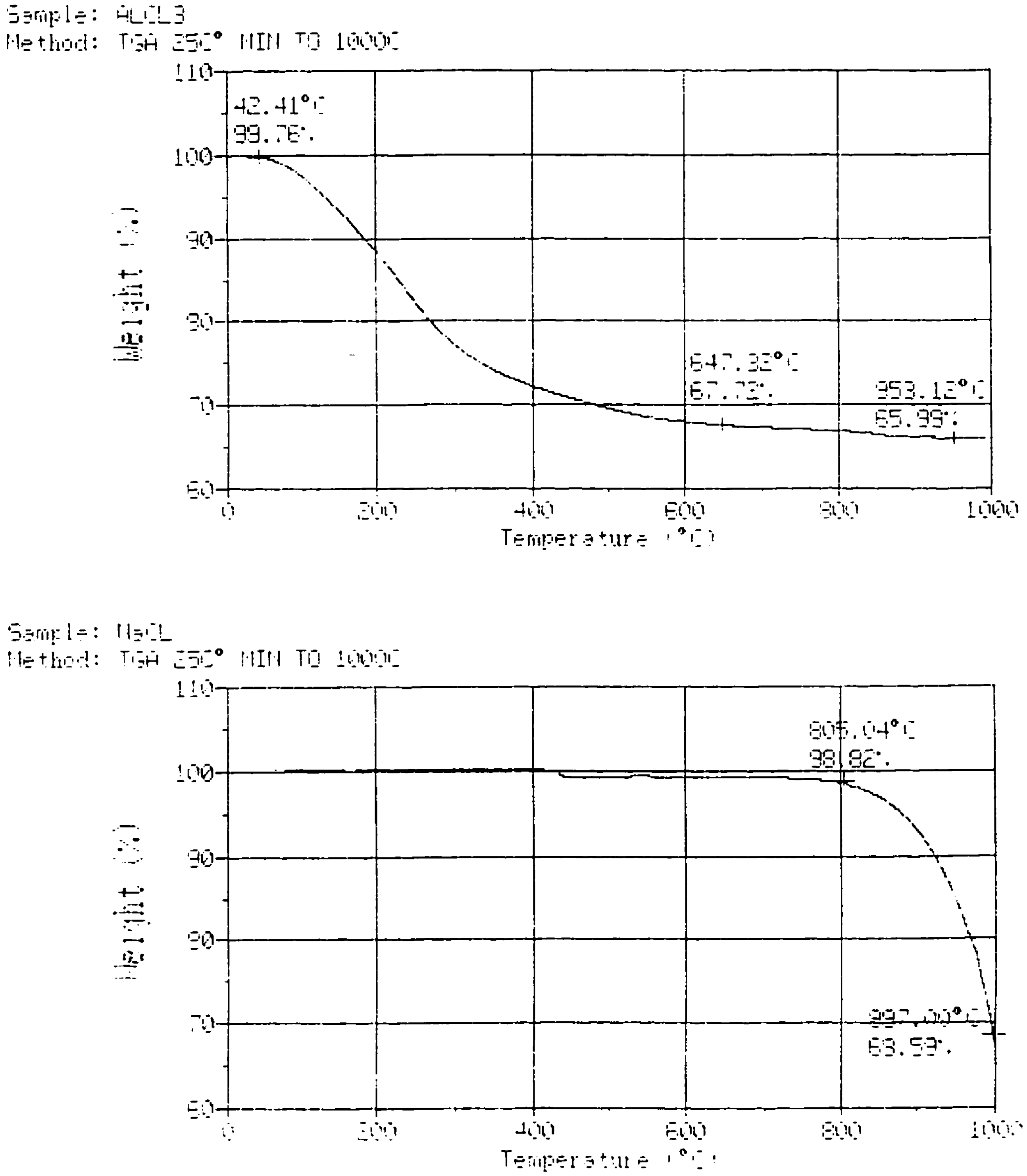


Fig. 7. Temperature dependence of equilibrium partial pressure of chlorine over different chlorination agents (Calculated from equation 18)

Fig. 8. Thermograms for $AlCl_3$ and NaCl samples in air



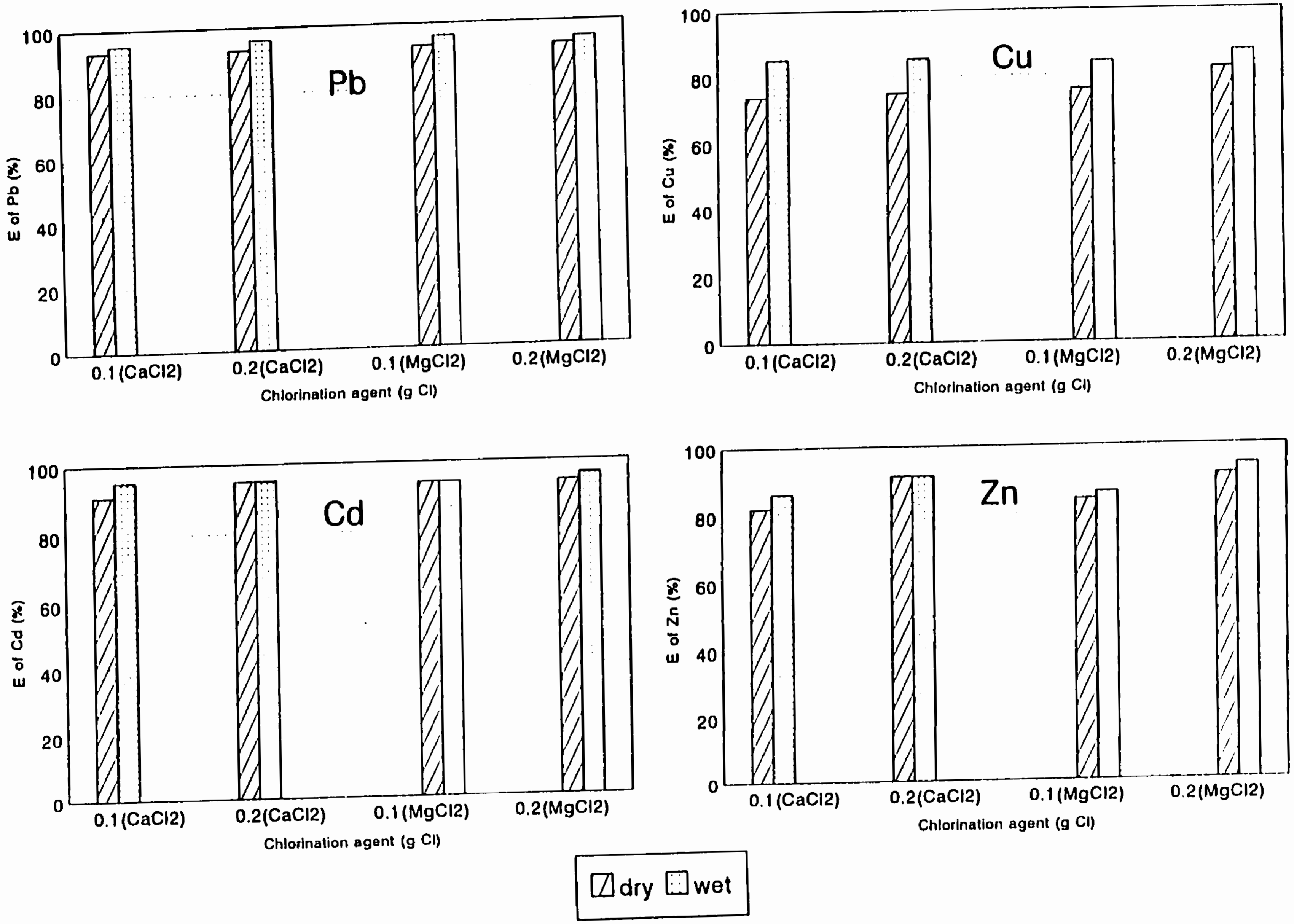


Fig. 9. Effect of contact pattern on heavy metal removal (holding at 1000 °C for 60 minutes)

Fig. 10. Absorption of moisture in dried fly ash
(a) Moisture absorbed vs. time
(b) Moisture absorbed vs. $\sqrt{t}$

