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CHARACTERIZATION AND THERMAL TREATMENT OF FLUE DUST GENERATED DURING IRON AND STEEL MANUFACTURING

by

Ghassan Abouatallah

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto

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The flue dust generated during steelmaking contains Zn (6 wt.%) and Pb (1 wt.%) originating from the recycling of galvanized scrap metal. These contaminants render the flue dust both environmentally hazardous and unsuitable for internal recycling. The physical and chemical characteristics of different types of dust were examined in this study. The distribution and the associations of these contaminants depended on the type of flue dust. The selective removal of Zn and Pb was accomplished through thermal treatment using a Cl₂/air mixture at 1 atm. and temperatures between 500 and 900 °C. The extent of removal was found to increase with temperature reaching 95% for Zn and 100% for Pb at 900 °C. Kinetic modeling was used to deduce the activation energies of Zn and Pb removal. These activation energies exceeded 50 kJ/mol in all cases, indicating that the rate determining step of the removal process is chemically controlled.
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"Εν οίδα στι ουδεν οίδα"

"I know one thing, that I do not know anything"
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1. INTRODUCTION

1.1 Statement of the problem

The production of iron and steel in integrated steel mills equipped with standard blast furnace (BF) and basic oxygen furnace (BOF) generates a large amount of solid waste totaling about 500 kg/tonne of steel produced [Piret, 1991]. Flue dust, which constitutes about 10% of this waste, is usually recycled back into the steelmaking process due to its high Fe content. Unfortunately, the total recycling of flue dust is no longer a desirable option due to the increase in the level of contaminants which interfere with steel production and quality [Noro, 1997]. This contamination problem has emerged as a result of metal recycling which involves the introduction of scrap metal into the steelmaking process. The recycling of scrap metal causes the amount of heavy metal contaminants such as Zn and Pb to increase in the flue dust, rendering it both environmentally hazardous and unsuitable for internal recycling. Zn, for example, interferes with the steelmaking process since it tends to concentrate in the gaseous phases due to its relatively low temperature of volatilization (1180 °C) then condenses back once it reaches the colder zone of the furnace (693 °C). This condensation is detrimental to the normal operation of the furnace since it prevents the free circulation of the gases generated during steelmaking [Defays, 1991]. It is therefore necessary to minimize the level of Zn in the furnace feed. Natural iron ore contains minor amounts of Zn, namely about 0.05 wt. %, thus it is not the main source of Zn that is found in the BOF flue dust at concentrations up to 6%. The origins of Zn and Pb have been traced back to the introduction of galvanized scrap into the steelmaking process as make-up raw material, thus explaining the exceptionally high levels of Zn (20%) in EAF dust, which charge is usually comprised of 100% galvanized scrap metal. This is a significant problem in the case of the EAF flue dust where the leachability of its non-ferrous contaminants led to its designation as hazardous waste by the US Environmental Protection Agency (US EPA) and European Community legislation [Ronald, 1996].
Before addressing the decontamination problem, it is important to understand the origin of the flue dust in the steelmaking process as outlined in the following section.

### 1.2 Overview of the iron and steelmaking process

The iron and steelmaking process requires different stages as outlined in Figure 1. Different kinds of flue dust are generated at the third and the fourth stage, with the former one involving the use of a blast furnace (BF) for ironmaking. The flue dust generated during this stage usually contains low levels of contaminants. Thus, it is often recycled almost totally back into the steelmaking process.

The fourth stage (highlighted in bold in Figure 1) involves the use of a basic oxygen furnace (BOF) where the scrap metal is usually introduced. The dust generated from the BOF is of concern since it contains high levels of Zn and Pb as mentioned above, thus preventing any internal recycling. The BOF flue dust is collected through the use of either electrostatic precipitators (BOF-Oxide) or wet scrubbers (BOF-Sludge) as detailed in section 4.1.

In addition to dust generation, over 80% of the solid waste is slag, namely about 390 kg slag/tonne of crude steel. The slag is currently collected and sold for use as road filler. Other gaseous and liquid wastes streams have been carefully examined by the industry and currently mitigated by adequate control methods capable of safeguarding the environment and complying with environmental legislation [Russel, 1976].
1 - COKING
In this stage, coke is produced from coal. Coke is then used as a fuel in Stage 2 as well as a fuel and a reducing agent in Stage 3.

2 - SINTERING
Ore fines and recycled BF dust are heated at 1200 °C to form coarse particles (agglomerates) suitable for charging into the BF.

3 - IRONMAKING
The sintered mixture is heated up to 2000 °C in order to reduce and melt the iron metal. Most of the impurities concentrate in the slag which floats on top of the molten iron and is periodically removed from the BF.

4 - STEELMAKING
The molten iron is further purified in refractory-lined basic oxygen furnaces by oxygen lancing in order to remove any remaining tramp elements.

5 - PRODUCT FINISHING
The molten steel is poured into ingots, followed by hot rolling, acid pickling (for surface cleaning), then cold rolling of finished steel products.

Figure 1. Overview of the iron and steelmaking process
1.3 Remedial methods

The hazardous nature of the flue dust has been the impetus for many scientific investigations aimed at devising techniques capable of reducing the leachability of heavy metals once the unrecyclable flue dust is landfilled. Some of these techniques include solidification/stabilization processes using either high temperature sintering or chemical binders which immobilize the heavy metals in the waste [Andres, 1994]. High temperature sulphatizing is also used to convert lead oxide into insoluble lead sulphates, thus allowing the landfiling option [Chaubal, 1982]. However, the disposal of the flue dust is becoming a less attractive option due to the tightening of environmental laws and the reduction of available landfill space. Furthermore, the internal recycling option is advantageous because it reduces the need for virgin iron ore, eliminates disposal costs, and lowers the risk of future environmental liabilities. Nonetheless, the commercial viability of the recovery of heavy metal contaminants from the flue dust is governed both by financial considerations related to the quantity of the target metal required for economic attractiveness when sold and by the degree of separation required for rendering the dust suitable for recycling. The best candidate for such recovery is the electric arc furnace (EAF) dust since its heavy metal content is typically four to five times that of BF and BOF flue dusts [Andres, 1994] because the EAF charge is often comprised of 100% scrap metal. However, even low-Zn residuals have been considered for treatment technologies capable of producing virtually contaminant-free recyclable flue dust [Piret, 1991].

In an effort to divert from landfiling, many hydrometallurgical and pyrometallurgical technologies have been devised to remove the non-ferrous metals from the flue dust which can then be recycled back into the steelmaking process [Nyierenda, 1991][Fray, 1986]. Many attempts were made at using low temperature hydrometallurgical processes including sulphuric, caustic and chlorine leaching. Sulphuric acid leaching is one process that achieved 80% removal of Zn but with considerable co-extraction of Fe [Cruells, 1992]. Caustic leaching was also capable of removing Zn from its oxide form but not from its ferrite form [Fray, 1986]. Chlorine leaching was more effective at
leaching Zn from its oxide form as well as from its ferrite which had formed at low temperatures and not the Zn ferrite formed at higher temperatures [Thomas, 1981]. In addition to leaching, physical separation methods such as hydrocycloning have been used to separate the extremely fine particles containing the majority of Zn, rendering the coarser fraction which constitutes the majority of the flue dust suitable for recycling. [Rawlins, 1993]. This alleviates the contamination problem by allowing the recycling of the majority of the dust but does not address the decontamination of the finer fraction which accumulates with every tonne of steel produced. Alternatively, pyrometallurgical processes are capable of treating all dust fractions. The most widely used technique is the Waelz process where the dust is mixed with coke fines and introduced into a rotary kiln producing gaseous Zn under reducing conditions [Serbent, 1975]. The Zn produced is converted to Zn oxide at less reducing regions of the kiln and the vapours collected downstream in a baghouse. An iron rich slag containing Pb and Cd is also produced, and further decontamination requires another calcine kiln. Furthermore, complete removal of Zn requires elevated temperatures reaching 1300 °C, a costly procedure. Similar high temperature electrothermal processes such as HTR, Tectronics Arc Plasma, and Plasmadust are used to volatilize the non-ferrous contaminants at high temperatures using coke as a reducing agent [Yatsunami, 1981]. A more attractive thermometallurgical process based on chlorination under oxidizing conditions can be used to selectively remove all of the non-ferrous contaminants in a single stage at much lower temperatures. The application of this technique and its high efficiency in decontaminating steelmaking flue dust obtained from a major Canadian steel manufacturer are detailed in this work.

Regardless of the treatment method, understanding the physical and chemical nature of the flue dust would facilitate the development of the most efficient and economical recovery process. Naturally, the EAF dust has been the most extensively characterized flue dust since it contains the highest level of hazardous materials [Lopez, 1993] [Cruells, 1992]. BF and BOF dusts, on the other hand, have rarely been characterized [Hay, 1993] since more emphasis has been placed on determining their leaching characteristics as opposed to their chemical characteristics [Dresinger,
This work presents a detailed study of the physical and chemical of the Canadian steel flue dust (mentioned above) whose characteristics may be considered to be similar to BOF dust produced in other integrated steel mills.

2. LITERATURE SURVEY AND BACKGROUND

2.1 Previous work: application of chlorination

Metal extraction through chlorination roasting has been used on ores and concentrates to isolate and recover the metal values [Habashi, 1986]. Chlorination is based on the conversion of most non-ferrous metal oxides into chlorides whose stability and volatility allows for selective separation. The basis of the chlorination process is described in Section 2.2. Prior to detailing the chlorination process, it is important to present practical applications where chlorination has been successfully applied. The extraction of Ni from an Indian laterite using chlorination at 900 °C serves as a good example [Mehrotra, 1994]. The process is initiated by the reaction of a solid chlorinating agent, namely CaCl₂, with steam and SiO₂ to form HCl which then chloridizes the NiO present in the ore grains to form volatile NiCl₂ as illustrated below:

\[
\text{CaCl}_2(s) + \text{H}_2\text{O}(g) + \text{SiO}_2(s) \rightarrow \text{CaO} \cdot \text{SiO}_3(s) + 2\text{HCl}(g) \quad \text{[R.1]}
\]

\[
\text{NiO}(s) + \text{HCl}(g) \rightarrow \text{NiCl}_2(g) + \text{H}_2\text{O}(g) \quad \text{[R.2]}
\]

The presence of controlled moisture is essential to this process since water vapour is reacted with C to produce H₂ gas which in turns reduces the NiCl₂ to metallized Ni as illustrated below:

\[
\text{C}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g) \quad \text{[R.3]}
\]

\[
\text{NiCl}_2(g) + \text{H}_2(g) \rightarrow \text{Ni}(s) + \text{HCl}(g) \quad \text{[R.4]}
\]
The application of this process yielded Ni recovery as high as 85% at 900 °C within 1 hour. Ericson et al. [1984, 1987] reported that this process was successfully tested on a pilot plant scale using a rotary kiln.

In addition to extracting Ni, CaCl₂ is also used to treat low-grade minerals which are unsuitable for conventional metallurgical treatment. For example, the recovery of Sn using casseterite reduction by solid carbon at temperatures exceeding 1200 °C requires a minimum Sn concentration of 56% [Wright, 1972]. This high level is not always easy to get, particularly in mineral with concentration difficulties due to mineral paragenesis and liberation like casseterite. Garcia et al. [1993] investigated low-grade minerals where Sn level was less than 2%. They were able to achieve 99% Sn removal by reacting SnO₂ with CaCl₂ in the presence of SiO₂, C and O₂ without the need for H₂O according to the following overall reaction:

\[
\text{SnO}_2(g) + \text{CaCl}_2(s) + \text{SiO}_2(s) + C(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SnCl}_2(g) + \text{CO}_2(g) + \text{CaSiO}_3(s) \quad [R.5]
\]

The process described above operated at 900 °C. Lower temperatures, however, are sometimes sufficient to remove certain elements whose chlorides have a boiling point less than 570 °C. Sb, As, and Bi constitute a good example of such elements. Holmström [1988] considered their removal from concentrates rich in Cu, Ag and Au by reacting the mixture with CaCl₂ under S0₂-rich weekly oxidizing conditions at 600 °C. The selective removal of As, Sb, and Bi was very satisfactory at 95%, 98%, >90%, respectively. In other cases, chlorination was used to recover Au when conventional processes including cyanidation were only able to recover between 60 to 70% of the Au. Deng [1987] was able to recover 94 to 97% of Au from Chinese quartz vein ores by using CaCl₂ chlorination under oxidizing conditions at 1000 to 1050 °C. The fumes were subsequently chemically treated in order to separate other elements that co-volatilized along with Au such as Ag, Cu, Zn and Pb, leading to virtually pure Au.
In addition to CaCl₂, other chlorinating agents are used for the purpose of selective chlorination. Parkeh et al. [1988] found NaCl to be the best chloridizing agent capable of extracting 90% of Ni, Co, and Cu from deep sea nodules. NaCl is also the chloridizing agent of choice in the Torco Cu segregation process mainly because of its economic attractiveness [Brittan, 1971]. Other solid chlorinating agents including FeCl₃·6H₂O and MgCl₂·6H₂O were used to obtain mercuric and mercurous chlorides from cinnabar ores. Roca et al. [1990] chose these reagents mainly because the more conventional NaCl and CaCl₂ do not react at temperatures sufficient to decompose cinnabar HgS (400 °C) and because solid chlorinating agent are easier to handle than the gaseous ones such as Cl₂(g). These hydrated chlorinated agents release HCl upon heating and depending on the operating temperature. For example, FeCl₃·6H₂O releases 2 moles of HCl in the 127 to 213 °C temperature range, with the third mole of chloride released in the 432 to 472 °C range. Once evolved, the HCl reacts with cinnabar to produce HgCl₂ according to the following reaction:

\[
\frac{1}{2}\text{HgS} \ (s) + \text{HCl} \ (g) + \frac{3}{2}\text{O}_2 \ (g) \rightarrow \frac{1}{2}\text{HgCl}_2 \ (s) + \frac{3}{2}\text{SO}_2 \ (g) + \frac{1}{2}\text{H}_2\text{O} \ (g) \quad [R.6]
\]

Other researchers preferred the use of Cl₂(g) as a chlorinating agent especially in cases where the introduction of Ca (from CaCl₂) or Na (from NaCl) is not desirable. Nair [1988] took such an approach and was able to remove 99% of Mo from low grade Indian molybdenite using a 10% Cl₂/air mixture in a fluidized bed at 275 °C. The use of a fluidized bed, in this case, enhanced the ore/Cl₂ contact, thus allowing the extent of Mo removal to reach completion in less than half hour. Djona et al [1995] also used a Cl₂/air mixture to selectively remove virtually all of Ni, Co, Mo and V (initially in their oxide form) from spent hydrorefining catalysts for the purpose of decontamination prior to disposal. They also determined an optimal selectivity window of 18 to 22% Cl₂ and 425 to 475 °C beyond which a decrease in selectivity occurs.

The chlorination processes described above highlight the versatility, efficiency, and advantages of this metal separation technique. Thus, the merits of this technique encouraged its
application to the iron and steel industry. Nunez et al [1984] reported that Cl₂, CaCl₂ and FeCl₃ had been proposed as suitable chlorinating agents for the removal of impurities from pyrite ashes. They favored CaCl₂ because it was easier to handle and because it yields CaO during chlorination which is favourable since CaO is a flux in the ironmaking process. The laboratory scale chlorination experiments with CaCl₂ as a chlorinating agent achieved 97% Pb removal and 93% As removal from an iron ore concentrate where Pb and As are the main non-ferrous contaminants. Similarly, Yazawa et al. [1967] achieved almost complete removal of impurities including Cu, Zn, and Pb through chlorination roasting of pyrite cinders. Even though 1100 °C was sufficient to remove the non-ferrous contaminants, they favoured a higher temperature of 1200 °C which strengthens the pellets by sintering, thus rendering them readily amenable to recycling. CaCl₂ was selected as the chlorinating agent because the pellets obtained by this process are commonly used in the iron blast furnace. Unlike the previous cases, the liberation of Cl₂ did not occur from the reaction of CaCl₂ with silica since the former is not available. Yazawa concluded that the reaction of CaCl₂ with SO₂ caused the liberation of Cl₂ which then reacted with the oxide contaminants (MO) to form their more volatile chlorides as shown below:

\[
\text{CaCl}_2(g) + \text{SO}_2(g) + \text{O}_2(g) \rightarrow \text{CaSO}_4(s) + \text{Cl}_2(g) \quad [R.7]
\]

\[
\text{MO}(s) + \text{Cl}_2(g) \rightarrow \text{MCl}_2(g) + \frac{1}{2}\text{O}_2(g) \quad [R.8]
\]

Lippert et al. [1969] substituted CaCl₂(s) with Cl₂(g) when the pyrite cinder was treated on a pilot plant scale because Cl₂ was cheaper and more effective than CaCl₂(s) at treating cinders containing a higher level of contaminants due to better mixing properties. They reported that a large scale German pilot plant (100 t/day) was successfully able to remove impurities including Zn, Cu, and Pb from pelletized cinder pellets. The outcome of trials showed that over 95% of these impurities can be selectively removed in a 1100 to 1250 °C range. Such success encouraged the design and development of a larger chlorination furnace capable of decontaminating 500 t/day of pyrite cinder.
In addition to treating iron ore, chlorination can be applied to decontaminate ironmaking by-products such as flue dust which contains significant amounts of non-ferrous contaminants including Zn, Pb, and Cu, as mentioned in Section 5.2. Fray [1986] showed that a 5% Cl\textsubscript{2}/air mixture is capable of reducing Zn, the most abundant contaminant in EAF dust, from 10.2% to 0.7%, a 93% reduction without loss of Fe. The overall chlorination reaction responsible for the removal of Zn from the EAF dust is shown below:

\[ \text{ZnO} (s) + \text{Cl}_2 (g) \rightarrow \text{ZnCl}_2 (g) + \frac{1}{2}\text{O}_2 (g) \]  

[R.9]

Fray [1993] also proposed that the generated ZnCl\textsubscript{2} vapour be dissolved in water and electrolyzed at high current density to yield high purity Zn. The remaining iron-rich flue dust was devoid of non-ferrous impurities and thus suitable for recycling back into the steelmaking process. In fact, the chlorination process is so versatile that it was successfully applied to remove heavy metal from other contaminated fine grained material such as incinerated municipal solid waste fly ash [Chan 1996] [Jakob, 1996].

The majority of the chlorination processes briefly explained above focused on the extent of removal of target metals as well as the operating conditions necessary to establish the metal removal efficiently and selectively. Very few studies, however, examined the reaction kinetics of the metal removal process with an attempt to describe the rate determining step governing the chlorination/volatilization process. This is mainly due to the complexity inherent to most industrial samples which complicates any theoretical studies. Some researchers attempted to circumvent such difficulty by conducting chlorination of pure oxides including ZnO [Orlov 1969] and NiO [Fruehan, 1973]. It is important to note that the behaviour of actual samples during chlorination may differ greatly from that of synthetic experiments due to non-ideality, heterogeneity, and complexity of industrial samples. In this study, more focus was placed on examining the reaction kinetics governing chlorination/volatilization of the non-ferrous elements from steelmaking flue dust. The kinetic
information obtained by examining the experimental data was used to investigate the nature of the rate determining step governing the metal removal process. But prior to examining the reaction kinetics, it is important to clarify the basis of the chlorination process itself.

2.2 Theoretical background

2.2.1 Thermodynamics of the chlorination process

The effectiveness of chlorination is based on the ability of Cl\textsuperscript{-} originating from a chlorinating agent to displace the O\textsuperscript{2-} from the metal oxide as illustrated below:

\[
\text{MO(s)} + \text{Cl}_2(g) \rightarrow \text{MCl}_2(g) + \frac{1}{2}\text{O}_2(g) \quad [R.10]
\]

Thermodynamically, the chlorides of most elements including Zn, Pb, Cu, Ni, Cd, Co, and Cr are more stable than their oxides at all temperatures, while the reverse applies to the hematite and magnetite [Fray, 1993]. This stability causes the equilibrium of reaction R.10 to shift to the right, thus favouring the formation of volatile chlorides and pushing the chlorination of all the important metal oxides close to completion under normal industrial operating conditions where the temperature is 500 to 1000 °C [Raynor, 1979].