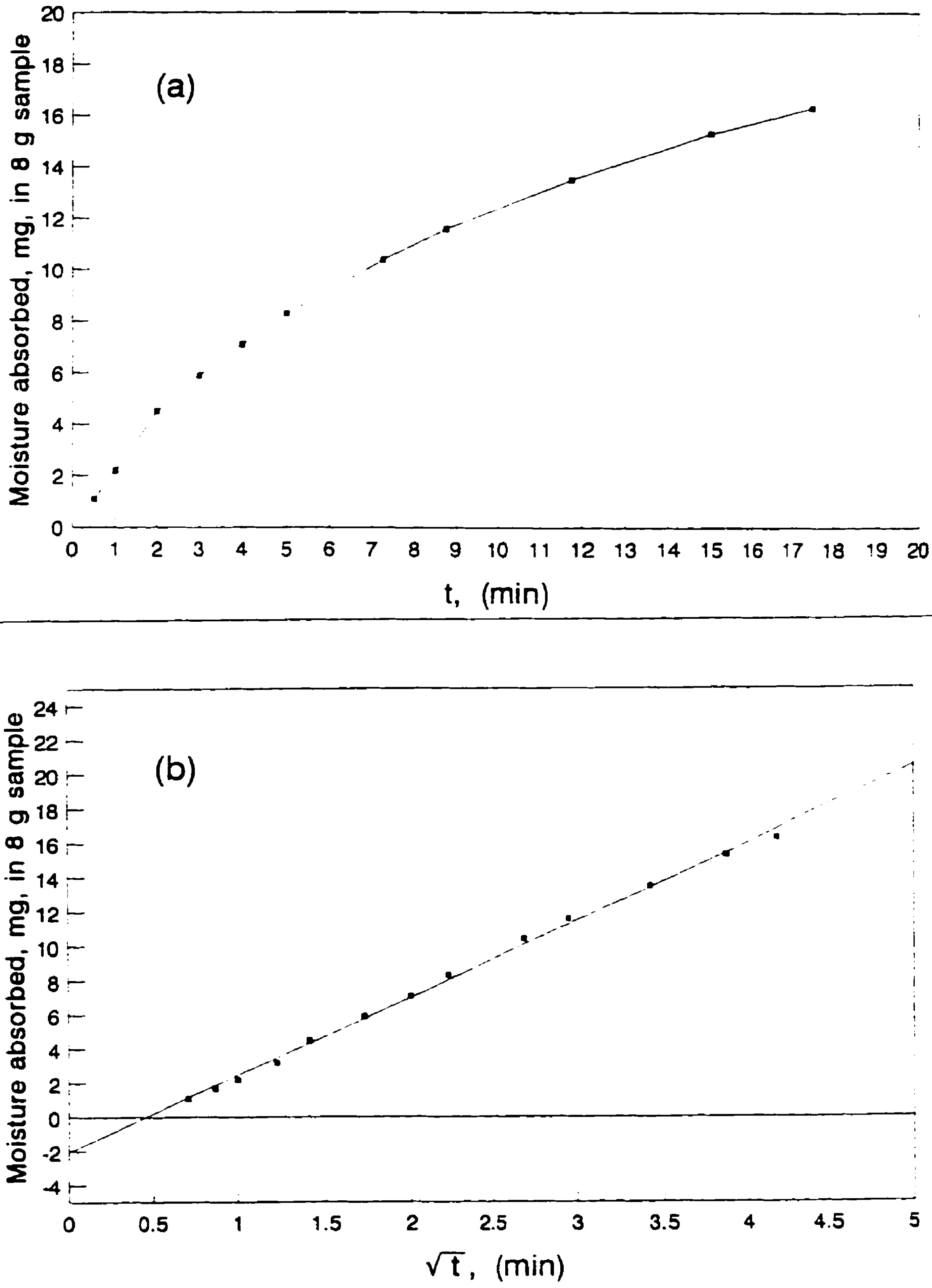


Fig. 11 XRD spectrum of a volatile matter sample

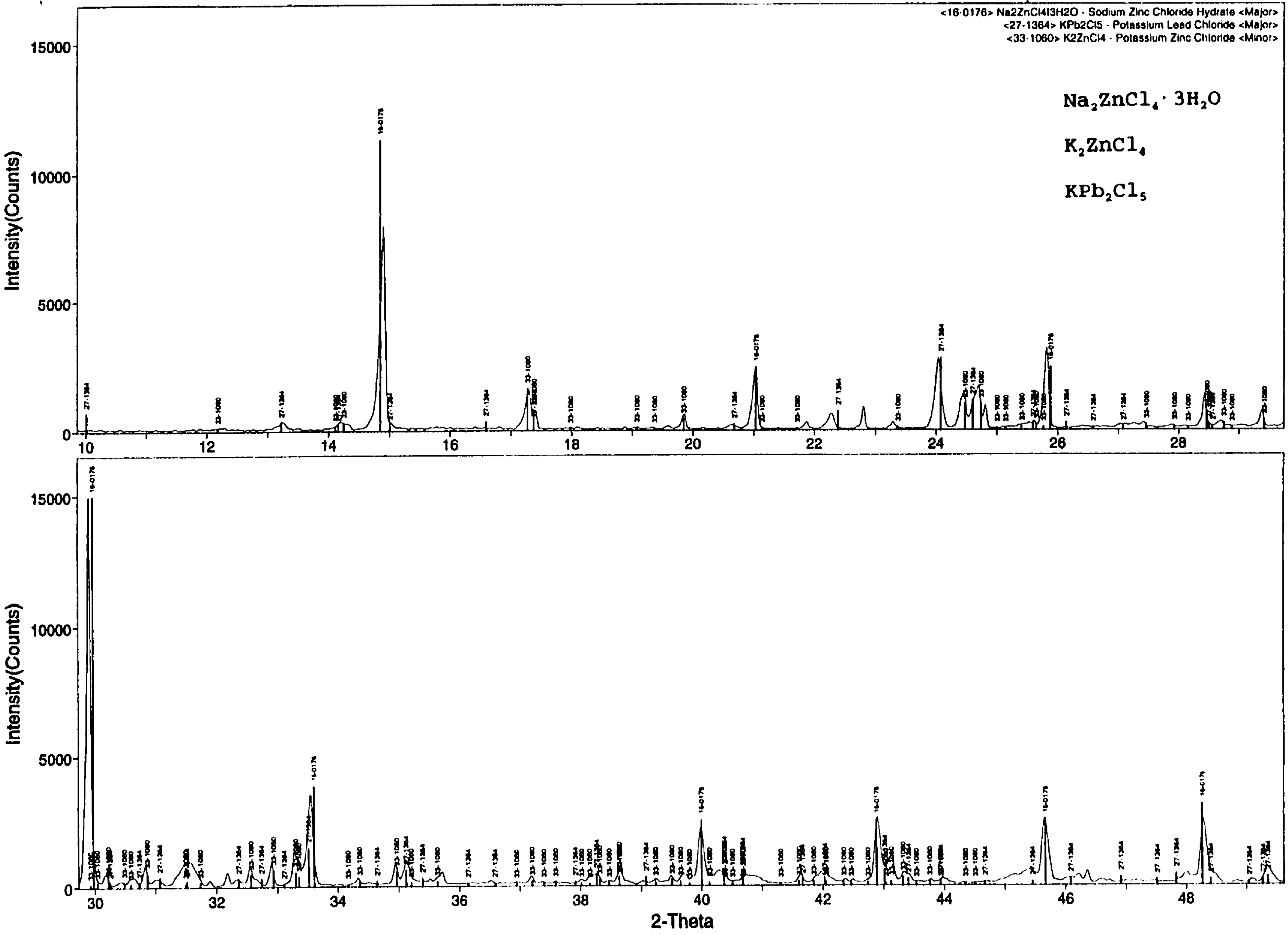


Fig. 12. XRD spectrum of a fly ash sample

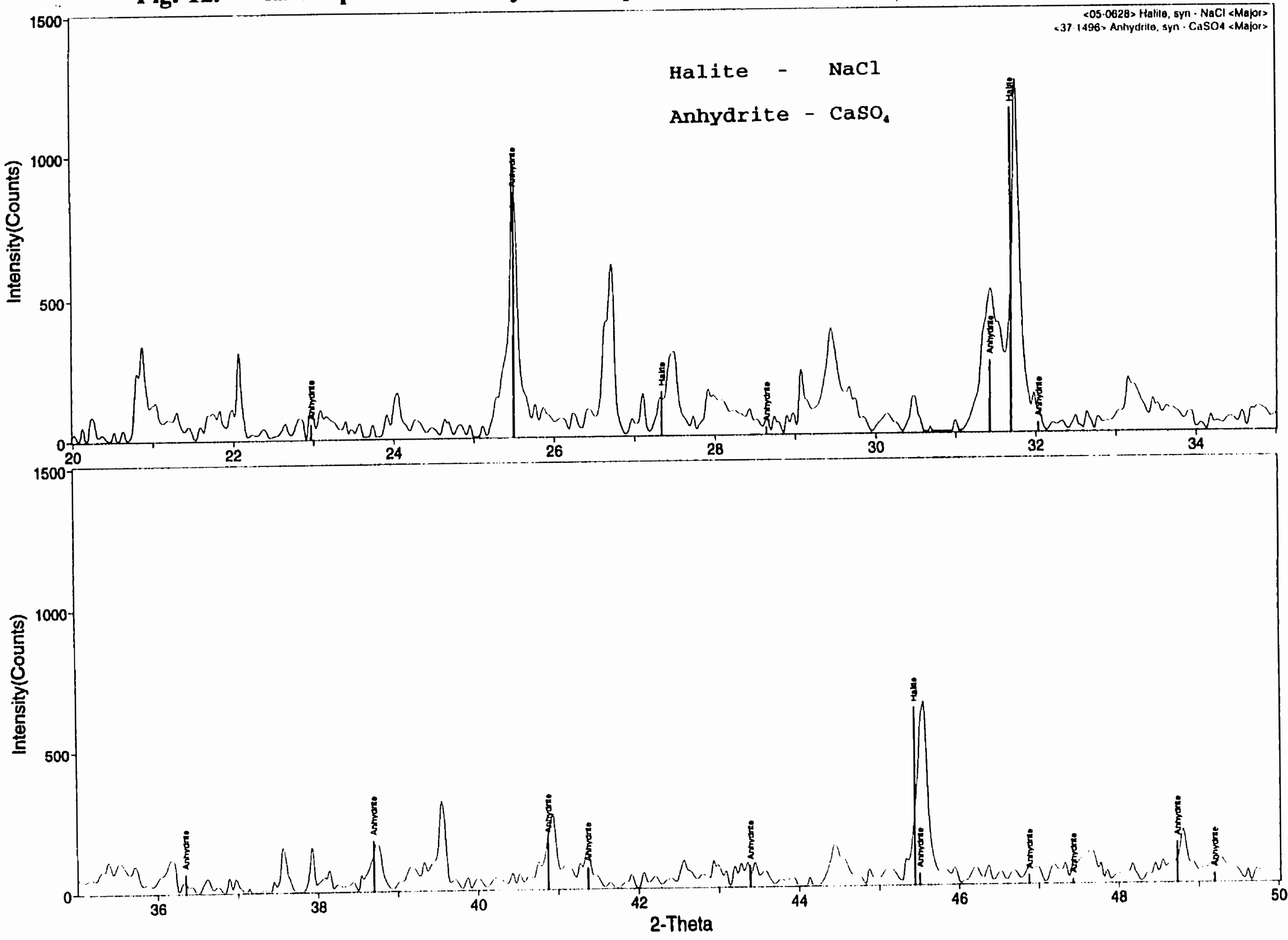


Fig. 13. XRD spectrum of a heat-treated fly ash sample

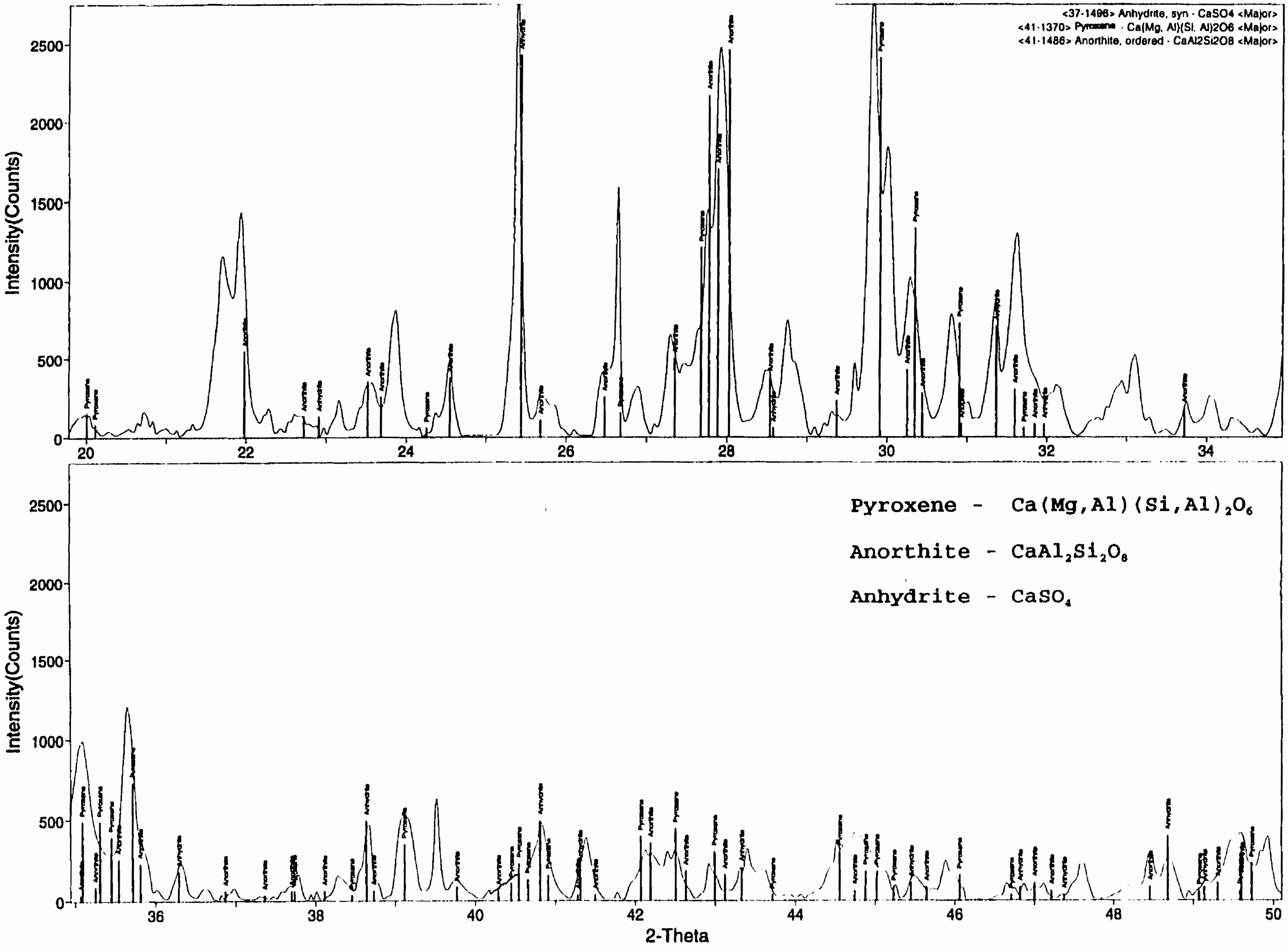
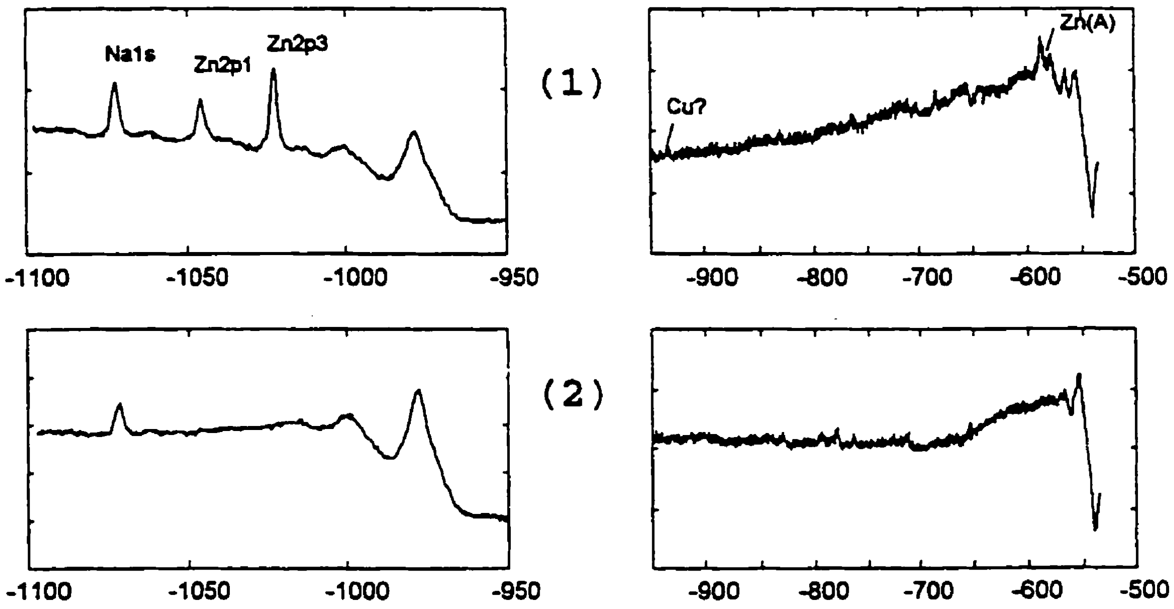


Fig. 14. **XPS spectra of surface of particles of (1) fly ash, (2) heat-treated fly ash.**