The attractiveness of chlorination is illustrated by the negative value of the standard Gibbs free energy change (ΔG\textsuperscript{o}) associated with the chlorination of all the important metal oxides as illustrated in the Ellingham diagram shown in Figure 2. A negative ΔG\textsuperscript{o} value highlights the higher affinity of the metal for chlorine rather than oxygen during chlorination according to reaction R.10. The ΔG\textsuperscript{o} values represent the difference between the sum of the free energies of formation of products and the sum of the free energies of reactants under standards conditions (i.e., each element is at its most stable form at 1 atmosphere and at the temperature specified). Thermodynamic data [Barin,
can be used to compute $\Delta G^\circ$ at a given temperature as illustrated in the following sample reactions:

\[
\begin{align*}
\text{ZnO (s) + Cl}_2 (g) & \rightarrow \text{ZnCl}_2 (s) + \frac{3}{2} \text{O}_2 (g) & \Delta G^\circ_{298K} = -54.8 \text{ kJ/mole} & \text{[R. 11]}\\
\text{PbO (s) + Cl}_2 (g) & \rightarrow \text{PbCl}_2 (s) + \frac{3}{2} \text{O}_2 (g) & \Delta G^\circ_{298K} = -106 \text{ kJ/mole} & \text{[R. 12]}\\
\text{CdO (s) + Cl}_2 (g) & \rightarrow \text{CdCl}_2 (s) + \frac{3}{2} \text{O}_2 (g) & \Delta G^\circ_{298K} = -97.6 \text{ kJ/mole} & \text{[R. 13]}\\
\text{Fe}_2\text{O}_3 (s) + 3\text{Cl}_2 (g) & \rightarrow 2\text{FeCl}_3 (s) + 3/2 \text{O}_2 (g) & \Delta G^\circ_{298K} = 68.5 \text{ kJ/mole} & \text{[R. 14]}\\
\end{align*}
\]

The thermodynamic relationships governing the chlorination process have been closely examined [Kellog, 1950]. It was noted that values of $\Delta G^\circ$ is a measure of feasibility of the reaction with a favourable reaction corresponding to a negative value of $\Delta G^\circ$. Nonetheless, it is the value of $\Delta G$ that determines the actual driving force of the reaction, or in other words, whether the reaction can occur spontaneously under a given set of condition. $\Delta G$ is related to $\Delta G^\circ$ value as follows:

\[
\Delta G = \Delta G^\circ + RT \ln K
\]

[E.1]

where is $K$ the reaction constant, which in the case of reaction R.11, is given by:

\[
K = \frac{a_{\text{ZnO}} \times P_{\text{Cl}_2}}{a_{\text{ZnCl}_2} \times P_{\text{Cl}_2}^{1/2}}
\]

[E.2]

Where $a_i$ and $P_i$ are the activity and the partial pressure of component $i$, respectively. The above equations are used to construct phase stability diagrams which demonstrate the effect of operating parameters like temperature and gas composition on metal separation. In the case of metal sulphide roasting, these stability diagrams are known as Kellog diagrams [Peek, 1996]. An example of the stability diagram applicable to the chlorination of flue dust under oxidative conditions for the purpose of removal of Zn in shown in Figure 3 [Peek, 1995]. It shows that for a 5 % Cl$_2$/air mixture
under atmospheric total pressure, the window of operation corresponds to zone E where ZnCl$_2$ and Fe$_2$O$_3$ are stable, thus favouring the extraction of Zn from Zn ferrite.

Note that this information describes equilibrium conditions without describing the kinetics of the actual chlorination/volatilization process. During actual operating conditions, a steady state is established rather than equilibrium especially in the case of continuous feed input. The stability diagram therefore merely indicates the state which the system tends to establish starting from non-equilibrium conditions. It is up to the reaction kinetics governing the process to determine how fast the system reaches equilibrium. The issue of reaction kinetics is addressed in details in Section 2.2.3. It is important to first investigate the reactants and the products of the chlorination process in order to better understand how their behaviour during chlorination affect the reaction kinetics.
Figure 2. Ellingham diagram: Gibbs free energy for metal oxide chlorination versus temperature: \( \text{MO (s) + Cl}_2 (g) \rightarrow \text{MCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) \)

\( M = \) melting, \( B = \) boiling, \( S = \) sublimation

[Yazawa, 1967]
2.2.2 Chlorination reactants and products

2.2.2.1 Chlorinating agents

The methods of chlorination are clearly explained in the literature [Habashi, 1986]. The chlorinating agents are also diverse including solids such as CaCl₂ and NaCl as well as gases such as HCl and Cl₂. The solid chlorinating agents, such as CaCl₂, were not utilized in this research because they require the presence of silica in order to be effective [Chan, 1997]. Silica reacts the CaCl₂ to release Cl₂ as follows:

\[ \text{CaCl}_2 (s) + \text{SiO}_2 (s) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{CaO} \cdot \text{SiO}_3 (s) + \text{Cl}_2 (g) \quad \Delta G^\circ_{1273K} = 16 \text{ kJ/mole} \quad [R.15] \]

The Cl₂ released then reacts with the MO to generate MCl₂, with the overall reaction having a negative \( \Delta G^\circ \). Without the presence of SiO₂, the release of Cl₂ is unfavourable:

\[ \text{CaCl}_2 (s) + \text{O}_2 (s) \rightarrow \text{CaO} (s) + \text{Cl}_2 (g) \quad \Delta G^\circ_{1273K} = 107 \text{ kJ/mole} \quad [R.16] \]

The samples examined in this study contain very little SiO₂, and thus the use of CaCl₂ or NaCl was not favoured. Furthermore, reaction R.15 represents an additional step which would complicate the determination of the rate determining step associated with the chlorination mechanism. It is for this reason that HCl was not used as a chlorinating agent since it is also requires an additional step in which Cl₂ is generated according to the following reaction:

\[ 2\text{HCl} (g) + \text{O}_2 (g) \rightarrow \text{Cl}_2 (g) + \text{H}_2\text{O} (g) \quad [R.17] \]

The thermodynamics of the above reaction, known as the Deacon process, have been thoroughly examined in the literature [Arnold, 1952]. In addition to the introduction of the Deacon reaction, the use of HCl produces water vapour which may introduce more complications since the chlorides formed are sensitive to moisture. The use of Cl₂, on the other hand, provides a more straight
forward alternative, especially since the chlorination of the majority of metal oxides has a more negative $\Delta G^\circ$ values at higher temperatures when Cl$_2$ is used instead of HCl. Using Cl$_2$ as a chlorinating agent is also advantageous because it allows fixing the partial pressure of Cl$_2$ during the process. A constant Cl$_2$ partial pressure is essential when studying reaction kinetics where only one variable is changed at a time during the process of determining kinetic parameters such as reaction rate constant. Fixing the partial pressure of Cl$_2$ is not as straightforward when using HCl or CaCl$_2$, especially that both of them require an additional step to liberate Cl$_2$ as mentioned above. Such additional reactions would complicate the determination of the rate determining step associated with the chlorination mechanism and are thus undesirable for this study.

2.2.2.2 Chloride properties

The effectiveness of chlorination is partially due to the stability of the target metals volatilized in their di- or trivalent state instead of metallic state. The metal chlorides generated during the chlorination process are very volatile at relatively low temperatures as demonstrated in Figure 4.

Moreover, the volatility of these chlorides differ from metal to metal. This allows for physical separation techniques such as selective volatilization and fractional distillation to be used when the recovery of the generated chlorides is sought. Fractional deposition is currently being investigated [Auer, 1997]. Fray [1993] even proposed the purification of ZnCl$_2$ through electrolysis which produces pure Zn metal and Cl$_2$(g) which can be recycled back into the chlorination process. If the recovery of volatilized metals is not sought, the generated chlorides can be scrubbed in an aqueous solution owing to their high solubility. The metals can later be separated from the solution by precipitation using caustic addition.
Figure 3. The Zn-O-Fe-Cl phase stability diagram at 1100 K in which every gaseous compound has a partial vapour pressure of $10^{-2}$ atmosphere. A = Fe(s) & ZnO (s), B = Fe(s) & ZnCl$_2$ (g), C = FeO (s) & ZnCl$_2$ (g), D = Fe$_3$O$_4$ (s) & ZnCl$_2$ (g), E = Fe$_2$O$_3$ (s) & ZnCl$_2$ (g) [Peek, 1996]

Figure 4. Vapour pressure of selected chlorides vs. Temperature [Toguri, 1975]
2.2.3 Reactions kinetics

2.2.3.1 Activation energy and rate determining step

The study of reaction kinetics reveals important information regarding the chlorination/volatilization mechanism such as the nature of the rate determining step. For example, the magnitude of the activation energy (Ea) obtained from reaction kinetics calculation can be used to establish whether the rate determining step is controlled by diffusion or by chemical reaction. This is possible because the magnitude of Ea for chemical reaction control is typically above 100 kJ/mole and only occasionally as low as 50 kJ/mole whereas diffusion control is associated with Ea typically less than 20 kJ/mole [Szekely, 1976] [Crowe, 1998].

In order to determine the Ea, it is first essential to determine the reaction rate constant. Customarily, researchers determine the reaction rate constant at a given temperature by drawing a straight line through the initial part of the curve generated by plotting fractional conversion versus time [Donald, 1996]. In this study, the more objective method of integrated equation (detailed in the Appendix C) is used to determine the reaction rate constant as follows [Walas, 1989]:

\[ aA + bB \rightarrow \text{products} \]  \hspace{1cm} [R.18]

The rate of disappearance of A is given by:

\[-dC_A/dt = k(C_A)^p(C_B)^q \]  \hspace{1cm} [E.3]

When B is present in excess (e.g. excess Cl₂), E.3 becomes:

\[-dC_A/dt = K(C_A)^p \]  \hspace{1cm} [E.4]

Where \( K = k(C_B)^q \). Replacing the concentration term by fractional conversion \( (f_A) \) and integrating yields the following (see details in the Appendix C):
\[-\ln (1 - f_A) = Kt \quad \text{for } p = 1 \quad \text{[E.5]}
\]
\[(1 - f_A)^{(1-p)} - 1 = (1 - p)Kt \quad \text{for } p \neq 1 \quad \text{[E.6]}
\]

The value of \(p\) is determined by plotting the left hand-side of the above equations versus \(t\) using the experimental \(f_A\) obtained for each element at a given temperature. The value of \(p\) that produces the most linear plot indicates the order of the rate determining step. The rate constant \(K\) can then be determined from the slope of the line. Once \(K\) is determined at different temperatures, the Arrhenius equation is used to determine \(E_a\) as follows [Song, 1979]:

\[K = K_0 e^{(-E_a/RT)} \quad \text{[E.7]}
\]

Where \(K\) is the reaction rate constant (units of mol L\(^{-1}\) min\(^{-1}\) for a first order reaction and mol\(^p\) L\(^{-p}\) min\(^{-p}\) for a reaction of order \(p\)), \(K_0\) is the frequency factor derived from the molecular collision theory (units same as \(K\)), \(E_a\) is the activation energy (kJ/mol), \(R\) is the gas law constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \(T\) is the temperature (K). A plot of \(\ln K\) versus \(1/T\) should yield a straight with a slope of \(-E_a/R\), thus giving the value of \(E_a\).

The procedure described above constitutes an empirical fitting of the experimental data for the purpose of obtaining useful kinetic such as reaction rate constant, reaction order, and activation energy. However, the reaction order obtained through this procedure does not uniquely determine the actual mechanism of the reaction. Other kinetic models based on certain mechanistic assumptions can be used to obtain more insight regarding the actual mechanism of the chlorination/volatilization process. One of these models are described in the following section.

2.2.3.2 Gas-solid reaction models

Models describing the reaction kinetics of non-catalytic heterogeneous solid-gas reaction include uniform internal reduction [Turkdogan, 1971], nucleation and growth [Matyas, 1974], and
shrinking core model [Levenspiel, 1972]. The last model is of the most widely used for gas-solid reactions. It is chosen over the first two models whose assumptions and boundary conditions do not apply to the chlorination/volatilization examined in this study. The shrinking core model assumes that as the reaction between a gaseous reactant and a densely packed solid reactant first occurs at the surface, then as the reaction proceeds, the surface of the reaction will shrink or move into the interior of the solid, leaving behind an inert ash layer. The progress of the reaction as well as the different layers surrounding the particle are illustrated in Figure 5. The illustration is based on a generic non-catalytic gas-solid reaction below:

\[ aA(g) + S(s) \rightarrow \text{Products (s,l)} \]  

[R.19]
The steps involved in gas-solid surface reaction described by the shrinking core model are the following [Levenspiel, 1972]:

1. Diffusion of the fluid reactants across the fluid film surrounding the solid
2. Diffusion of the fluid reactants through porous solid layer
3. Chemical reaction with the solid surface
4. Diffusion of the product away from the reaction surface through the porous solid media and through the film surrounding the solid

The mathematical equations describing the shrinking core model have been developed and thoroughly examined in the literature [Wen, 1968]. A brief explanation is provided here to better understand the model and the associated assumptions.

Using material balance around a reacting particle, the fundamental equation is given by equation E.8 and the boundary conditions given by equations E.9 and E.10:

\[ \varepsilon \frac{\partial C_A}{\partial t} = D_{st} \left( \frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right), \quad R > r > r_c \]  

\[ D_{st} \left( \frac{\partial C_A}{\partial r} \right)_{r = R} = k_{ma} (C_{Ao} - C_{As}) \]  

\[ D_{st} \left( \frac{\partial C_A}{\partial r} \right)_{r = r_c} = a_k C_{So} C_{Ac} \]  

Where \( C_{Ao}, C_{As}, C_{Ac}, C_{So} \) are the concentration of reactant A in the bulk of the fluid stream, at the surface of the particle, and at the surface of the core, the concentration of reactant S in the unreacted core, respectively. \( R, r_c, r \) are the radius of the particle, radius of the unreacted core, and
radius at any point from the center of the particle, respectively. \( \varepsilon, D_{eA}, k_{ma}, k_s \) are the voidage fraction of the porous layer, effective diffusivity of A in ash layer, mass transfer coefficient across fluid film, reaction rate constant, respectively.

An analytical solution of the given equations can not be obtained except for a few special cases. An approximate solution, however, can be obtained by applying the pseudo-steady state assumption where \( \varepsilon \frac{\partial C}{\partial t} = 0 \) which is reasonable since the shrinkage of the unreacted core is slower than the flow rate of A toward the unreacted core by a factor of about 1000 roughly obtained from the ratio of densities of solid to gas. This assumption facilitates the calculation and yields the concentration profile equation shown on the following page:

\[
\frac{C_A}{C_{A0}} = \frac{\left(1 + \frac{D_{eA}}{ak_s C_{s0} r_e^3}\right)\frac{1}{r_e^3} - \frac{1}{r}}{\left(1 + \frac{D_{eA}}{ak_s C_{s0} r_e^3}\right)\frac{1}{r_e^3} - \left(1 - \frac{D_{eA}}{k_{ma} R}\right)\frac{1}{R}}
\]  

(E.11)

The time required for the particle to reduce the unreacted core from \( R \) to \( r_c \) is given by:

\[
t = \frac{aR_{s0}}{C_{A0}} \left[\frac{1}{3} \left(\frac{1}{k_{ma}} - \frac{R}{D_{eA}}\right) \left(1 - \frac{R^3}{r_c^3}\right) + \frac{1}{ak_s C_{s0}} \left(1 - \frac{r_c^3}{R^3}\right) + \frac{R}{2D_{eA}} \left(1 - \frac{r_c^2}{R^2}\right)\right]
\]

(E.12)

The above equations can be expressed in terms of fractional conversion as following:

\[
1 - 2/3 f_A - (1-f_A)^{2/3} = \alpha t \quad \text{(diffusion control)}
\]

(E.13)

\[
1 - (1-f_A)^{1/3} = \pi t \quad \text{(chemical control)}
\]

(E.14)
Where $\epsilon_A$ is the fractional conversion of $A$, $t$ is time, and $\alpha$ is a proportionality constant that is directly proportional to the size of particle and inversely proportional to the fluid film mass transfer coefficient, the ash layer diffusion coefficient, and the reaction rate constant at the solid reactant surface. Equations E.13 and E.14 can be used to clarify the reaction mechanism by plotting the left hand-side versus time and checking the linearity of the plot to determine whether diffusion or chemical control apply.

3. OBJECTIVES

The objectives of this study are twofold:

1. To characterize various steelmaking flue dust samples by investigating their particle size distribution, chemical composition, thermal behaviour, phases, morphology and metal associations. The findings will provide a better understanding of the chemical and physical nature of the flue dust samples. This understanding is essential in predicting the outcome of any treatment process aimed at removing heavy metal contaminants such as Zn, Pb, and Cu for the purpose of internal recycling of the flue dust.

2. To investigate the thermal treatment of the flue dust using chlorination roasting under oxidizing conditions in order to remove Zn, Pb, and Cu in the form of volatile chlorides. The data will reveal whether this thermal treatment process is capable of producing contaminant-free flue dust suitable for internal recycling. As well, the data will be used to investigate the kinetics of the chlorination/volatilization process by estimating the activation energies and reaction rate constants associated with the removal of each of the aforementioned contaminants. The findings will be used to determine whether the rate determining step of the chlorination/volatilization process is under diffusion or chemical control.
4. EXPERIMENTAL PROCEDURES

4.1 Materials

The flue dust samples were obtained from a major steel manufacturer whose annual production of five million tonnes of steel accounts for about 30% of the total steel produced in Canada. The two manufacturing facilities where the flue dust is generated are integrated steel mills equipped with standard blast furnace (BF) and basic oxygen furnace (BOF). The BF flue dust is classified into two categories depending on the method of collection which differs between the two facilities. In the first collection method, the high pressure air blast escaping from the top of the furnace is channeled to a bag house where the flue dust (BF-FD) is cooled and collected. The second collection method involves the use of a wet gas scrubbing system which produces a wet solid mass of the BF flue dust (BF-FC). Similarly, the BOF flue dust is collected through two methods. The first collection method involves the use of a wet scrubber system which produces a wet sludge (BOF-OG). In the second collection method, the BOF flue dust is collected by means of electrostatic precipitators which produces an extremely fine dust (BOF-OX). Currently, the BOF-OX is collected and pugged (i.e. mixed with water and compressed into coarser fractions) in order to facilitate its transport and storage on site pending treatment. Representative samples of BF-FD, BF-FC, pugged BOF-OX (pBOF-OX), unpugged BOF-OX (uBOF-OX), and BOF-OG were collected on site and placed in air-tight containers. The composition of these samples is typical of those from other mills (see Section 4.2).

In this study, emphasis will be placed on the characterization of pBOF-OX as well as the BOF-OG, accompanied by a partial characterization of BF-FD and BF-FC for purpose of comparison. The uBOF-OX samples were received at a later stage of the study and were thus partially characterized. More emphasis was placed on thermally treating the uBOF-OX samples.
4.2 Characterization

The cone-and-quarter technique was used to obtain representative sub-samples from the original flue dust sample containers. The moisture content was determined from the weight loss caused by drying the flue dust samples at 110°C for a period of 12 hours until constant dry weight is reached.

The particle size distribution of the pBOF-OX was determined by sieve analysis down to 53 μm (Canadian Standard Sieves) using a mechanical shaker for a period of 20 minutes per dehydrated sample. For the finer uBOF-OX dust with diameter less than 53 μm, a sedimentation method was used to obtain the particle size distribution. The Andreasen pipette illustrated in Figure 6 was manufactured and used for this purpose [Chen, 1986][Allen, 1990]. The operation of this apparatus is based on Stoke’s law as detailed in Appendix A. The pipette consists of a one liter graduated sedimentation vessel (6 cm I.D.) into which a 10 mL calibrated pipette (1 mm I.D.) dips down to a 4 cm distance from the bottom. The tip of the pipette is at the zero level mark and its stem is fused to a ground-glass socket which fits into the neck of the sedimentation vessel. A three-way valve is provided above the socket to allow for interval sampling of suspension into the 10 ml pipette container which is then emptied into a 30 ml receiving flask. An additional 0.5 ml container is located between the socket and the 10 ml container to allow for rinsing before each sample is withdrawn. The liquid suspension from which samples are withdrawn consisted of an aqueous solution containing 1.5 wt.% uBOF-OX solids. The suspension is thoroughly mixed prior to sampling by inverting the container several times without stirring since stirring causes persistent vortices. The timer is started at the end of the agitation period and samples are withdrawn at pre-determined intervals and later dried for weighing.

In addition to size analysis, the chemical composition of flue dust samples was determined by analytical methods conducted both locally and at commercial laboratories when required. The accuracy of the results obtained by commercial analysis was verified by sending standards of known
concentrations to be analyzed along with the unknown samples. The deviation between the reported value and the actual concentrations were used to calibrate the results, thus increasing their reliability. The concentration of the most common elements present in flue dust samples was determined by inductively coupled plasma spectrometry (ICP - Perkin Elmer Optima 3000). This analysis was conducted on flue dust samples that were fused with Na$_2$O$_2$ prior to analysis in order to solubilize elements that would otherwise be trapped within a silicate matrix. The fused flue dust samples were digested with 5% nitric acid prior to ICP analysis. X-ray fluorescence spectrometry was used to analyze Na and Si, whereas C and S were analyzed thermally by combusting flue dust samples and analyzing the evolved gases (LECO method). A specific ion electrode was used to measure the chloride content in the flue dust samples.

The behavior of the samples with increasing temperature was investigated by thermogravimetric analysis (TGA - DuPont Instruments Model 951) interfaced with a mass spectrometer (VG Model EGA 300 MM) used to determine the composition of the gas generated during thermal decomposition. The dehydrated flue dust samples were typically heated in air as well as argon at 25 °C per minute up to 1200 °C. The mineralogical phases of flue dust samples were qualitatively determined by powder x-ray diffraction (XRD – Phillips Model PW 1120-60) equipped with LiF filter and using copper Kα radiation. Additional mineralogical and morphological studies were conducted using polished thin sections of the flue dust samples examined under a polarized light microscope (Olympus) and a scanning electron microscope (SEM - Hitachi S570) equipped with an energy dispersive x-ray spectrometer (EDX – Leybold Model MAX 200).
Figure 6. The Andreasen pipette (not to scale)
4.3 Thermal treatment

4.3.1 Apparatus

The thermal treatment apparatus used to treat the oxide fines is shown in Figure 7. It consists of a quartz tube (90 cm long, 4 cm I.D. inlet and 1 cm I.D. outlet) held by firebricks inside a furnace (Carbolite Model TZf 12/75) equipped with a programmed temperature controller (Model 808P). Chlorine (diluted with air) is delivered to the tube from a lecture bottle, and a sparger containing 5% HNO₃ is attached to the outlet nozzle to absorb the volatile metal chlorides.