Top - Flyash
Bottom - Heat-treated flyash



Top - Flyash
Bottom - Heat-treated flyash

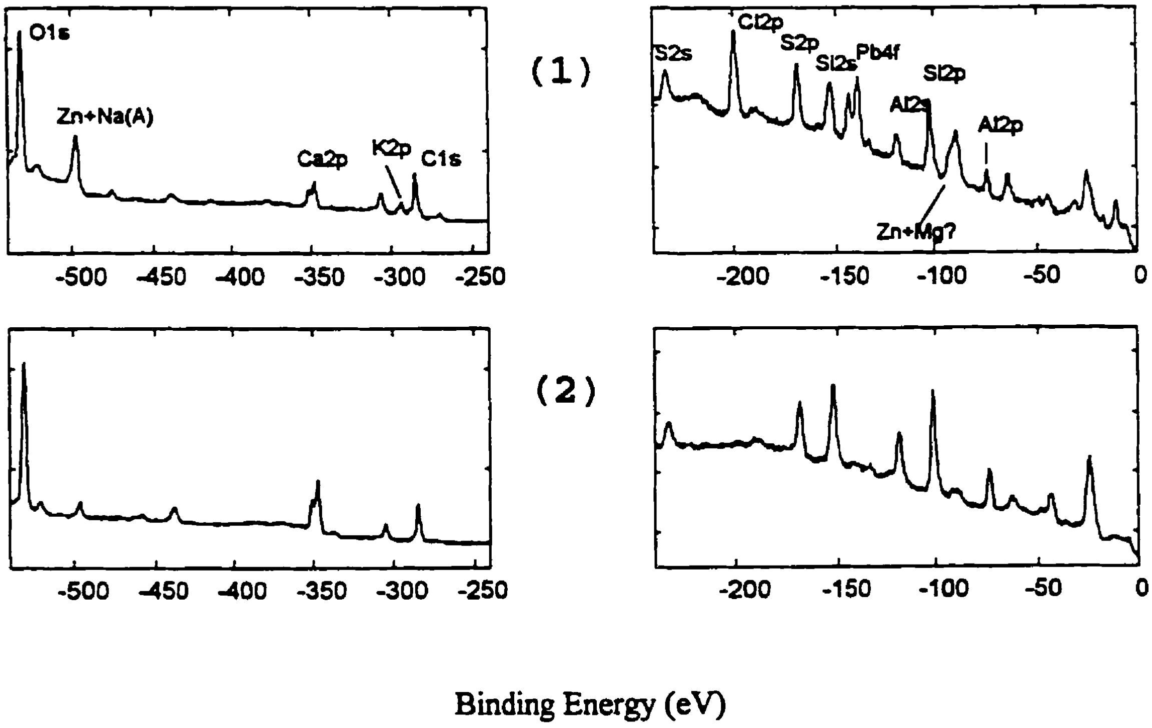
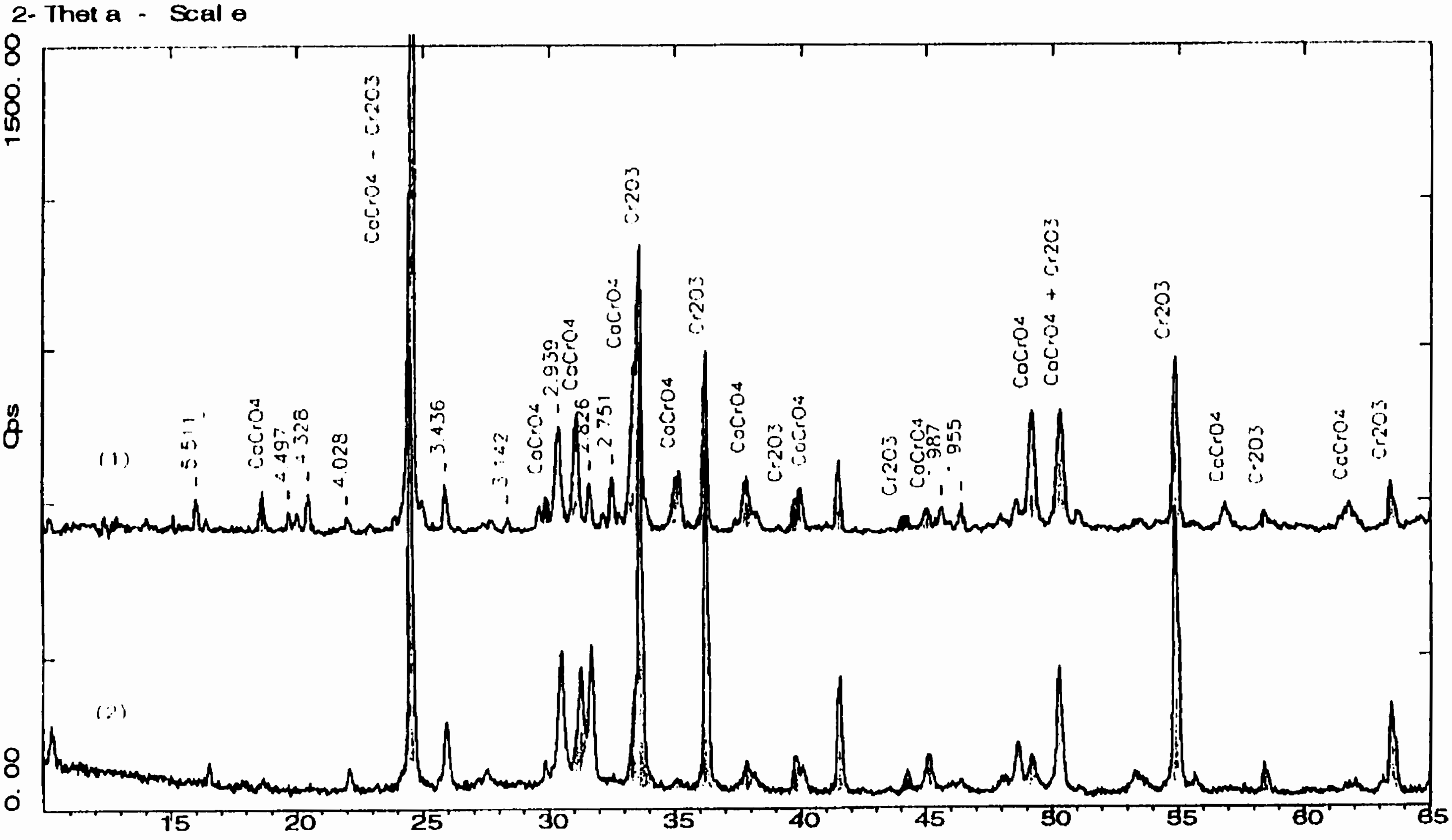


Fig. 15 X-ray Diffraction Patterns of samples from
(1) heating Cr_2O_3 and CaO at 1000°C
(2) heating Cr_2O_3 and $CaCl_2$ at 1000°C

Identified phases: $CaCrO_4$ and Cr_2O_3



The diffraction patterns of both samples were checked out for the other possible compounds: $CrCl_3$, CrO_2, CrO_3 and $Ca_3(CrO_4)_2$. None of those compounds were identified in either samples.

Fig. 16 X-ray Powder Diffraction Pattern of sample from heating Al_2O_3 with CaO at 1000°C.

Identified phases: $Ca_{12}Al_{14}O_{33}$ - ☐ $CaAl_2O_4$ - ☐ Al_2O_3 - ▨ CaO - ☐

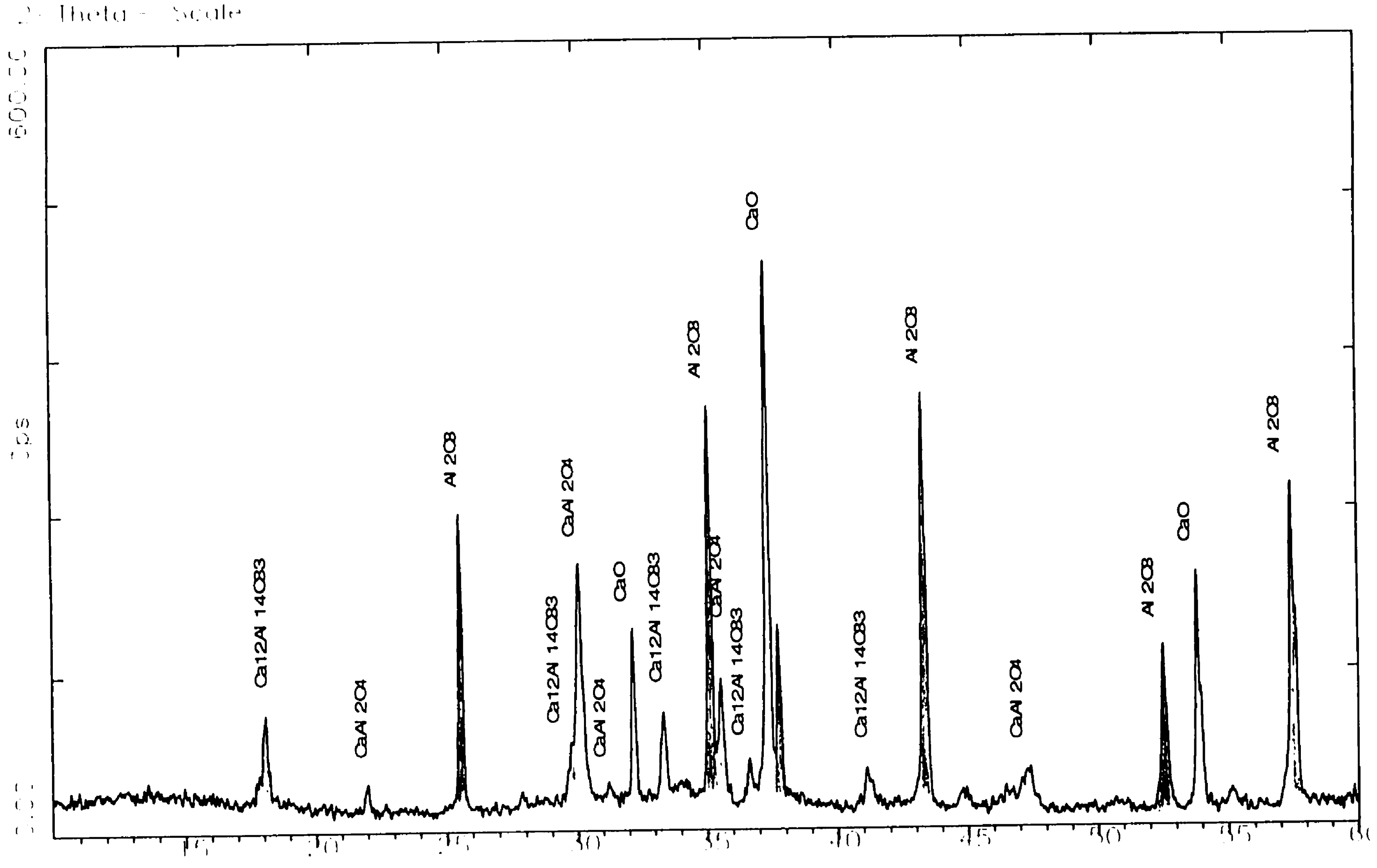


Fig. 17 X-ray Powder Diffraction Pattern of sample from heating Al_2O_3 with $CaCl_2$ at 1000°C.

Identified phases: $Ca_{12}Al_{14}O_{33}$ - ▨ Al_2O_3 - ■ and a cubic phase- □

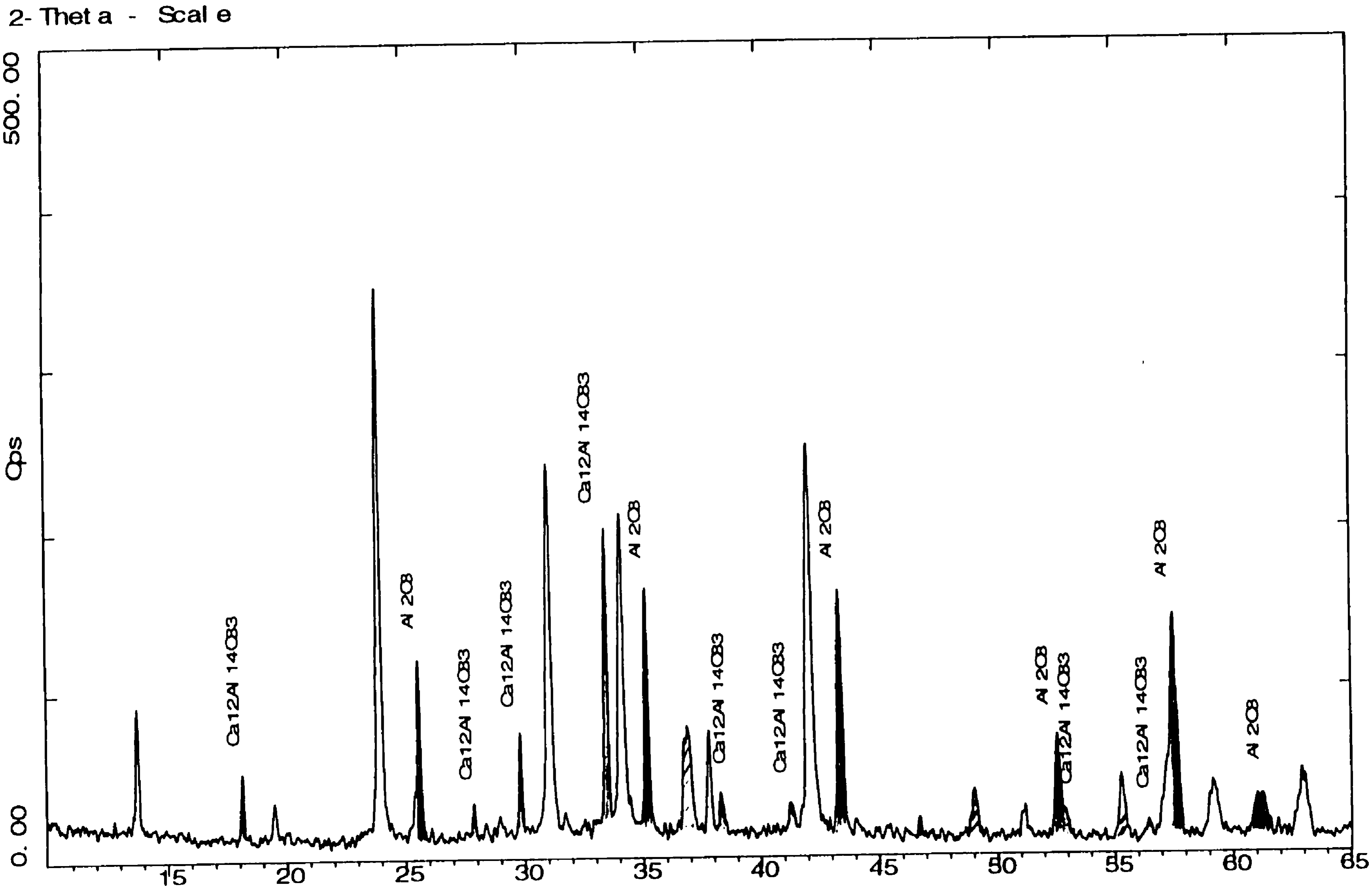


Fig. 18. A thermogram for a $CaCl_2$ sample in air

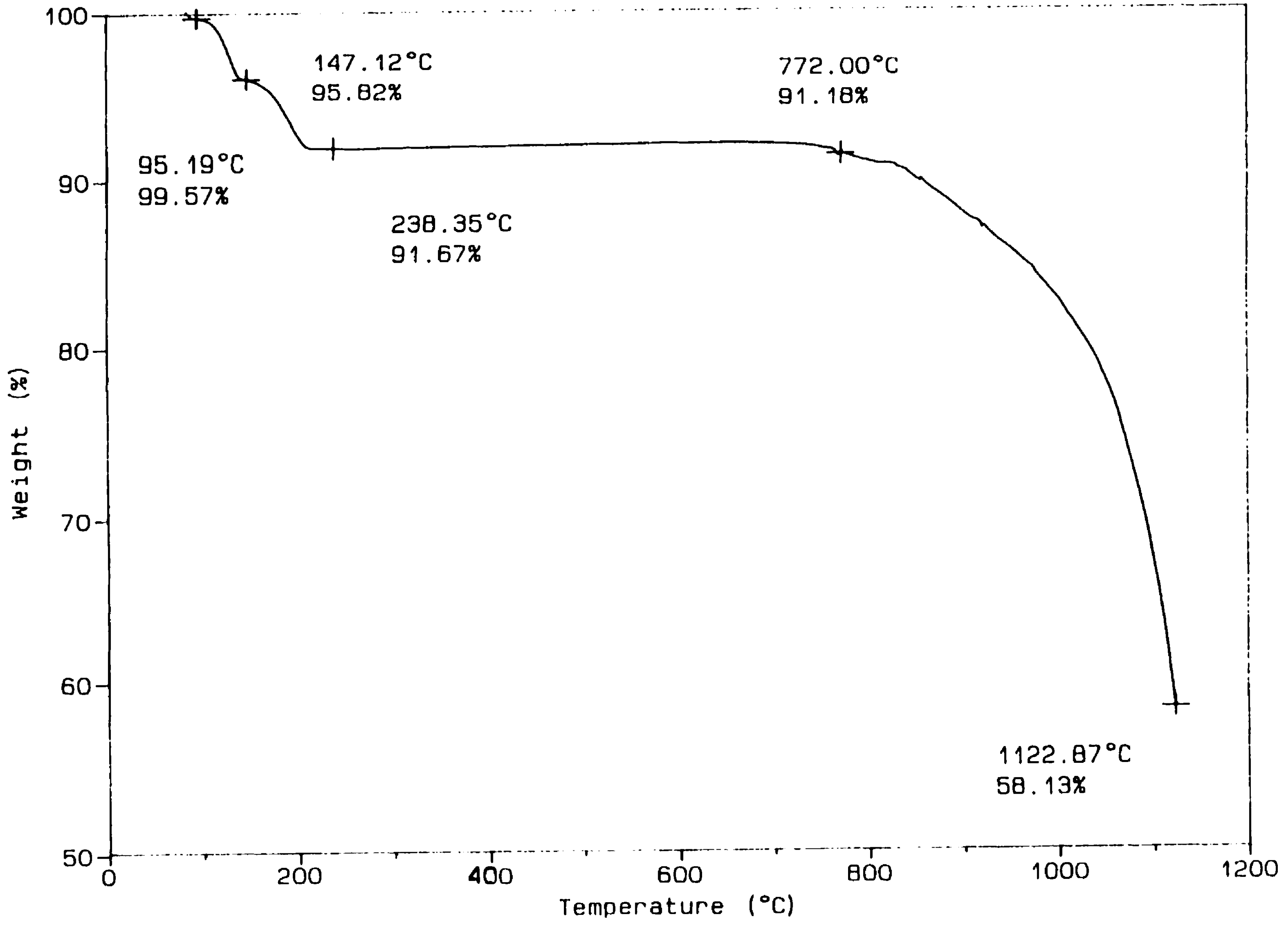


Fig. 19. Effect of heating time on metals volatilized Cl flow rates, 3 ml/min and 6 ml/min

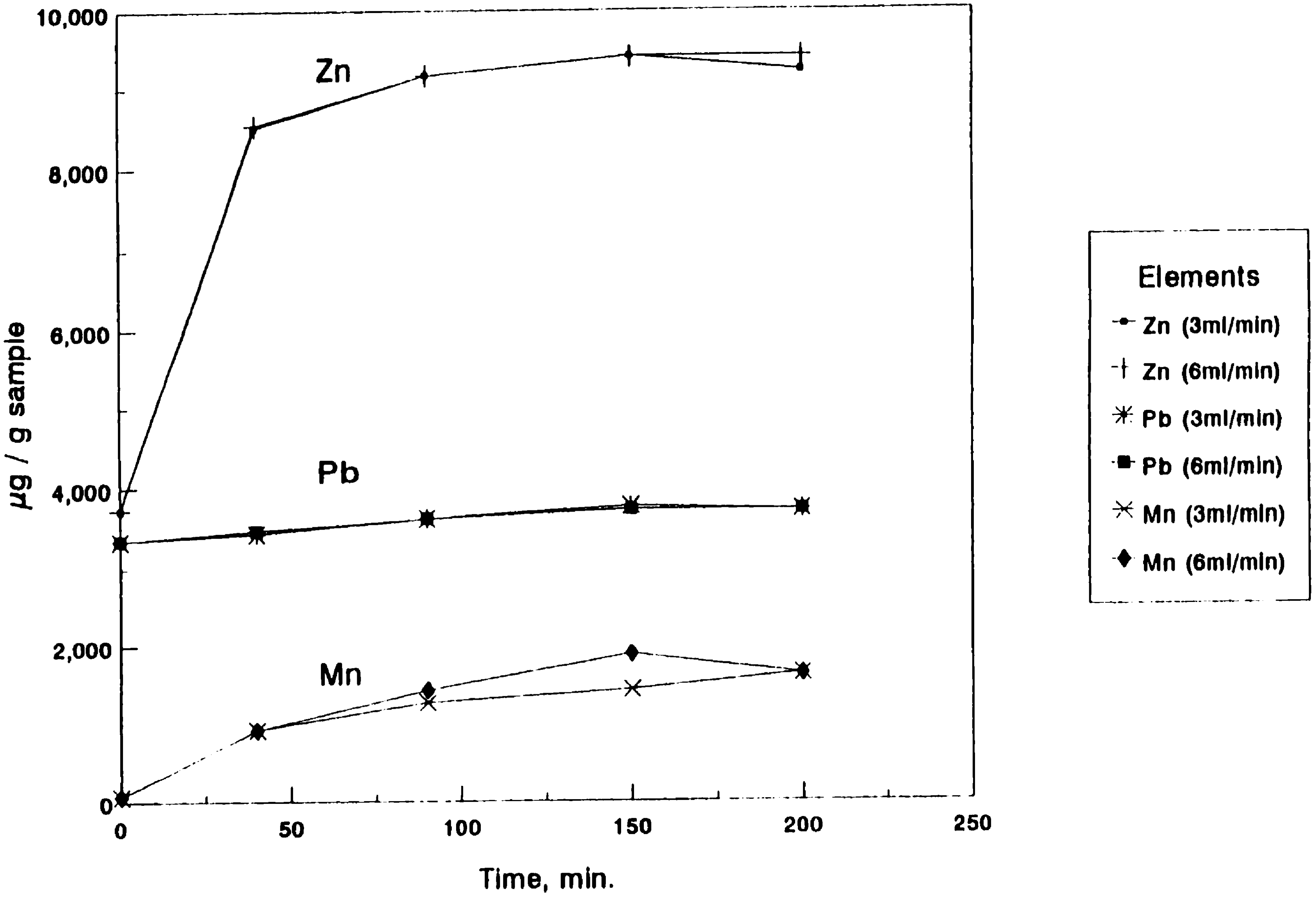


Fig. 20. Effect of heating time on metals volatilized Cl flow rates, 3 ml/min and 6 ml/min

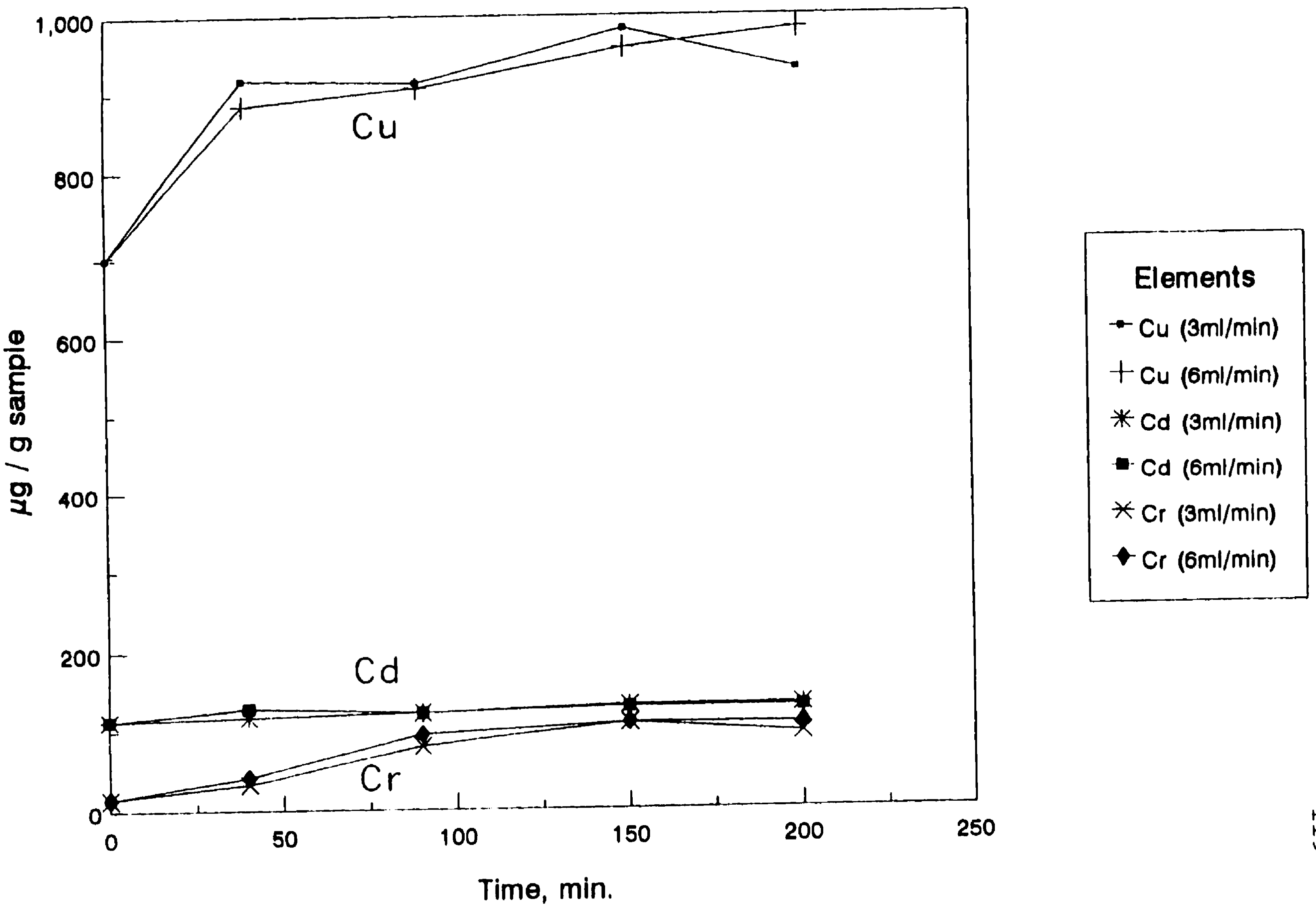


Fig. 21. Dependence of E on ΔG° for reactions between metal oxides and chlorine to form metal chlorides and oxygen

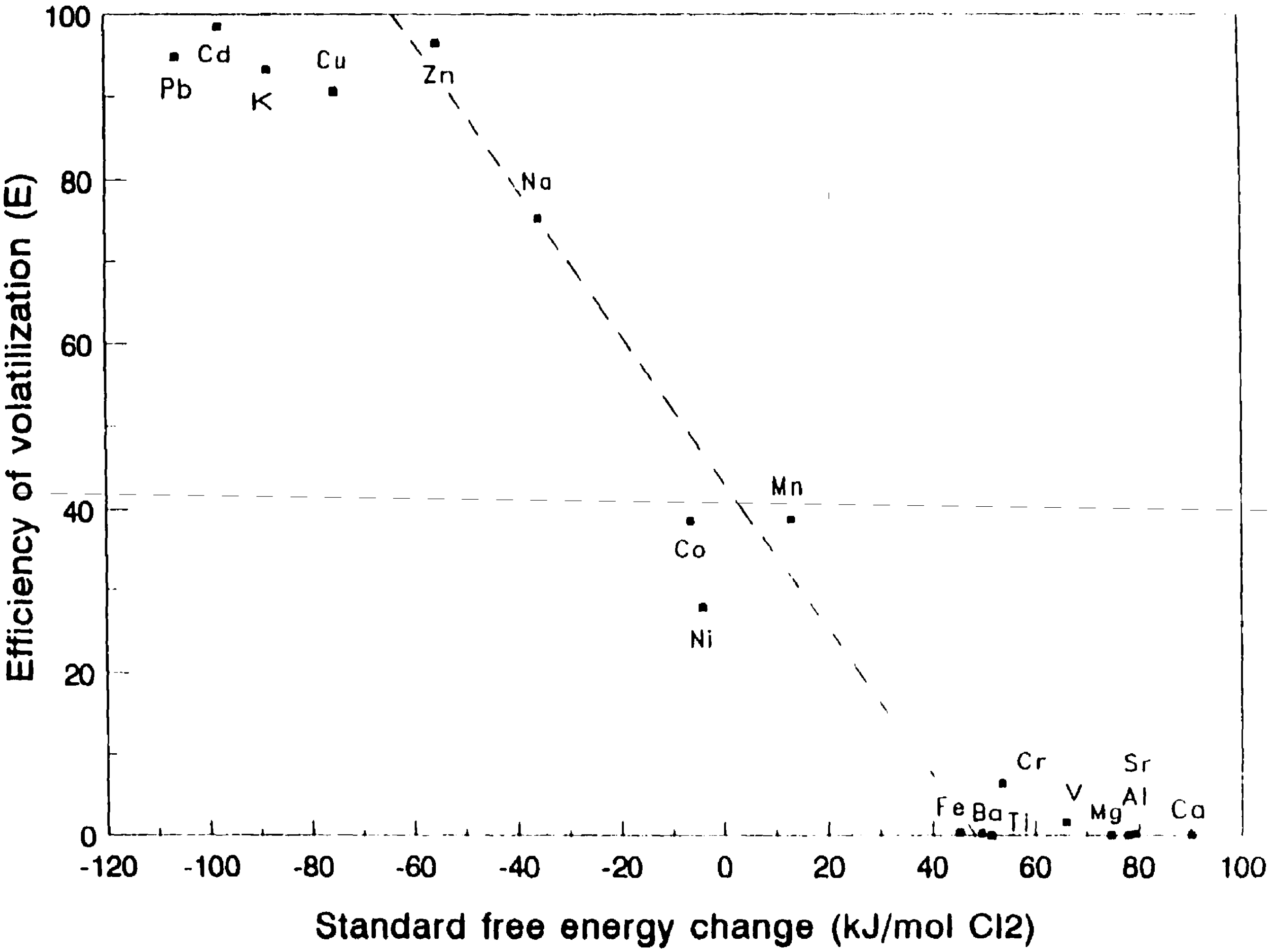
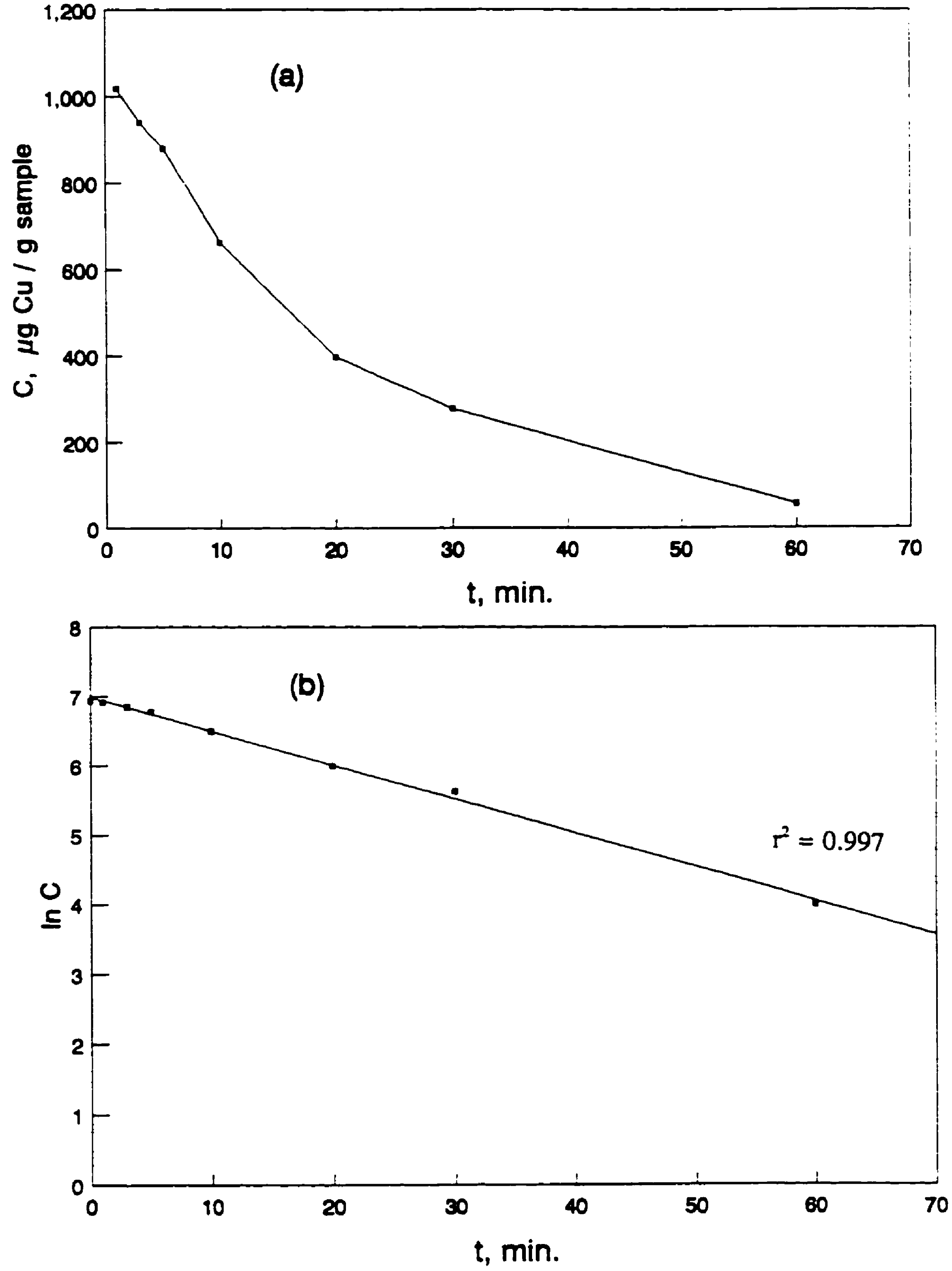