4.3.2 Temperature profile

A chromel-alumel thermocouple was used to locate the zone inside the quartz tube where the temperature varied by less than 5 °C from the chosen temperature (Tₘₐₓ) in the 500 to 900 °C range. For example, the location of the thermally stable zone corresponding to a set temperature of 800 °C is illustrated in Figure 8. This thermally stable zone was found to be the same for all set temperatures. A 10 cm long alumina boat containing 3 g of oxide fines averaging 1 mm in height was inserted into that zone along with the chromel-alumel thermocouple contacting the solids. This allowed the estimation of the time required to heat the sample from room to Tₘₐₓ. This pre-heating time was found to vary between 10 to 12 minutes for Tₘₐₓ in the 500 to 900 °C range.

4.3.3 Operation

The chlorination/volatilization of the heavy metal contaminants contained in the oxide fines was achieved by passing an air/chlorine mixture (5 to 10 vol.%) flowing at 110 mL/min and one atmosphere over the oxide fines when the sample had reached a chosen Tₘₐₓ. The gaseous mixture
exiting the tube was captured by sparging into a 5% nitric acid solution and samples were taken periodically at predetermined time intervals throughout the length of each experiment. The use of two spargers made this sequential sampling possible by allowing rapid switching from one sparger to the other at the end of each sampling interval while the gaseous flow was stopped. ICP was then used to determine the heavy metal content of the solution.

4.3.4 Troubleshooting

The main operational difficulty was the condensation of chloride species occurring at the delivery nozzle of the quartz tube which was several hundred degrees lower than the set temperature. This problem was solved by inserting hollow quartz cylinders (0.7 cm I.D.) when switching spargers into the delivery nozzle as illustrated in Figure 9. The inserted cylinders covered 75% of the delivery nozzle's length for the purpose of capturing the condensate.

The efficiency of this novel method was determined by evaporating synthetic ZnCl₂ (s) under inert N₂ atmosphere as well as air. It was found that over 95% of the evaporated ZnCl₂ was captured by the inserted cylinders and the sparger, with the former capturing 1/3 of the total condensate. These results indicate that this mitigation method is capable of capturing virtually all the condensate and thus is adequate for sequential sampling. Mass balances conducted on Zn (the most abundant contaminant) during thermal treatment of flue dust samples also yielded very satisfactory results as indicated in Table 1.
Figure 7. Experimental apparatus (not to scale)

Figure 8. Temperature profile inside furnace for $T_{\text{set}} = 800 \, ^{\circ}\text{C}$

Figure 9. Hollow cylindrical insert in the delivery nozzle
5. RESULTS AND DISCUSSION

5.1 Characterization

5.1.1 Moisture content

The moisture content of flue dust samples are recorded in Table 2. Duplicate samples were dried and the moisture content was found to be within ± 5% of the reported figures in Table 2.

The results indicate that the moisture content of the flue dust samples depends on the collection and handling method. The highest moisture content is thus associated with the wet scrubbing of the flue dust. The moisture content of the pBOF-OX (10.8%) is 100 times greater than that of uBOF-OX (0.10%) because the former is intentionally mixed with water for transportation and storage purposes. This practice causes the moisture level of pBOF-OX to exceed 30% initially. The decrease in the moisture level of the pBOF-OX is due to 2 factors: natural drying which gradually occurs during on-site storage as well as water consumption by cementation reactions which convert lime into slaked lime as described on page x.

In the case of BF flue dust, the BF-FC moisture content is almost double that of BF-FD mainly because the former is collected through a wet scrubbing system.

5.1.2 Particle size analysis

The particle size distribution of BF-FD and pBOF-OX are given as cumulative volume percent in Figures 10 and 11, respectively. An arbitrary size cut-off of 2000 μm was used for the largest size fraction. No such analysis was conducted for flue dust samples collected by wet scrubbers, namely BF-FC and BOF-OG, due to the unavailability of sieves with a mesh fine enough to separate these very fine (d<10 μm) ash-like dust particles.
5.1.2.1 BF-FD

The size distribution of BF-FD follows a normal S-shaped trend as shown in Figure 10. The cumulative size distribution plot indicates that 80% of the particles are less than 400 μm in diameter and 10% are less than 75 μm. This is expected since, unlike the pBOF-OX particles, the BF-FD particle are collected and stored without mixing with water, thus eliminating the formation of large solid particles.

5.1.2.2 BOF flue dust

The presence of large particles is illustrated in Figure 11 which shows that 80% of the pBOF-OX particles are less than 1.5 mm in diameter and 7% less than 100 μm. This distribution is in sharp contrast with the uBOF-OX examined in a similar study where over 90% of the particles were found to be less than 100μm in diameter [Peek, 1996]. This is expected since, in the case of the pBOF-OX, the mixing of the dust particles with water leads to the formation of agglomerates which harden into large solid particles upon drying. No such particles were found in the case of uBOF-OX since water was not used to agglomerate the fine fraction.

The size distribution of the uBOF-OX was determined using the Andreasen pipette. The results illustrated in Figure 12 indicate that the 90% of the particles are less than 32 μm. The precision of the results was verified through a duplicate experiment, and the data from both experiments were found to be within ± 5%. The results also show that over 70% of the uBOF-OX particles are between 25 and 32 μm. This is indicative of aggregation of particles less than 30 μm into agglomerated particles which sediment faster than individual particles due to their higher weight. The occurrence of agglomeration was noted in a characterization study conducted on similar flue dust samples [Mikhail, 1994].
The nature of the agglomeration driving force was further investigated. Surface attraction due to electrostatic forces was ruled out since the use of various anionic and cationic surfactants including IGEPAL CA-630 (tert-Octylphenoxy poly(oxyethyleneethanol)) (suitable for iron oxide materials) did not reduce agglomeration which persisted even when the samples were ultra-sonified. Switching the dispersing medium from polar (water) to less polar (ethanol) had a negligible effect on the number and size of agglomerates, thus ruling out the possibility of agglomeration caused by liquid/solid interaction. Visual examination under a microscope revealed that the agglomerates, both irregular and strand-like ones, had a random like orientation as shown in Figure 13. These agglomerates, however, lined up in the direction of a magnetic field created when a magnet was placed close to the sample. The response of the agglomerates to the rotation of the magnet around the particles as illustrated in Figures 14 to 16 indicate that the particles are held together by magnetic forces. Further investigation detailed in Section 5.1.5 showed that the uBOF-OX is primarily comprised of iron oxides, namely magnetite and hematite, which have significant magnetic properties. This supported the hypothesis that magnetic forces led to the formation of agglomerates. Several attempts were made to degauss the uBOF-OX by heating it beyond the Curie temperature of magnetite (585 °C) and hematite (575 °C). It was found that temperatures exceeding 800 °C are required to reduce the magnetism of the uBOF-OX. This was deemed undesirable since such high temperatures may cause recrystallization of some phases as well as sintering, thereby changing the shape and size of the particles and ultimately altering the original size distribution. The agglomeration problem thus prevented the establishment of accurate particle size distribution for the uBOF-OX samples. Furthermore, the results indicate that gravity sedimentation is not adequate for selectively separating uBOF-OX particles less than 10 μm which agglomerate with bigger particles and sediment together. Such selective separation is desirable because when the pBOF-OX was further investigated (Section 5.1.6.1), it was found that Zn, the main heavy metal contaminant of the flue dust, is associated with particles not exceeding 1 to 2 μm in diameter. This agglomeration problem was solved by the use of industrial hydrocyclones which
Table 1. % mass balance based on Zn for chlorination experiments in the 500 to 900 °C range

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>625</th>
<th>650</th>
<th>700</th>
<th>700</th>
<th>800</th>
<th>800</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>% mass balance</td>
<td>92</td>
<td>98</td>
<td>104</td>
<td>99</td>
<td>99</td>
<td>101</td>
<td>102</td>
<td>100</td>
<td>101</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2. Moisture content of flue dust samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BOF-OG</th>
<th>BF-FC</th>
<th>pBOF-OX</th>
<th>BF-FD</th>
<th>uBOF-OX</th>
</tr>
</thead>
<tbody>
<tr>
<td>% H₂O</td>
<td>36.2</td>
<td>13.2</td>
<td>10.8</td>
<td>7.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 10. Cumulative size distribution of dehydrated BF-FD (volume basis)
Figure 11. Cumulative size distribution of dehydrated pBOF-OX (volume basis)

Figure 12. Cumulative size distribution of dehydrated uBOF-OX (volume basis)
Figure 13. uBOF-OX agglomerates in aqueous solution

Figure 14. uBOF-OX agglomerates in a magnetic field oriented at +45°
Figure 15. uBOF-OX agglomerates in a magnetic field oriented at $+180^\circ$

Figure 16. uBOF-OX agglomerates in a magnetic field oriented at $-45^\circ$
produce large centrifugal forces capable of overcoming the magnetic forces [Rawlins, 1993]. Further details on the association of Zn and other heavy metal contaminants in flue dust samples are provided in Section 5.1.5.

5.1.3 Chemical analysis

The chemical composition expressed as weight % of the flue dust samples is shown in Table 3. The accuracy of the results was verified as described in Section 4.2. In addition, some of the flue dust samples were re-analyzed to check the precision of the data obtained from commercial laboratory analysis of the flue dust samples. An example illustrating this validation is provided in Table 3 and the results show that the concentrations of the most abundant BOF-OG elements obtained from commercial and local analyses are in agreement within ± 10%.

5.1.3.1 BF flue dust

The results indicate that Fe, originating from the iron ore used in the steelmaking process, is the most abundant element (apart from oxygen) in all flue dust samples except BF-FD where the C concentration (54%) is more than twice that of Fe (24.9%). Carbon is also the second most abundant element in BF-FC and the combination of its concentration (29%) with that of Fe (40%) constitutes the majority of BF-FC. The abundance of C in BF-FD and BF-FC is probably caused by the entrainment of the low density coke with the upward draft of gases generated within the blast furnace. The coke fines are originally added to the solid mixture of the blast furnace as a source of fuel and carbon monoxide [Russel, 1976]. Their presence in the dust particles reflects an inefficient combustion process since not all the C was combusted as desired. In addition to Fe and C, Ca is present almost equally (about 3%) in both BF-FD and BF-FC. It originates from the addition of lime CaO or dolomite CaMg(CO₃)₂ which, when added to the blast furnace, acts a basic flux needed to balance the acid constituents (silica SiO₂ and alumina Al₂O₃) from the coke and iron ore
These oxides, along with periclase MgO originating from dolomite, constitute the four primary oxides which form the slag. Si, most likely entrained from the silica in the slag, is thus found in both BF-FD and BF-FC at 2.7% and 2.1% respectively. Other minor elements present in both flue dust sample include Mn, Zn, Pb, Al, Cu and Na. The target heavy metal contaminants, namely Zn, Pb, and Cu, are present at a level low enough (<0.5%) to allow for total internal recycling of BF-FD and BF-FC without additional treatment. This is not the case for the BOF flue dust described below.