Fig. 22. Cu conc. in sample as a function of time of heating

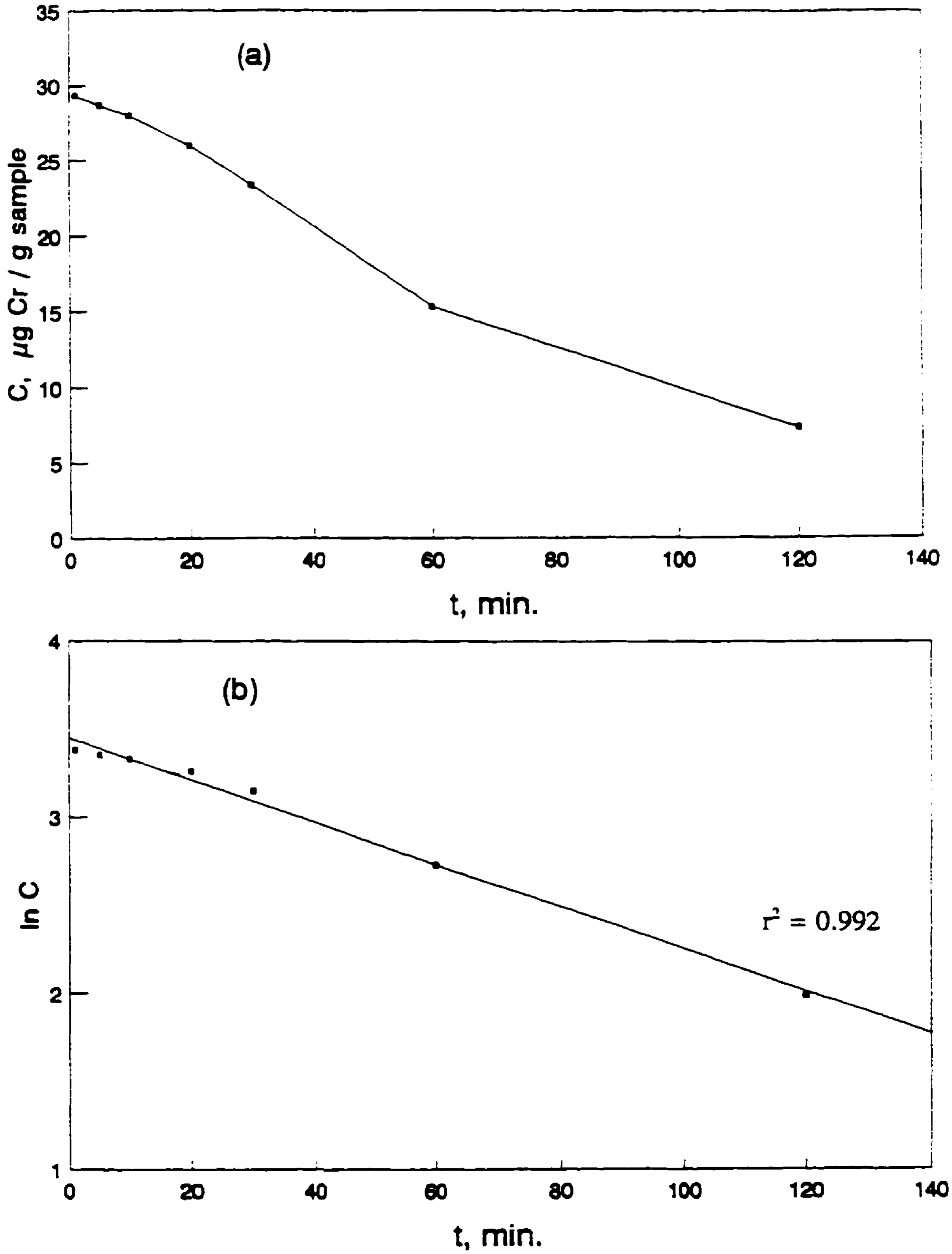
(a) C (μg Cu / g sample) vs. t

(b) ln C vs. t (test for a first-order reaction)



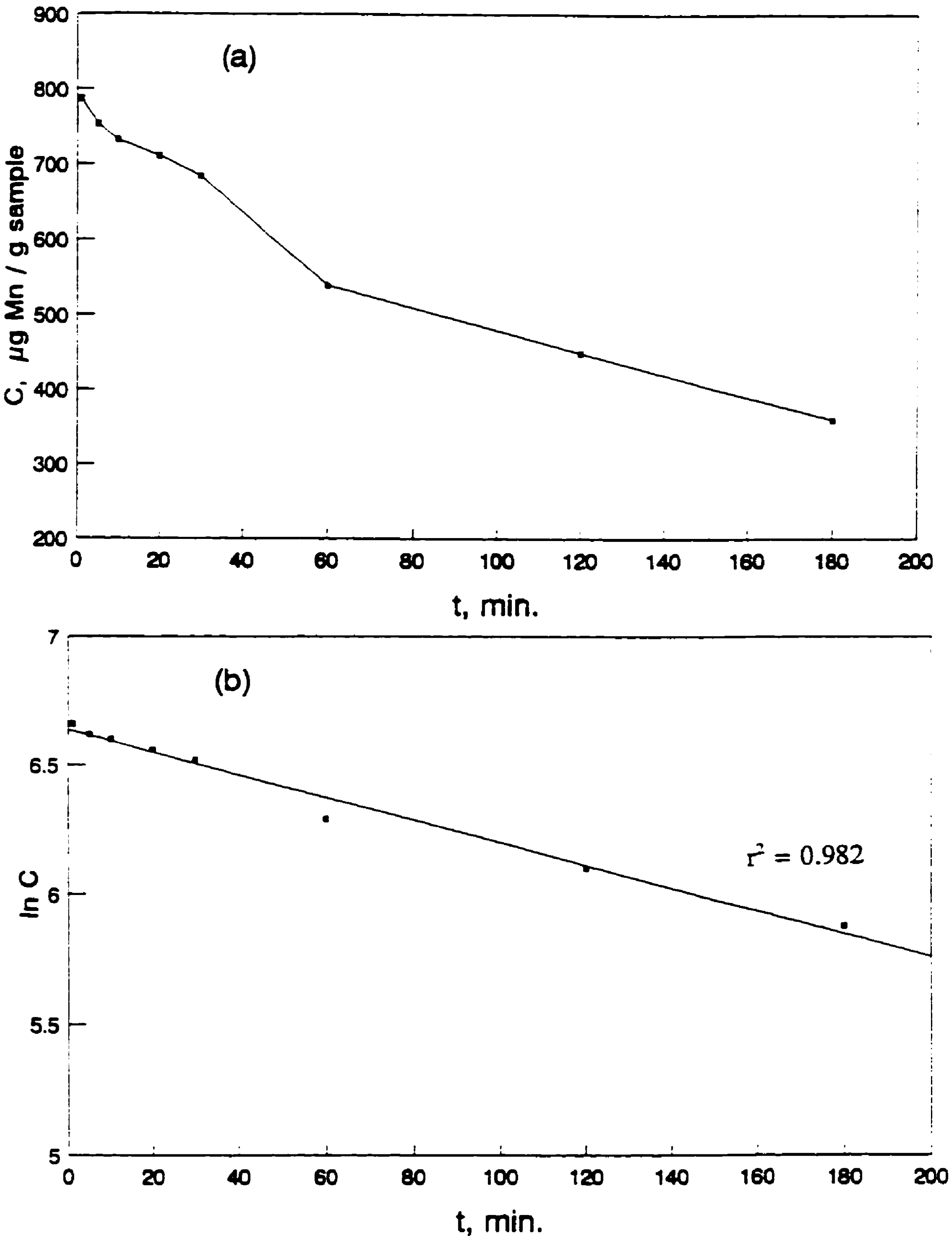
Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

Fig. 23. Cr conc. in sample as a function of time of heating
(a) C (μg Cr / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



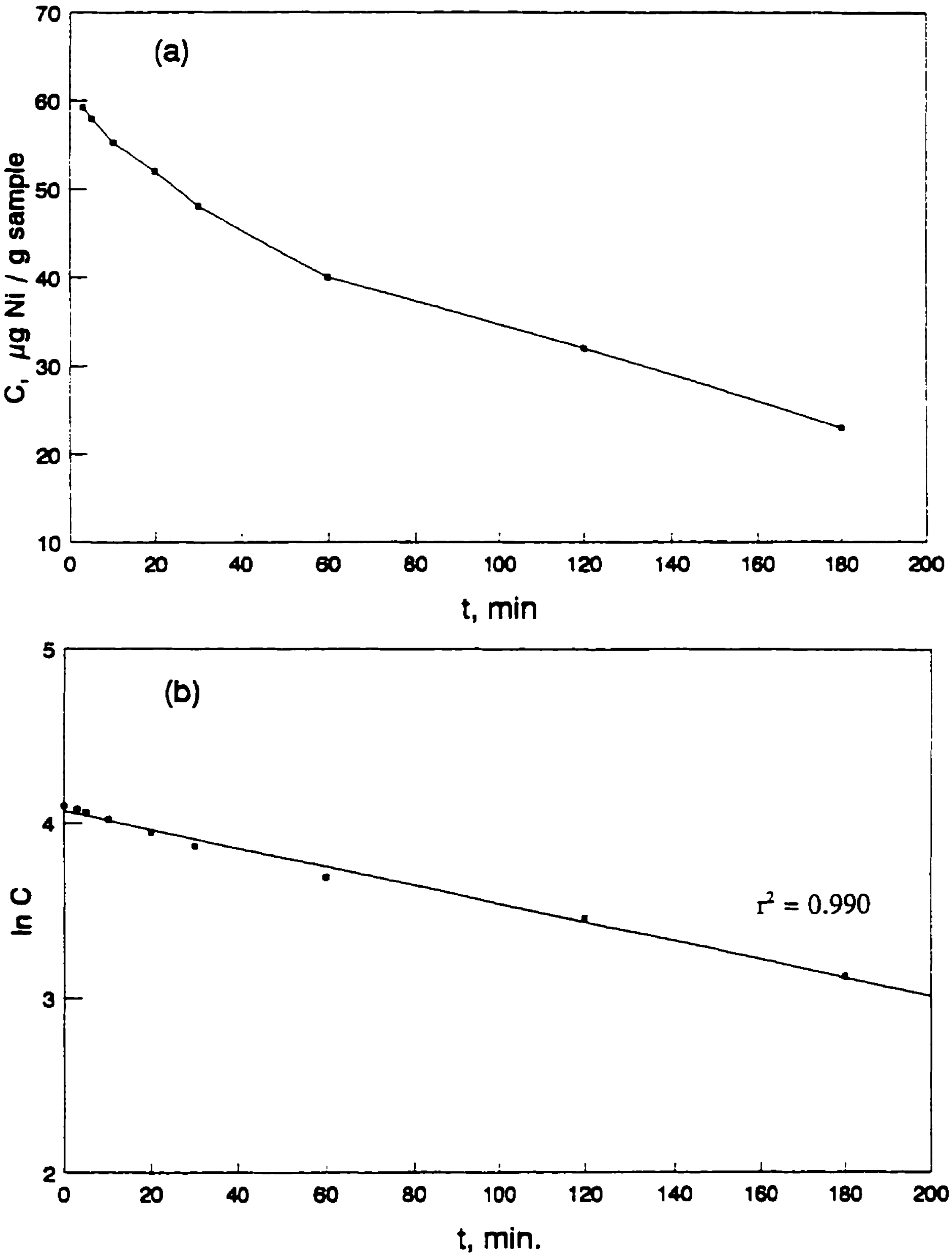
Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

Fig. 24. Mn conc. in sample as a function of time of heating
(a) C (μg Mn / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



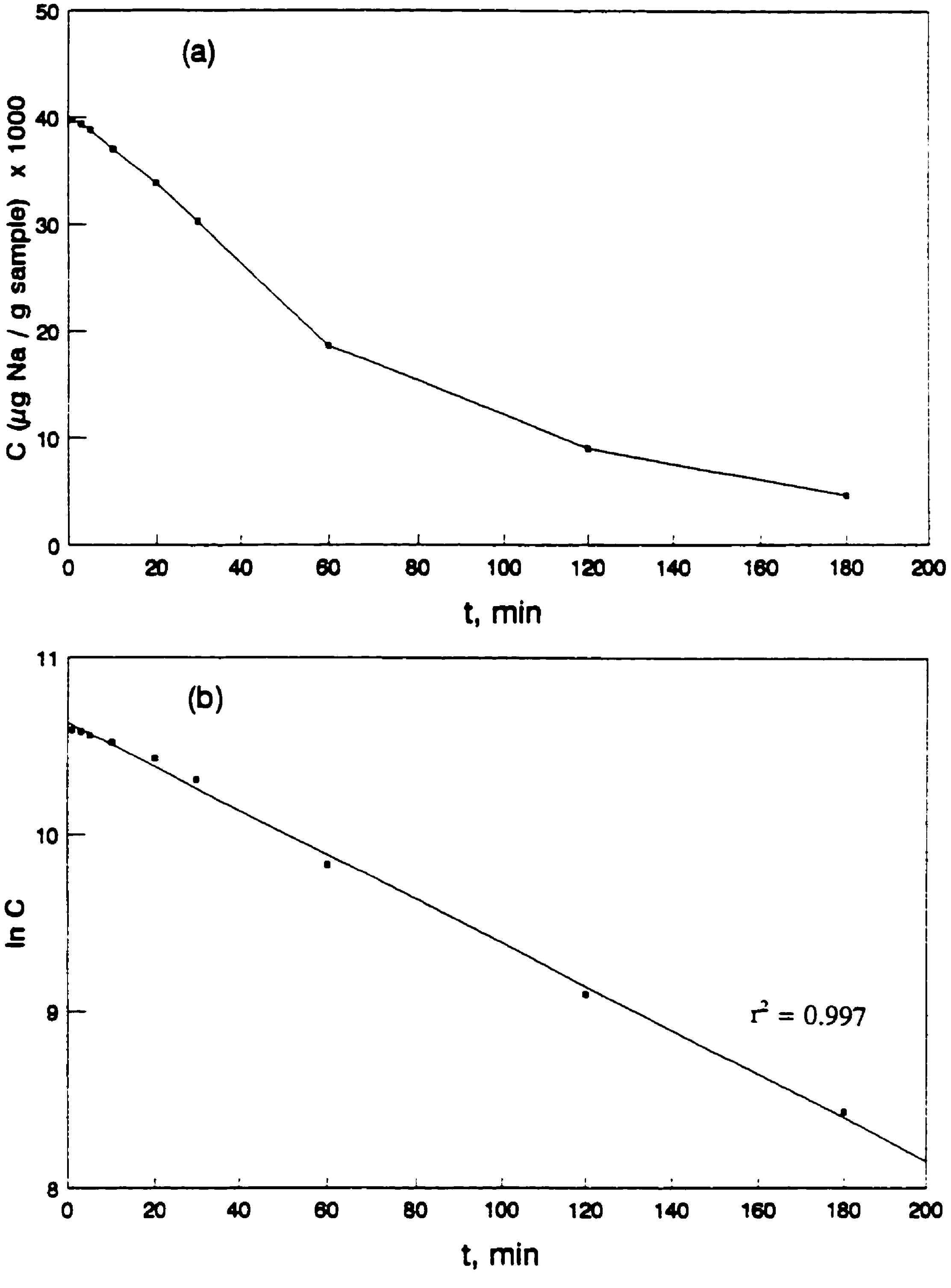
Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

Fig. 25. Ni conc. in sample as a function of time of heating
(a) C (μg Ni / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



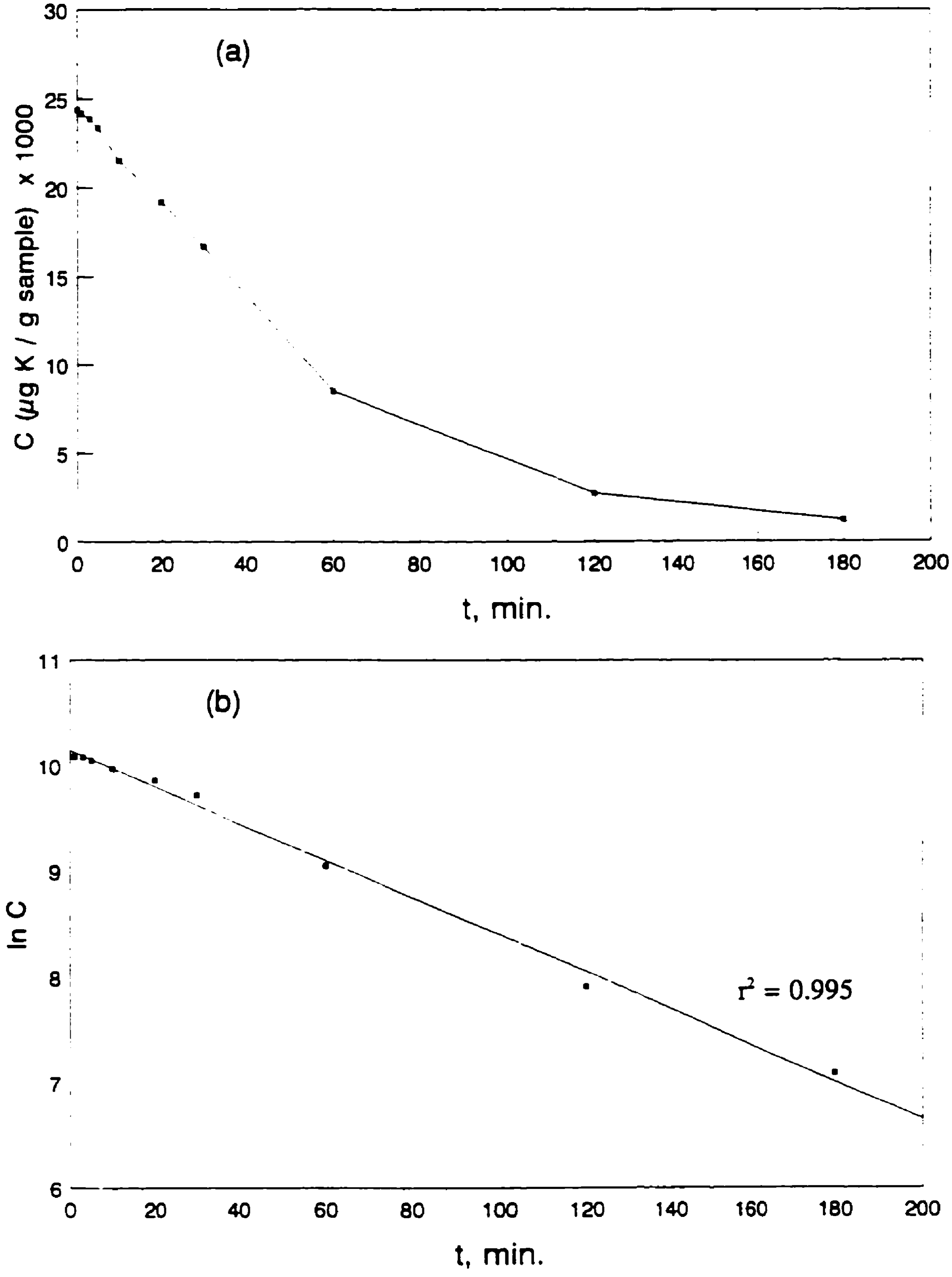
Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

Fig. 26. Na conc. in sample as a function of time of heating
(a) C (μg Na / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



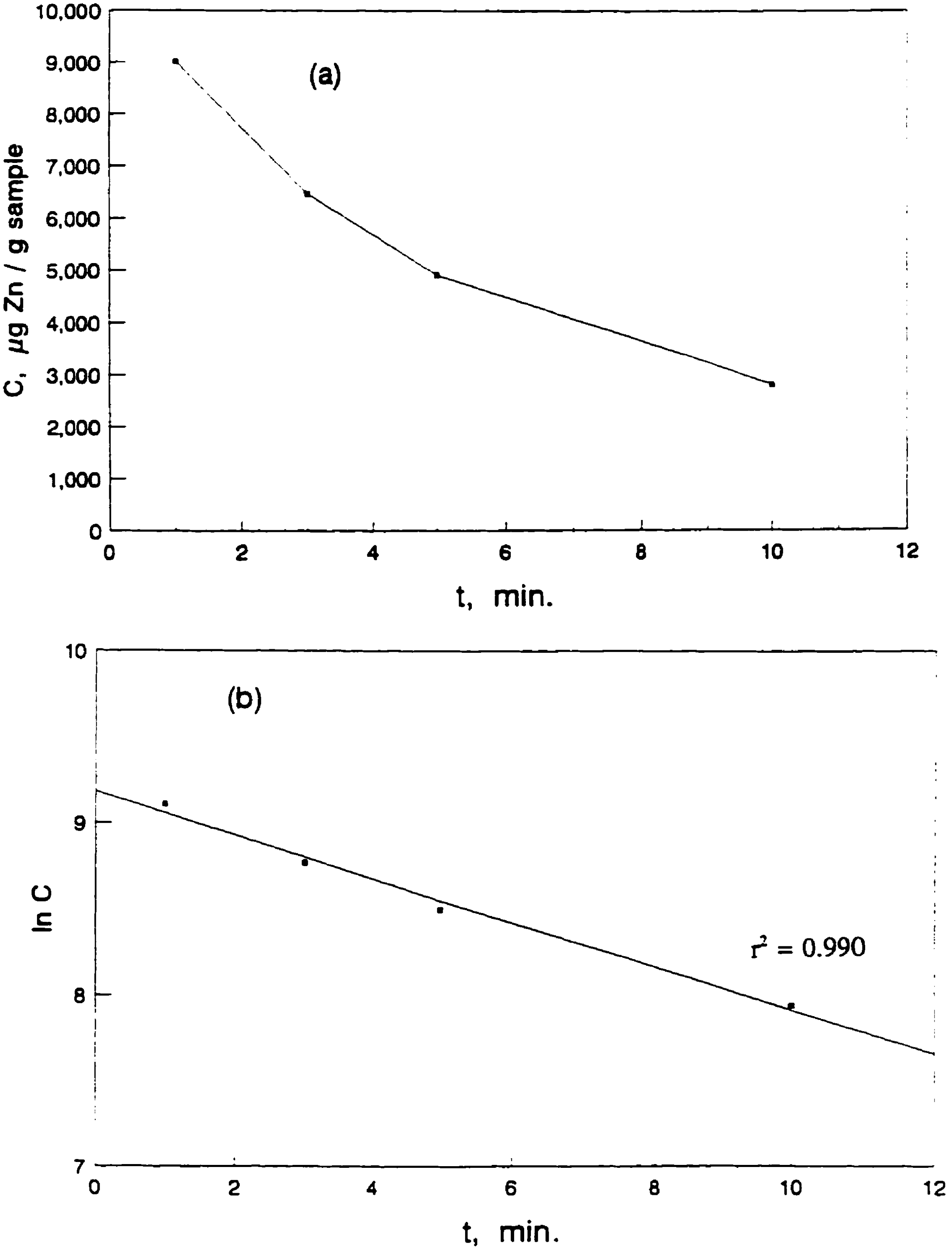
Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

Fig. 27. K conc. in sample as a function of time of heating
(a) C (μg K / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



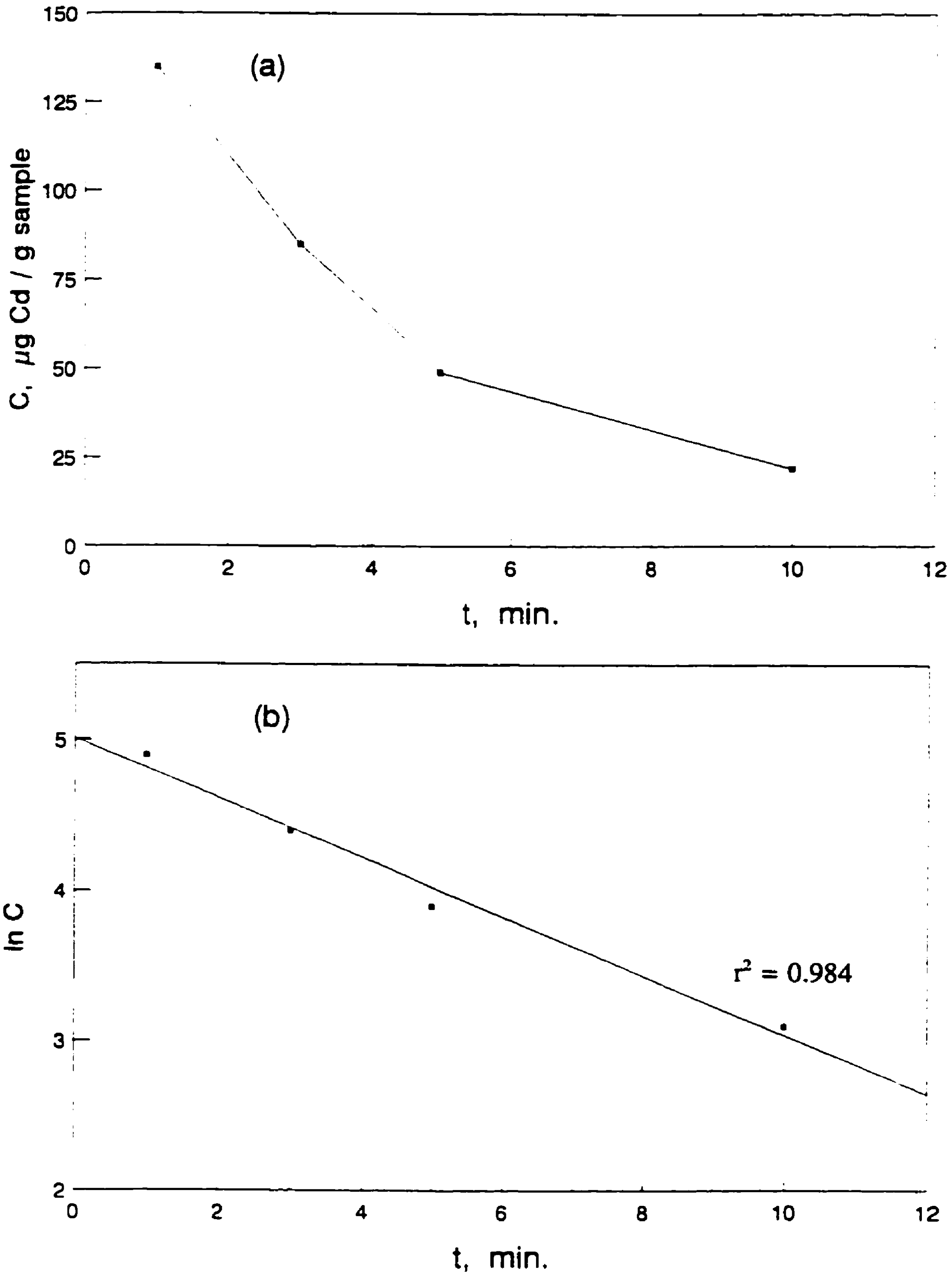
Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