5.1.3.2 BOF flue dust

Similar to BF flue dust, the results indicate that Fe (up to 56%) is the most abundant element (apart from oxygen) followed by Ca (up to 8.5%) and Mg (up to 2.7%) in BOF flue dust samples. This is expected since the raw materials from which the BOF dust is generated are iron ore and dolomite (Ca,Mg)(CO₃)₂. The latter is added to the molten ore during the steelmaking process as a source of MgO and CaO needed to balance the acid constituents as described above. Degradation of the refractory lining inside the furnace may also have contributed to the MgO content. Carbon is present in both pBOF-OX and BOF-OG at a level of about 2%, much lower than that of the BF flue dust samples. Other elements such as Mn, Na, Al, and Si are also present in all BOF-OX flue dust samples with concentrations ranging from 0.8 to 1.5%. Note that the difference in composition between BOF-OX (pugged and unpugged) and BOF-OG is probably due to the variation in the BOF’s feed composition. More scrap was most likely introduced into the furnace in the case of the BOF-OG, causing a higher level of contaminants. This difference is apparent in the level of the fourth most abundant element, namely Zn, which is nearly four five times higher in BOF-OG (5.4%) than in pBOF-OX (1.2%) and uBOF-OX (1.6%). The same trend is also noted in the case of Pb. Other heavy metals contaminants including Cu, Cd, Ni, and Cr are present as minor elements in all BOF-OX flue dust samples with concentrations less than 1%. Nevertheless, the level of these heavy metal
contaminants are consistently greater than their counterpart in the BF flue dust samples. The relatively high level of Zn, Pb, and Cu prevents the direct recycling of the BOF flue dust. The removal of these heavy metal contaminants is thus essential in order to allow for the desirable recycling of the BOF-OX flue dust back into the steelmaking process. In addition to these heavy metal contaminants, elements such as S, Cl, and P are also present as minor elements with concentrations below 0.1%. The balance is mostly comprised of oxygen.

The close agreement between the composition of the pBOF-OX and uBOF indicates that the difference in handling method did not affect the overall composition of the flue dust sample. This would be otherwise had the BOF-OX contained a large fraction of soluble substances which would not be detected in the case of pBOF-OX flue dust where water is added to the dust for handling and storage purposes. Furthermore, the elemental abundances are in close agreement with analyses conducted on flue dust samples obtained from other steel mills [Goskel, 1971][Serbent, 1975], thus confirming that the BOF flue dust samples studied here are typical. The main difference between the dust examined in this study and described in the literature is the higher level of Ca and Mg in the samples examined here, probably due to a greater addition of dolomite to the BOF during steelmaking.

5.1.4 Thermal characterization

5.1.4.1 pBOF-OX

The thermal analysis of dehydrated pBOF-OX and BOF-OG samples heated in dry air at 25 °C per minute is illustrated in Figures 17 and 18, respectively. The decomposition of pBOF-OX started at 25 °C with the sample losing its residual adsorbed water and water of hydration during gradual heating (0.9%). This was verified by the detection of H₂O by the mass spectrometer during the dehydration range of 25 °C to 200 °C. Another decomposition occurred in the 300 to 420 °C
Table 3. Chemical composition expressed as weight % of dehydrated flue dust samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Method</th>
<th>BF-FC*</th>
<th>BF-FD*</th>
<th>pBOF-OX*</th>
<th>BOF-OG*</th>
<th>uBOF-OX**</th>
<th>BOF-OG**</th>
<th>%***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>ICP</td>
<td>40.0</td>
<td>24.9</td>
<td>48.1</td>
<td>55.7</td>
<td>53.02</td>
<td>56.76</td>
<td>2%</td>
</tr>
<tr>
<td>Ca</td>
<td>ICP</td>
<td>2.84</td>
<td>3.21</td>
<td>8.44</td>
<td>4.93</td>
<td>7.68</td>
<td>5.02</td>
<td>2%</td>
</tr>
<tr>
<td>Mg</td>
<td>ICP</td>
<td>0.76</td>
<td>1.08</td>
<td>2.44</td>
<td>1.82</td>
<td>2.62</td>
<td>1.96</td>
<td>7%</td>
</tr>
<tr>
<td>Zn</td>
<td>ICP</td>
<td>0.19</td>
<td>0.04</td>
<td>1.22</td>
<td>5.37</td>
<td>1.57</td>
<td>4.97</td>
<td>-8%</td>
</tr>
<tr>
<td>Mn</td>
<td>ICP</td>
<td>0.75</td>
<td>0.84</td>
<td>1.41</td>
<td>1.13</td>
<td>1.60</td>
<td>1.04</td>
<td>-8%</td>
</tr>
<tr>
<td>Pb</td>
<td>ICP</td>
<td>0.02</td>
<td>0.005</td>
<td>0.04</td>
<td>0.76</td>
<td>0.06</td>
<td>0.70</td>
<td>-9%</td>
</tr>
<tr>
<td>Al</td>
<td>ICP</td>
<td>0.76</td>
<td>0.94</td>
<td>0.17</td>
<td>0.10</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>XRF</td>
<td>0.04</td>
<td>0.03</td>
<td>0.30</td>
<td>0.91</td>
<td>0.22</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>ICP</td>
<td>0.04</td>
<td>0.05</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>ICP</td>
<td>0.01</td>
<td>0.01</td>
<td>0.04</td>
<td>0.02</td>
<td>0.005</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>ICP</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>ICP</td>
<td>0.003</td>
<td>0.003</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>ICP</td>
<td>0.09</td>
<td>0.11</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.10</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>ICP</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Spec. Ion Electrode</td>
<td>0.05</td>
<td>0.31</td>
<td>0.07</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>XRF</td>
<td>2.10</td>
<td>2.72</td>
<td>1.22</td>
<td>0.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>LECO</td>
<td>29.00</td>
<td>54.60</td>
<td>1.99</td>
<td>1.81</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>LECO</td>
<td>0.28</td>
<td>0.41</td>
<td>0.07</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>ICP</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>ICP</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>ICP</td>
<td>0.05</td>
<td>0.07</td>
<td>0.03</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* = Analysis conducted by commercial laboratory
** = Analysis conducted at university laboratories using ICP
*** = % difference between the commercial and university results obtained for BOF-OG

BF-FC = Blast furnace filter cake
BF-FD = Blast furnace flue dust
pBOF-OX = Pugged basic oxygen furnace oxide (flue dust)
BOF-OG = Basic oxygen furnace overhead gas (slags)
uBOF-OX = Unpugged basic oxygen furnace oxide (flue dust)
range. The weight loss was attributed to the dehydration of Ca(OH)$_2$ according to the following reaction:

$$\text{Ca(OH)}_2(s) \rightarrow \text{CaO}(s) + \text{H}_2\text{O}(g)$$  \hspace{1cm} [R.20]

The amount of water generated through this decomposition was very small and thus difficult to detect on the mass spectrometer. The associated weight loss (1.1%) was used to estimate Ca(OH)$_2$ at 4.8%. The fraction of Ca originally present in the sample as Ca(OH)$_2$ was thus estimated at 30%. Ca(OH)$_2$ was most likely formed through the hydration of CaO originally present in the sample. The decomposition of Ca(OH)$_2$ in this temperature range was also reported in other studies [Mikhail, 1994]. The dehydration of Ca(OH)$_2$ was closely followed by another minor decomposition in the 450 to 500 °C range. This was attributed to the oxidation of carbon according to the following reaction:

$$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$$  \hspace{1cm} [R.21]

The evolution of CO$_2$ was detected by the mass spectrometer. The associated weight loss (0.5%) was much lower than the expected loss (2%). The discrepancy is probably due to incomplete oxidation of all of the available carbon in the sample. A more significant weight loss occurred in the 560 to 775 °C range which was associated with the decomposition of CaCO$_3$ according to the following reaction:

$$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$$  \hspace{1cm} [R.22]

Similar to reaction R.21, the CO$_2$ generated according to reaction R.22 was detected by the mass spectrometer. The associated weight loss (6.7%) was used to estimate the CaCO$_3$ at 14.8%. The fraction of Ca originally present in the sample as CaCO$_3$ was thus estimated at 70%. No further decomposition or weight gain due to oxidation of iron compounds was detected up to 1000 °C. The
lack of oxidation was confirmed by a similar pattern of weight loss obtained when the sample was heated under an inert argon atmosphere.

5.1.4.2 BOF-OG

The thermal decomposition of dehydrated BOF-OG exhibited a more complex pattern due to alternating weight loss and weight gain sequences. Similar to pBOF-OX, the two main weight losses occurred in the 25 to 200 °C range and the 560 to 700 °C range. The former was associated with the loss of residual adsorbed water (0.3%) and water of hydration (0.8%) whereas the latter was associated with the decomposition of CaCO₃ (2.7%). The weight loss associated with the carbonate decomposition was used to estimate CaCO₃ at 6.1% with about 50% of the Ca originally present in the sample as CaCO₃. Another weight loss (1.2%) occurred in 975 to 1130 °C range but could not be associated with a specific compound since no evolved gas was detected by the mass spectrometer.

The weight loss ranges were closely followed by weight gain ranges occurring in the 250 to 550 °C range (5.2%) and the 690 to 970 °C range (1.6%). The latter interfered with the weight loss associated with CaCO₃ decomposition since it commenced before the end of CaCO₃ decomposition, thus causing the CaCO₃ originally present in sample to be underestimated. All weight gains were associated with the oxidation of various iron species according to the following reactions:

\[
\begin{align*}
    \text{Fe(s)} + \frac{1}{2}\text{O}_2(g) & \rightarrow \text{FeO(s)} \quad [R.23] \\
    2\text{FeO(s)} + \text{O}_2(g) & \rightarrow \text{Fe}_2\text{O}_3(s) \quad [R.24] \\
    3\text{FeO(s)} + \frac{3}{2}\text{O}_2(g) & \rightarrow \text{Fe}_3\text{O}_4(s) \quad [R.25] \\
    2\text{Fe}_3\text{O}_4(s) + \frac{3}{2}\text{O}_2(g) & \rightarrow 3\text{Fe}_2\text{O}_3(s) \quad [R.26]
\end{align*}
\]

The total weight gain due to oxidation of iron species was estimated at 6.8%. The results were used to estimate the original Fe at 32% in the metallic (elemental) form, 22% in the FeO form, and 47% in other forms including Fe₃O₄ (see Section 5.1.5 below). It was assumed that the 5.2%
Figure 17. Thermal decomposition of dehydrated pBOF-OX in dry air

Figure 18. Thermal decomposition of dehydrated BOF-OG in dry air
weight gain due to $O_2$ consumption was associated with reaction R.23 and the 1.6% weight gain associated with reactions R.24 and R.25. It was assumed that reaction R.26 did not occur in the examined temperature range. This is a reasonable assumption since there was no weight gain in the case of the pBOF-OX where Fe is present mainly as $Fe_3O_4$. Furthermore, no weight gains occurred when the sample was gradually heated under argon atmosphere, thus confirming that the weight gains were due to oxidation.