Fig. 28. Zn conc. in sample as a function of time of heating
(a) C (μg Zn / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



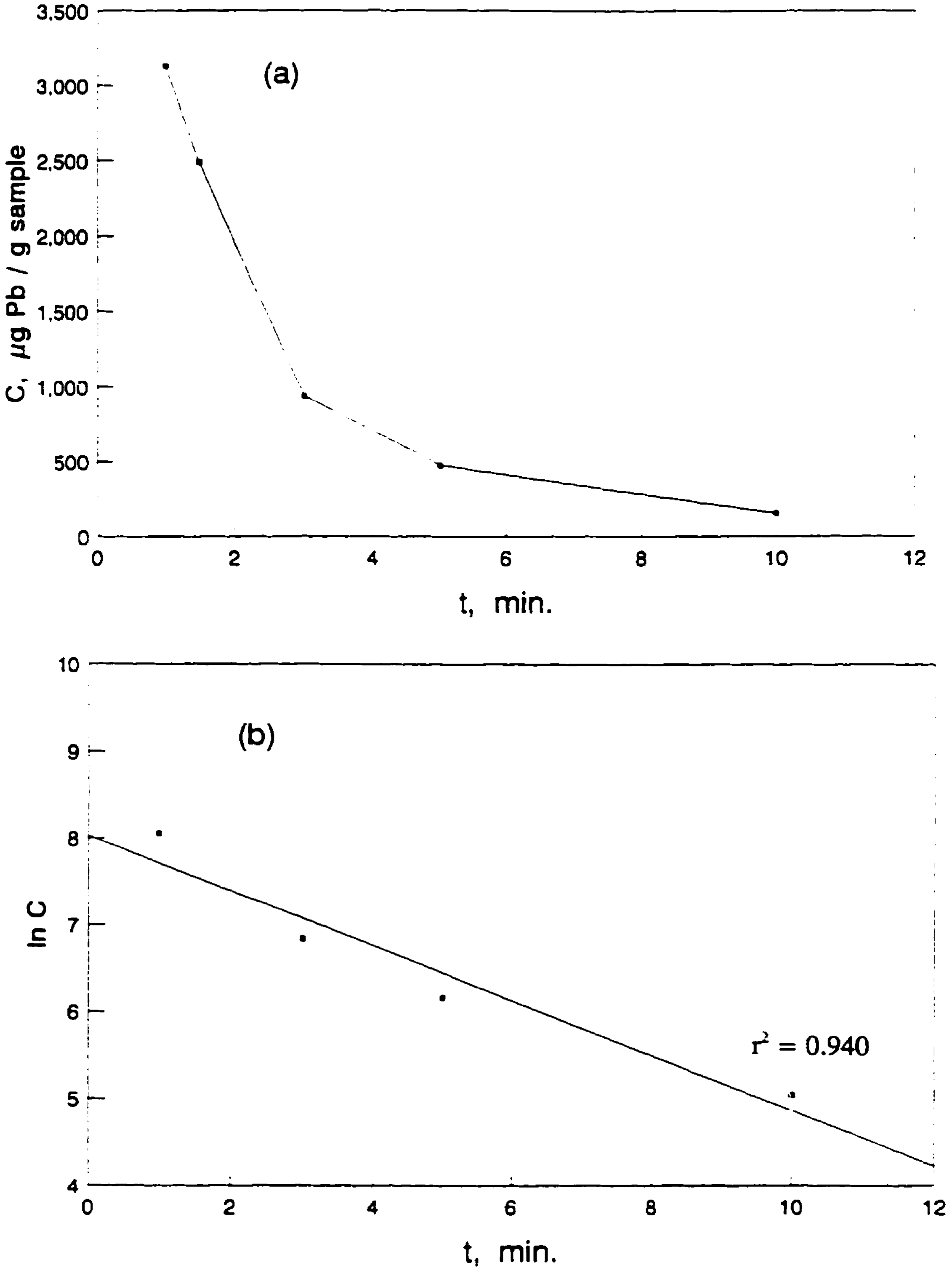
Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

Fig. 29. Cd conc. in sample as a function of time of heating
(a) C (μg Cd / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



Heating conditions: 3 g sample was heated with CaCl2 (0.3g Cl) at 1000°C

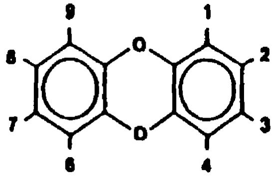
Fig. 30. Pb conc. in sample as a function of time of heating
(a) C (μg Pb / g sample) vs. t
(b) ln C vs. t (test for a first-order reaction)



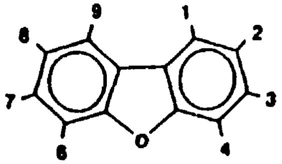
Heating conditions: 3 g sample was heated with $CaCl_2$ (0.3g Cl) at 1000°C

Fig. 31. Dioxins and furans

(a) Chlorinated Dibenzo-p-dioxins (Dioxins) and Dibenzofurans (Furans): Structure and Numbers of Isomers



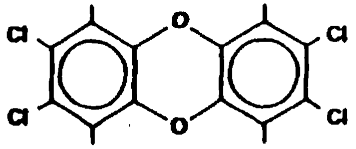
Dibenzo-p-dioxin



Dibenzofuran

NUMBER OF CHLORINES	NUMBER OF COMPOUNDS Dioxins	Furans
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1
TOTALS	75	135

(b) The Seventeen 'Toxic' Dioxins and Furans and Toxic Equivalent Factors



2,3,7,8-Tetrachlorodibenzo-p-dioxin (2378-TCDD)

COMPOUND	TEF*
Dioxins:	
2,3,7,8-TCDD	1.0
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.001
Furans:	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.001

* NATO/CCMS

11. APPENDICES

APPENDIX A

Quality control data for ICP analysis, ppm (µg/mL).
All analytes in the calibration-check solutions (standards NIST 3171a and NIST 3172a) were at 0.200 or 2.000 ppm, and K 10.00 ppm.

	NIST 3171a	NIST 3172a
Mo	2.0477	
Sr		0.2022
Al	2.0819	
Cu		2.0553
Be	0.2038	
V	1.9564	
Mg	2.0359	
Cr	2.0168	
Fe	1.9874	
Mn	2.0489	
Ni	2.0055	
Co		2.0071
Cd	2.0225	
Pb		2.0126
Zn		2.0197
K	10.3522	
Ba		0.2012

APPENDIX B

Ranges of concentrations of inorganic constituents in fly ash from municipal waste incinerators in µg/g (ppm)

Constituent	Concentration (ppm)
Arsenic	15 - 750
Barium	80 - 9,000
Cadmium	5 - 2,210
Chromium	21 - 1,900
Lead	200 - 26,600
Mercury	0.9 - 35
Selenium	0.48 - 15.6
Silver	ND - 700
Aluminum	5,300 - 176,000
Antimony	139 -760
Beryllium	<4
Bismuth	36 - 100
Boron	35 - 5,654
Bromine	21 - 250
Calcium	13,960 - 270,000
Cesium	2,100 - 12,000
Cobalt	2 - 1670
Copper	187 - 2,380
Iron	900 - 87,000
Lithium	8 - 34
Magnesium	2,150 - 21,000
Manganese	171 - 8500
Molybdenum	9 - 700
Nickel	10 - 1,966
Phosphorous	1,770 - 9,300
Potassium	11,000 - 65,800
Silicon	1,783 - 266,000
Sodium	9,780 - 49,500
Strontium	98 - 1100
Tin	300 - 12,500
Titanium	<50 - 42,000
Vanadium	22 - 166
Yttrium	2 - 380
Zinc	2,800 - 152,000
Chloride	1,160 - 11,200
Sulphate	3,200 - 32,800 (sulphur)

Ref. [33]

APPENDIX C

Physical properties of selected metal compounds

Compound	Melting point, °C	Boiling point, °C
Metal chlorides		
$PbCl_2$	501	951
$CdCl_2$	564	960
$ZnCl_2$	290	732
$CuCl_2$	630 d.	
CuCl (or Cu_2Cl_2)	430	1400, 1690[a]
Cu_3Cl_3		1595[a]
$CrCl_2$	814	1300
$CrCl_3$	1152	1300 d.
$NiCl_2$	1009	subl.
Metal oxides		
PbO	888	--
CdO	900 d.	--
ZnO	1975	--
CuO	1446	--
Cr_2O_3	2330	3000
CrO_3	197	250 d.
FeO	1377	--
Fe_2O_3	1565	--
CaO	2580	2850
MgO	2800	3600
Al_2O_3	2045	
Na_2O	1275 subl.	--
NiO	1955	--
Metal sulphates		
$PbSO_4$	1170	--
$CdSO_4$	1000	--
$ZnSO_4$	680 d. to ZnO	
$CuSO_4$	650 d. to CuO	
Chlorinating agents		
$CaCl_2$	775	1935, 2000[a]
$MgCl_2$	714	1412
$FeCl_2$	677	1023
$FeCl_3$	304	316
$AlCl_3$	192	190 subl.
NaCl	801	1465

Sources: CRC Handbook of Chemistry and Physics (Lide 1996);
a: Kubaschewski, 1979 [18].

APPENDIX D

Distribution of the volatile matter along the condensation route. Elemental analytical results on the volatile matter (µg/g sample) from duplicate fly ash samples A by ICP and AAS.

Element		ICP		AAS		Av
		Sample 1	Sample 2	Sample 1	Sample 2	
	* (1)	969	1074	983	1129	
	* (2)	943	861	929	839	
	* (3)	1510	1428	1475	1398	
Pb	Sum	**3422**	**3363**	**3387**	**3366**	**3385**
	(1)	245	225	238	225	
	(2)	410	399	395	385	
	(3)	407	415	386	408	
Cu	Sum	**1062**	**1039**	**1019**	**1018**	**1035**
	(1)	3847	3530	4000	3333	
	(2)	1680	1575	1733	1580	
	(3)	3107	3689	3133	3500	
Zn	Sum	**8634**	**8794**	**8866**	**8413**	**8677**
	(1)	9	4	2	2	
	(2)	13	2	2	0	
	(3)	5	5	4	0	
Cr **	Sum	**27**	**11**	**8**	**2**	**12**
	(1)	45	43		43	
	(2)	40	32		33	
	(3)	41	50		42	
Cd	Sum	**126**	**125**	--	**118**	**123**
	(1)	118	132			
	(2)	445	470			
	(3)	188	208			
Mn	Sum	**751**	**810**			**780**
	(1)	14	13			
	(2)	19	21			
	(3)	25	23			
Ni	Sum	**58**	**57**			**57**
	(1)	10	11			
	(2)	28	38			
	(3)	57	45			
Mg	Sum	**95**	**94**			**94**

Con't

	(1)	59	71	
	(2)	372	395	
	(3)	299	293	
Ca	Sum	**729**	**759**	**744**
	(1)	28	19	
	(2)	5	8	
	(3)	37	35	
Fe	Sum	**70**	**62**	**66**
	(1)	1371	1351	
	(2)	11560	10050	
	(3)	4416	3872	
K	Sum	**17350**	**15270**	**16310**
	(1)	1789	1794	
	(2)	20750	17840	
	(3)	6280	5333	
Na	Sum	**28820**	**24970**	**26890**

* (1) = on the wall of the quartz tube.
(2) = in the connecting tube between the quartz tube and the absorbing solution.
(3) = in the solution of the absorber.

** Cr concentrations are close to detection limit.

APPENDIX E (1)

Metal concentrations in leachate(2) before and after the fly ash(3) was heat treated at 1000°C for 5 h.

Element	Untreated fly ash (mg/L)	Heat treated fly ash (mg/L)	Regulatory limit(4) (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	-

(1) This Appendix is quoted from Ref. [26].

(2) The leachate was tested by the standard testing procedure according to Ontario Regulation 347.

(3) This sample of MSW incinerator fly ash was obtained from an incinerator in U.S.A.

(4) MOE Regulation 347

APPENDIX F

Calculation of ΔG° values for chlorination reactions at 1000°C.