5.1.5 X-ray diffraction analysis

Samples of BOF flue dust were examined by x-ray diffraction and the results of typical diffractograms are listed in Table 4. Both mineral name and formula are listed together with the height of the strongest peak for each phase. The peak heights give a qualitative indication of the relative abundance of each phase. The absolute abundances are not known since no internal standard was used. Furthermore, the presence of multiple phases inevitably caused overlapping of peaks, thus making individual peak height measurements difficult. As well, most of the phases were present in low amounts, often near the detection limit (about 1 wt.%). Thus, the abundances are only indicative, and the relative intensities of the strongest line of different phases can vary by a factor of about two.

5.1.5.1 BOF flue dust

The XRD results indicate that magnetite is the dominant phase in the case of pBOF-OX. This is expected because the BOF dust is mainly comprised of iron which, when exposed to highly oxidizing conditions at the top of the BOF vessel, will readily oxidize into magnetite. Zn is mainly present in the form of zinc ferrite which is probably generated when the volatilized zinc reacted with airborne iron oxide particles. Zn can also be found as zinc oxide but to a much lesser extent. Other minor phases were also detected, namely periclase, calcite, and portlandite. Periclase is most likely derived from the decomposition of added dolomite or from the erosion of the refractory lining inside
the furnace. Similarly, calcite probably originates from the decomposition of dolomite, whereas portlandite was formed from the hydration of CaO as mentioned earlier. These results are in agreement with the ones obtained through thermal characterization. No specific phase containing Pb or other minor elements was identified since their low concentrations put them below the detection limit.

Almost all the phases mentioned above were detected in the case of uBOF-OX with the exception of calcite substitution with lime. The abundances of the non-ferric species, however, were lower than their counterparts in the pBOF-OX case, thus making their identification more difficult.

5.1.5.2 BOF-OG

In the case of BOF-OG, Fe is present in a multitude of phases including metallic iron, wustite, and magnetite. The presence of iron in its lowest oxidation state, namely metallic iron, indicates that the BOF-OG dust was probably generated in less oxidizing conditions compared to pBOF-OX, possibly because of lack of excess oxygen or presence of extra CO in the gas above the BOF vessel at the time the BOF-OG was generated. Other phases detected include lime and calcite. Similarly to the BOF flue dust case, the phases detected through XRD are in agreement with the ones deduced from the thermal characterization. Unlike pBOF-OX, no periclase or portlandite were detected in this case. Zn, on the other hand, is present mainly as zinc ferrite and to a lesser extent as zinc oxide. Both zinc ferrite and zinc oxide are also found in pBOF-OX, thus indicating the same process of zinc condensation during the formation of both flue dusts. Other minor BOF-OG phases include lime and calcite. Phases containing Pb and other minor elements were not detected due their low concentration.

The phases mentioned above were also detected in similar studies [Goskel, 1971][Mikhail, 1994] which also reported the presence of zinc silicate, a phase not detected in this study possibly because of the rarity of silica-rich slag droplets entrained in the gas above the BOF vessel.
Table 4. Phases detected by x-ray diffraction and their relative abundances

<table>
<thead>
<tr>
<th>Phase</th>
<th>Main Peak</th>
<th>Name</th>
<th>Formula</th>
<th>Height *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frankline</td>
<td>ZnFe₂O₄</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Periclase</td>
<td>MgO</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Portlandite</td>
<td>Ca(OH)₂</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zincite</td>
<td>ZnO</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase</th>
<th>Main Peak</th>
<th>Name</th>
<th>Formula</th>
<th>Height *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frankline</td>
<td>ZnFe₂O₄</td>
<td>4</td>
<td>N.A.**</td>
<td></td>
</tr>
<tr>
<td>Periclase</td>
<td>MgO</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime</td>
<td>CaO</td>
<td>&lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Portlandite</td>
<td>Ca(OH)₂</td>
<td>&lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zincite</td>
<td>ZnO</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase</th>
<th>Main Peak</th>
<th>Name</th>
<th>Formula</th>
<th>Height *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wustite</td>
<td>FeO</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frankline</td>
<td>ZnFe₂O₄</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime</td>
<td>CaO</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* = arbitrary units
** = Not available due to peak overlapping
5.1.6 Microscopy

Powder samples of pBOF-OG and BOF-OG were mounted into polished thin sections which were used to reveal the internal structure and morphology of the particles when examined under light and scanning electron microscopy. These mounts were used to obtain light microscope photographs of various common particles whose phases were identified by quantitative elemental x-ray microanalysis using EDX. The concentrations reported are normalized atomic percent of detected elements.

5.1.6.1 pBOF-OX

A typical view of the pBOF-OX flue dust is presented in Plate 1. The dust is mainly composed of spherical particles constituting 30 to 40 vol.% of the sample, with 10 to 20 vol.% of the sample comprised of irregularly shaped particles. Both spherical and irregular particles are contained in a matrix of sub-micron dust constituting 50 to 60 vol.% of the sample. The spheres range in size from less than 1 μm to occasional 300 μm particles, with a predominant size fraction less than 10 μm. This size distribution is in agreement with the uBOF-OX particle size distribution previously described in Section 5.1.2.2 which indicated that the majority of the particles are less than 32 μm in diameter.

Apart from oxygen, Fe is the major constituent of the dust and is thus found in almost all the particles. Fe is present in its metallic form either as inclusions in bigger particles as shown in Plate 1 or as separate particles often surrounded by an oxide layer as shown in Plate 2. It was found that metallic Fe (99%) contained trace elements such as Si (up to 0.5%) and Ca (up to 0.5%). In addition to a pure metallic phase, Fe is present as oxide in the form of hematite/magnetite cenospheres with minor amounts of Ca (up to 1.2%), Si (up to 0.6%), and Mg (up to 0.5%) as shown in Plate 3. These
spheres appear brighter than other particles in the light microscope and have occasional plucking due to polishing. The rim of the cenosphere in Plate 3 is comprised of hematite which is also found as lamellae in the particle's interior. These lamellae were formed by the inward diffusion of oxygen, the subsequent oxidation of part of the magnetite to hematite, and the exolution of hematite from magnetite. Magnetite particles which have partially oxidized to hematite along their octahedral crystallographic planes have been detected in characterization studies conducted on EAF dust [Hagni, 1995]. The abundance and identity of phases containing Fe was also confirmed by XRD results as indicated in Section 5.1.5.1.

Aside from iron oxide particles, multi-phase particles are present in significant numbers. The large angular particle shown in the top center of Plate 1 is comprised of dolomite with almost stoichiometric Ca (56%) and Mg (42%) content, along with a very small amount of Fe (0.6%), Si (0.8%), and S (0.4%). The most abundant two-phase particles are calcium ferrite ones shown in Plates 4 to 6. The rim of the calcium ferrite particle shown in Plate 4 is rich in Fe (87%) followed by Ca (8%) as well as minor elements including Mg (1.7%), Si (1%) and Mn (1%). The darker phase at the center of this particle contains less Fe (71%) and more Ca (25%) in addition to Si (1.5) and Mn (0.5). Other calcium ferrite particles such as the one shown in Plate 5 do not contain an Fe-rich rim. The higher Fe content, however, is found in the needle-like strand within the spherical particle. The overall composition of this particle is comprised of Fe (65%), Ca (29%), Si (2.3%), Mn (1.8%) and Mg (0.8%). This composition is similar to that of the core of the particle shown in Plate 4. In addition to spherical particle, some calcium ferrite particle can be dendritic as illustrated in Plate 6. No particle containing Ca solely in the calcite form was encountered, even though such phase was detected through thermal characterization as well as XRD. It is possible that the calcite content is associated with the very fine inter-particle dust discussed below.

An example of less common three phase particles is illustrated in Plate 7. This is a Ca-Fe silicate with overall composition includes Ca (43%) as the main component followed by Si (17%), Fe (13%), Mg (12%), and Mn (9.4%). The composition of each phase is detailed in on. The darkest
phase corresponding to the four large regions at the center of the particle are calcium silicate fragments comprised mainly of Ca (72%) and Si (15%) as well as Fe (5%), Mn (3%) and Mg (2%). These fragments are most likely inclusions which were ejected from the furnace and became incorporated in the bigger particles as they cooled. In contrast, the dark phase appears to be an integral component of the particle. That phase contains Ca (61%) as well as Si (17%), Fe (10%) and Mn (7%). It was most likely formed by exolution from a lighter phase which contains more Fe (32%) and Mn (19%) and less Ca (37%) and Si (5%). The phase with the medium shade, on the other hand, appears to be unrelated to the other two as indicated by its composition which is comprised of almost equal amounts of Ca, Fe, Mn, Mg and a minor amount of Si. This illustrates the limitation of light microscopy in identifying phase based only on their appearance. Additional information such as elemental composition is required to identify phases more accurately. Furthermore, the versatility of the particle described above indicates that the process by which these particles are formed is a complex one. Similar particles are distinguished as variably textured particles with a shade darker than that of iron oxide particles when viewed through a light microscope. They almost always contain small amounts of P (up to 2.5%) as well as trace amounts of S, Ti, Cr, V (< 2%, combined).

Other less common particles such as the one shown in Plate 8 have an angular shape and a high S content (56%) in addition to Si (14%) and equal amount of Fe (9%) and Ca (9%). These particles are probably the remnant of coke fines which did not combust. Organic contaminants are also occasionally found as fibrous material (Plate 9) containing Si (24%) and Fe (19). Equally rare non-ferrous particles include orthoclase with Si (63%) K (18%) shown in and Al (17%) Plate 10 as well as quartz with 97% Si shown in Plate 11.