Metal	Reaction and ΔG°, kJ/mol Cl_2
Pb	$PbO_{(l)} + Cl_2 \rightarrow PbCl_2 + \frac{1}{2} O_2$ $\Delta G^\circ = -199.5 - (-93.3)$ $= -106.2$
Cu	$6\ CuO_{(s)} + 3\ Cl_2 \rightarrow 2\ Cu_3Cl_{3(g)} + 3\ O_2$ $\Delta G^\circ = [\ 2(-237.6) - 6(-41.5)\ ] \div 3$ $= -75.4$
Zn	$ZnO_{(s)} + Cl_2 \rightarrow ZnCl_{2(g)} + \frac{1}{2} O_2$ $\Delta G^\circ = -259.4 - (-204.2)$ $= -55.2$
Cd	$CdO_{(s)} + Cl_2 \rightarrow CdCl_{2(g)} + \frac{1}{2} O_2$ $\Delta G^\circ = -199.1 - (-101.4)$ $= -97.7$
Cr	$Cr_2O_{3(s)} + 4\ Cl_2 \rightarrow 2\ CrCl_{4(g)} + 1\frac{1}{2} O_2$ $\Delta G^\circ = [\ 2(-293) - (-801)\ ] \div 4$ $= 53.7$
Mn	$Mn_2O_{3(s)} + 2\ Cl_2 \rightarrow 2\ MnCl_{2(g)} + 1\frac{1}{2} O_2$ $\Delta G^\circ = [\ 2(-299.3) - (-625)\ ] \div 2$ $= 13.2$
Fe	$Fe_2O_{3(s)} + 2\ Cl_2 \rightarrow 2\ FeCl_{2(g)} + 1\frac{1}{2} O_2$ $\Delta G^\circ = [\ 2(-197.7) - (-486.3)\ ] \div 2$ $= 45.5$
Al	$Al_2O_{3(s)} + 3\ Cl_2 \rightarrow 2\ AlCl_{3(g)} + 1\frac{1}{2} O_2$ $\Delta G^\circ = [\ 2(-514) - (-1262)\ ] \div 3$ $= 78.0$
Ti	$TiO_{2(s)} + 2\ Cl_2 \rightarrow TiCl_{4(g)} + O_2$ $\Delta G^\circ = [\ -606.3 - (-709.3)\ ] \div 2$ $= 51.5$
V	$V_2O_{5(l)} + 4\ Cl_2 \rightarrow 2\ VCl_{4(g)} + 2\frac{1}{2} O_2$ $\Delta G^\circ = [\ 2(-381.9) - (-1027.9)\ ] \div 4$ $= 66.0$
Co	$CoO_{(s)} + Cl_2 \rightarrow CoCl_{2(g)} + \frac{1}{2} O_2$ $\Delta G^\circ = -149.0 - (-142.7)$ $= -6.3$

con't

Ni $NiO_{(s)} + Cl_2 \rightarrow NiCl_{2(g)} + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -127.6 - (-123.6) \\ &= -4.0 \end{aligned}$$

Na $Na_2O_{(s)} + Cl_2 \rightarrow 2\ NaCl_{(g)} + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= 2(-241.0) - (-220.4) \\ &= -262.0 \end{aligned}$$

$Na_2SiO_{3(s)} + Cl_2 \rightarrow 2\ NaCl_{(g)} + SiO_2 + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= 2(-241.0) - 678.5 - (-1124.7) \\ &= -35.8 \end{aligned}$$

K $K_2O_{(l)} + Cl_2 \rightarrow 2\ KCl_{(g)} + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= 2(-259.7) - (-153.0) \\ &= -366.4 \end{aligned}$$

$K_2SiO_{3(l)} + Cl_2 \rightarrow 2\ KCl_{(g)} + SiO_2 + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= 2(-259.7) - 678.5 - (-1109.7) \\ &= -88.2 \end{aligned}$$

Mg $MgO_{(s)} + Cl_2 \rightarrow MgCl_{2(g)} + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -416.4 - (-458.1) \\ &= 41.7 \end{aligned}$$

$MgSiO_{3(s)} + Cl_2 \rightarrow MgCl_{2(g)} + SiO_2 + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -416.4 - 678.5 - (-1169.6) \\ &= 74.7 \end{aligned}$$

Ca $CaO_{(s)} + Cl_2 \rightarrow CaCl_{2(g)} + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -498.9 - (-498.7) \\ &= -0.2 \end{aligned}$$

$CaSiO_{3(s)} + Cl_2 \rightarrow CaCl_{2(g)} + SiO_2 + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -498.9 - 678.5 - (-1267.6) \\ &= 90.2 \end{aligned}$$

Sr $SrO + Cl_2 \rightarrow SrCl_{2(g)} + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -510.8 - (-459.7) \\ &= -51.1 \end{aligned}$$

$SrSiO_{3(s)} + Cl_2 \rightarrow SrCl_{2(g)} + SiO_2 + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -510.8 - 678.5 - (-1268.5) \\ &= 79.2 \end{aligned}$$

Ba $BaO + Cl_2 \rightarrow BaCl_{2(g)} + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -533.8 - (-426.8) \\ &= -107.0 \end{aligned}$$

$BaSiO_{3(s)} + Cl_2 \rightarrow BaCl_{2(g)} + SiO_2 + \frac{1}{2} O_2$

$$\begin{aligned} \Delta G^\circ &= -533.8 - 678.5 - (-1262) \\ &= 49.7 \end{aligned}$$

APPENDIX G

Calculation of ΔG for the chlorination of $PbCl_2$ at 1000°C.

(1) Using $CaCl_2$ as a chlorinating agent.

$$PbO_{(s)} + Cl_2 \rightarrow PbCl_{2(g)} + \frac{1}{2} O_2$$

$$\Delta G = \Delta G^\circ + RT \ln (p^{1/2}_{O_2} \cdot p_{PbCl_2} / p_{Cl_2}) \qquad (I)$$

ΔG° = -106 kJ/mol Cl_2
R = 0.008314 kJ deg^{-1} mol^{-1}
T = 1273°K
p_{O_2} = 0.21 atm
p_{Cl_2} = 0.0035 atm (see Sec. 5.8.1.3)
p_{PbCl_2} is calculated as follows:

- Pb volatilized from a 3 g sample D,
  3.666 mg Pb x 3 = 11.0 mg Pb
- atomic weight = 207.2
- theoretical volume of $PbCl_{2(g)}$ at 25°C and 1 atm,
  (11.0 / 207.2) x 24.47 mL = 1.3 mL
- average flow rate is 1.3 mL / 180 min = 0.0072 mL/min
- p_{PbCl_2} is 0.0072 / 150 = 4.8×10^{-5} atm.

Note: Volume ratio of $PbCl_{2(g)}$ and air is independent of temperature, and so is p.p. of $PbCl_2$.

Substitute all these values in equation (I)

$$\Delta G = -106 + 0.008314 \times 1273 \ln (0.21^{1/2} \times 4.8 \times 10^{-5} / 0.0035)$$
$$= -160 \text{ kJ/mol } Cl_2$$

Con't

(2) Using Cl_2 as a chlorinating agent.

p_{Cl2} = 0.02 atm (see Sec. 5.8.1.3) is substituted in eq. (I). The free energy change for the chlorination of $PbCl_2$ becomes

$$\Delta G = -106 + 0.008314 \times 1273 \ln (0.21^{½} \times 4.8 \times 10^{-5} / 0.02)$$
$$= -178 \text{ kJ/mol } Cl_2$$

Since the p_{Cl2} is larger (0.02 > 0.0035), while the p_{PbCl2} is substantially the same, the last term of the equation becomes smaller. Therefore, the ΔG is smaller or more negative, -178, compared with -160 when $CaCl_2$ is used as chlorinating agent.

APPENDIX H

Experimental data for metal concentrations after the samples were heated with $CaCl_2$ for various periods of time. Table (1)-(8). (The concentration of metal at t = 0 refers to the concentration of the total volatilizable metal in fly ash.)

Table (1)
Cr concentrations after heating sample for various periods of time.

Time, min	C, µgCr/g sample	ln C
0	30.0	3.40
1	29.3	3.38
5	28.7	3.35
10	28.0	3.33
20	26.0	3.26
30	23.3	3.15
60	15.3	2.73
120	7.3	1.99

Table (2)
Mn concentrations after heating sample for various periods of time.

Time, min	C, µgMn/g sample	ln C
0	800	6.68
1	787	6.66
5	753	6.62
10	732	6.60
20	711	6.56
30	684	6.52
60	539	6.29
120	449	6.10
180	360	5.88

con't

Table (3)
Ni concentrations after heating sample for various periods of time.

Time, min	C, µgNi/g sample	ln C
0	60	4.10
3	59	4.08
5	58	4.06
10	56	4.02
20	52	3.95
30	48	3.87
60	40	3.69
120	32	3.46
180	23	3.13

Table (4)
Na concentrations after heating sample for various periods of time.

Time, min	C, µgNa/g sample	ln C
0	40000	10.60
1	39770	10.59
3	39380	10.58
5	38840	10.56
10	37040	10.52
20	33870	10.43
30	30260	10.31
60	18600	9.83
120	9000	9.10
180	4600	8.43

Table (5)
K concentrations after heating sample for various periods of time.

Time, min	C, µgK/g sample	ln C
0	24400	10.10
1	24180	10.09
3	23870	10.08
5	23380	10.05
10	21500	9.97
20	19170	9.86
30	16660	9.72
60	8535	9.05
120	2736	7.91
180	1203	7.09

con't

Table (6)
Zn concentrations after heating sample for various periods of time.

Time, min	C, µgZn/g sample	ln C
1	9018	9.11
3	6468	8.77
5	4902	8.50
10	2802	7.94

Table (7)
Cd concentrations after heating sample for various periods of time.

Time min	C, µgCd/g sample	ln C
1	135	4.9
3	85	4.4
5	49	3.9
10	22	3.1

Table (8)
Pb concentrations after heating sample for various periods of time.

Time min	C, µgPb/g sample	ln C
1	3133	8.05
3	937	6.84
5	477	6.16
10	155	5.04

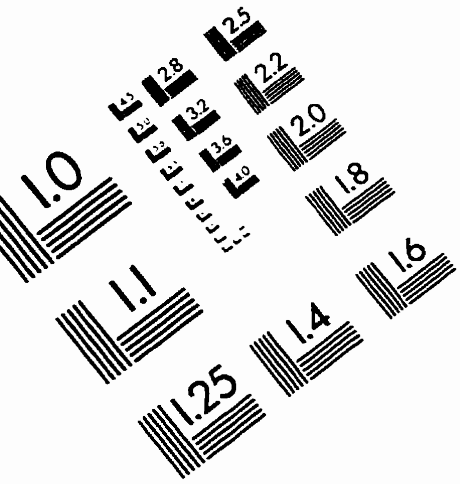
APPENDIX I

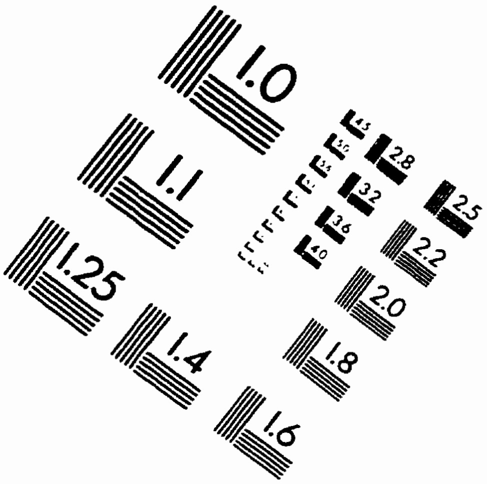
Analytical procedure for determination of dioxins and furans in fly ash samples. (Procedure used by the Laboratory Services Branch, Ontario Ministry of Environment and Energy)

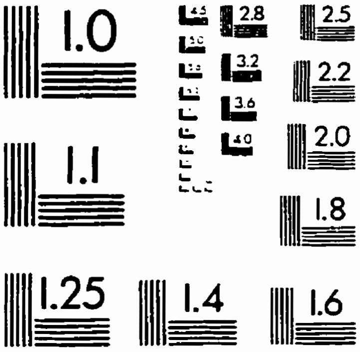
Before extraction, all samples are spiked with a mixture of fifteen carbon-13 labelled 2,3,7,8-substituted dioxins and furans to allow for isotope dilution quantitation (i.e., comparing the intensity of the native and carbon-13 labelled species, knowing the initial concentration of labelled species before extraction). A spiked (to add C-13 labelled species) blank matrix (sand), and a "precision and recovery" sample (consisting of a spiked blank matrix fortified with native dioxins and furans) are analyzed with each batch of samples for quality control purposes. Samples are extracted in refluxing toluene for sixteen hours using a Soxhlet extractor. The majority of interfering organic compounds are then removed from the sample extract by use of open-column liquid-solid chromatography (LSC). Four LSC sorbents are used: acid-modified silica, base-modified silica, silver nitrate-modified silica, and alumina. Following LSC, the extract is ready for gas chromatography/mass spectrometry (GC/MA) analysis.

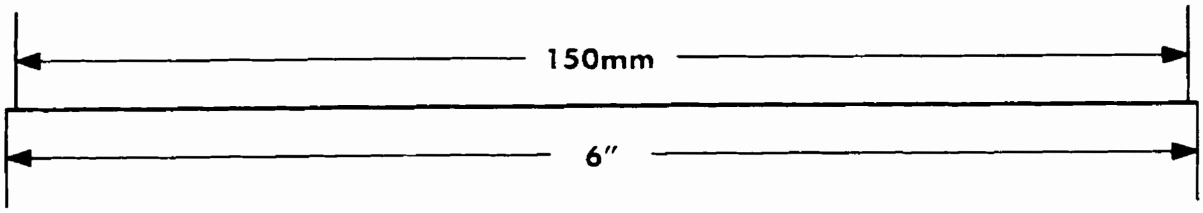
A VG AutoSpec high resolution mass spectrometer (HRNS) and a Hewlett-Packard gas chromatograph (Model HP5890 Series II) with a 60 m x 0.25 mm i.d., 0.25 µm film thickness DB-5 GC column are used for determination of the analytes. The temperature program of the gas chromatograph (GC) is arranged such that 2,3,7,8-TCDD is fully resolved from its nearest eluting isomers using helium carrier gas. Under these conditions, the tetra- through octa-chlorinated dioxins and furans elute between 25 and 50 minutes. The HRMS which is interfaced to the GC is operated in "selected ion" recording mode at 10,000 resolving power. The two most abundant chlorine isotope peaks in the molecular ion cluster are monitored for each of the native and carbon-13 labelled dioxin and furan congeners. Retention times and isotope ratios are used as identification criteria for the dioxins and furans.

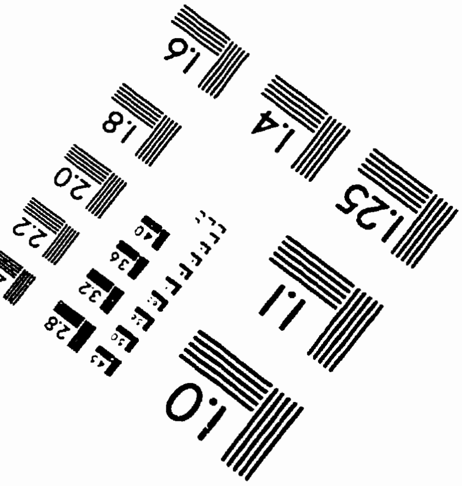
IMAGE EVALUATION TEST TARGET (QA-3)

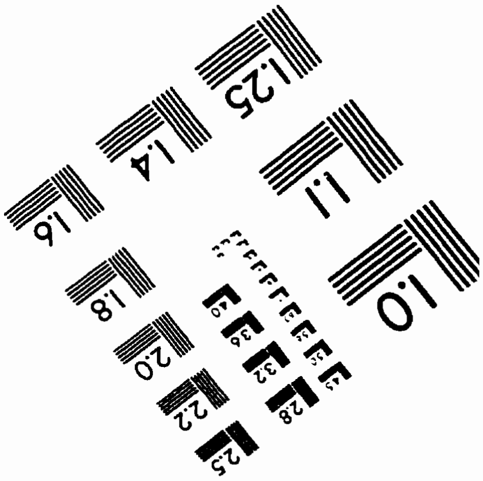












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