The interparticle sub-micron dust or matrix shown in Plate 12 is characterized by a high concentration of Fe (75%) as well as Ca (9%) and Mg (8%) with small amount of Mn (3%) and Si (1.5%). It is important to note that detectable levels of Zn (3.3%) were only found in the matrix and that no Zn was detected in any of the particles discussed above. This suggests that the majority of the Zn present in the sample is concentrated in particles with diameter less than 2 μm. This association
Plate 1. General view of pBOF-OX flue dust
1 = metallic Fe inclusion, 2 = dolomite particle

Plate 2. Irregularly shaped pBOF-OX iron oxide particle
The lighter phase is metallic Fe surrounded by an oxide layer
Plate 3  Magnetite/hematite pBOF-OX particle
The lighter phase is hematite (either at the rim or evolved)

Plate 4  Ca-Fe oxide pBOF-OX particle
The lighter phase is Fe-rich
Plate 5. Ca-Fe oxide pBOF-OX particle
The lighter phase is Fe-rich

Plate 6. Ca-Fe oxide pBOF-OX particle
Note the dendritic shape
Plate 7. Multi-component multi-phase pBOF-OX particle
comprised of Ca-Fe silicate with the following composition:

<table>
<thead>
<tr>
<th>Phase (elem%)</th>
<th>Ca</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darkest (i)</td>
<td>72</td>
<td>15</td>
<td>5</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Dark (d)</td>
<td>61</td>
<td>17</td>
<td>10</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Medium (m)</td>
<td>21</td>
<td>3</td>
<td>25</td>
<td>23</td>
<td>27</td>
</tr>
<tr>
<td>Light (l)</td>
<td>37</td>
<td>5</td>
<td>32</td>
<td>19</td>
<td>4</td>
</tr>
</tbody>
</table>

50 μm
Plate 8. Angular coke particle found in pBOF-OX
It contains a high sulfur content

Plate 9. Rare organic fibers found in pBOF-OX
Plate 10. Orthoclase particle found in pBOF-OX

Plate 11. Quartz particle found in pBOF-OX
Plate 12. Fine dust particles (matrix) constituting the interparticle material surrounding pBOF-OX particles
was also noted in other studies [Mikhail, 1994]. One of these studies found that Zn and Pb were concentrated at the surface of dust particles and proposed that these particles act as nuclei for Zn and Pb which condense upon cooling of the hot gas above the BOF vessel [Itoh, 1982]. Therefore, smaller particles with a large surface area per unit volume tend to have a larger concentration of Zn and Pb. This finding suggests that a cheap physical separation technique may be used in order to reduce the Zn content of the sample by segregating the finer particles from the coarse ones. This would allow the recycling of the virtually Zn-free Fe-rich dust fraction back into the steelmaking process without any further pre-treatment.

5.1.6.2 BOF-OG

A typical view of the dehydrated BOF-OG flue dust is presented in Plate 13. The dust is comprised of irregularly shaped particles (5 to 10 vol.%), spherical particles (10 to 20 vol.%), and a matrix of sub-micron particles (70 to 80 vol.%). The spheres range in size from less than 10 μm to occasional 250 μm particles, with a predominant size fraction less than 10 μm. This size distribution is similar to that of uBOF-OX described above.

The metallic Fe particles, such as the one shown in Plate 14, contain a high concentration of Fe (97%) with traces of Si (<2%) and Ca (<1%) and a diameter ranging from 1 to 100 μm. Some of these particles such as the ones shown in Plate 15 are surrounded by an oxide layer of up to 10 μm in thickness similar to the pBOF-OX case described above. They are the remains of oxidized metallic Fe droplets. In addition to metallic iron, Fe is found in magnetite cenospheres with evolved hematite as shown in Plate 16. These particles are comprised mainly of Fe (97%) and minor amounts Si (2%). Similar particles occasionally contain minor amounts of Ca (up to 3%) and/or Si (up to 4%). They are sparse and small with diameter less than 25 μm and some particles contain detectable amounts Zn (up to 1.1%). The abundance of Fe and its associations are in agreement with the results obtained through thermal characterization and XRD as described above.
Unlike the case of pBOF-OX, non-ferrous two-phase Ca-Fe oxide particles are rare. Ca-Mg-Fe oxide particles, on the other hand, are abundant and some have an interesting morphology characterized by a Swiss-cheese like texture such as the one shown in Plate 17. Its composition includes Ca (43%), Fe (36%), equal amounts of Mg and Si (8%) as well as detectable levels of Zn (1.5%) and Pb (1.2%). Similar Ca-Mg-Fe oxide particles contain a higher level of Fe (48%) and Mg (27%) and a lower level of Ca (21%). Their appearance is more uniform as shown in Plate 18.

Other multi-phase particles including Ca-Fe silicates are occasionally found. An example of such particles is shown in Plate 19. This particle contains two phases distinguished by light and dark phases when viewed under a light microscope. This is due to the difference in the composition of the two phases since the light phase at the rim is rich in Fe (71%) as well as Mg (13%) and Mn (11%) whereas the dark phase at the center is comprised mainly of Si (50%) as well as Ca (21) and Fe (17%). Both phases contained detectable levels of Pb and P of up to 1%. Some of these particles such as the one shown in Plate 20 contain significant levels of Mg and Mn. The lighter phase of the particle in Plate 20 is rich in Fe (50%) and Mg (33%) and contains Mn (8%), Ca (3%) and Si (3%); whereas the darker phase is rich in Ca (48%) and Si (30%) and contains Fe (11%), Mg (4.3%) and Mn (2.3%). This is similar to the pBOF-OX multi-phase particle shown in Plate 7. It was found that there is a general association of Mn, P, Cr, V, Ti whenever the particle contained silicate. Additionally, uncombusted coke fines are rarely detected. They are present as strand-like fibrous material as shown in Plate 21 and may contain metallic Fe trapped between the branches.

The fine dust particles constituting the matrix range from a few microns down to sub-micron size. This matrix illustrated in Plate 22 contains Fe (60%) as well as Ca (20%), Mg (6%), and Si (6%) with minor amounts of Mn, S, Cr and P. Zn (up to 5%) and Pb (up to 1.1%) were also detected in the matrix which contains more of these heavy metals than large particles. This is contrary to the pBOF-OX case, where Zn and Pb were exclusively found in the matrix. Zn (up to 4%) is also found in MgO fragments scattered in the matrix originating from the degradation of the furnace lining or from the decomposition of added dolomite. The non-selective distribution of Zn and Pb in this case indicates
Plate 13. General view of BOF-OG flue dust
1 = metallic Fe, 2 = MgO fragment

Plate 14. Metallic Fe particle (top center) found in BOF-OG
Plate 15. Metallic Fe found in BOF-OG (1,2,3)
Note the oxidized rim of the Fe particles

Plate 16. Magnetite/hematite particles found in BOF-OG (1,2,3)
The lighter phase within each particle corresponds to hematite
Plate 17. Ca-Fe-Mg oxide particle found in BOF-OG
It contains detectable levels of Zn and Pb

Plate 18. Ca-Fe-Mg oxide particle found in BOF-OG (center particle)
It is similar to the above particle with a more uniform appearance
Plate 19. Ca-Fe silicate particle found in BOF-OG
The lighter phase is Fe-rich

Plate 20. Ca-Fe silicate particle found in BOF-OG
The evolved lighter phase is Fe-rich
Plate 21. Rare organic fibers found in BOF-OG
Note the trapped metallic Fe particles (1,2,3)

Plate 22. Fine material (matrix) constituting the interparticle dust surrounding BOF-OG particles
that a physical separation method capable of isolating Zn and Pb from the rest of the BOF-OG flue dust may not be suitable.

5.1.7 Characterization summary

The characterization of BF BOF flue dust samples revealed that the material is iron-rich and thus its re-introduction into the steelmaking process is desirable. The results obtained through the characterization study will be useful when examining the suitability of the treatment process as well as the behaviour of the material when it undergoes thermal treatment as detailed in Section 5.2. For example, the elemental analysis of the BF-FD and BF-FC revealed that, in this case, the material contains only minor amounts of contaminants such as Zn, Pb, and Cu. A thermal treatment would thus be unnecessary in this case, especially since it would lead to the combustion of the abundant carbon content of the BF flue dust which would provide fuel value if the BF flue dust is recycled internally. In the case of BOF flue dust collected through a dry scrubber, the microscopic analysis revealed that Zn, the most abundant contaminant, is associated with the fine particles (d< 2 μm). Therefore, the treatment of the dust need only be applied to the fine fraction. The separation of the fine fraction can not, however, be conducted based solely on gravity sedimentation since the particle size analysis revealed that the finer uBOF-OX particles are arranged into agglomerates held together by magnetic attraction. A more energetic method, such as hydrocycloning would thus be required to separate the fine fraction. Furthermore, the microscopic analysis conducted on BOF-OG revealed that, unlike the pBOF-OX and pBOF-OX case, Zn is distributed more uniformly. Therefore, physical separation prior to thermal treatment is not effective since Zn is not just confined to the fine fraction of the dust. Furthermore, XRD analysis revealed that, in the case of BOF-OG, most of the Fe is present in the metallic or wustite form. These phases would be oxidized at higher temperatures in oxidizing conditions as indicated by the thermal characterization. Such oxidation is not desirable
since the objective of recycling the dust is to produce metallic iron. Therefore, the thermal treatment process should be conducted under non-oxidizing conditions in the case of BOF-OG.

Aside from Fe and Zn, the characterization provided valuable information regarding non-ferrous phases. These phases play an influential role in the kinetics and the outcome of the thermal treatment. For example, XRD indicated that the uBOF-OX contains CaO as well as Ca(OH)$_2$, with the latter decomposing to CaO and H$_2$O upon heating as indicated by the thermal characterization. The presence of CaO during thermal treatment, as discussed later, is responsible for delaying the chlorination/volatilization of the heavy metal contaminants. Furthermore, the elemental analysis showed the existence of silicates in which some of the heavy metals may migrate if their diffusion occurs at high temperature [Massilamany, 1993]. Such heavy metal entrapment would lower the efficiency of the removal process since the goal of thermal treatment is to produce virtually contaminant free flue dust suitable for internal recycling. It will be shown later that the diffusion of metal into silicates is mainly restricted to Fe which diffuses into the silicate matrix at temperatures greater than 700 °C.

The arguments presented above illustrate how a thorough characterization of the material at hand is useful in choosing the optimal conditions for the proposed thermal treatment process, namely chlorination/volatilization. It also provides useful information pertaining to the composition of the material. Such information will be used in examining the kinetics and the extent of the thermal treatment process discussed in the following section.
5.2 Thermal treatment

The main objective of conducting the thermal treatment is to assess the efficiency of removal of heavy metal contaminants from uBOF-OX flue dust samples through selective chlorination under oxidizing conditions. The apparatus used for this purpose is described in Section 4.3. The focus was placed on examining the removal of the two most abundant contaminants, namely Zn, Pb, as well as Cu, with the additional aim of investigating the rate determining step of the chlorination/volatilization process and the factors affecting the mechanism of this process. Other minor heavy metal contaminants including Ni, Cr, V, and Cd did not volatilize appreciably (i.e. < 50%) under the examined experimental conditions, thus their behavior was not thoroughly analyzed. The parameters affecting the chlorination/volatilization process, hereinafter referred to as the removal process, of Zn, Pb and Cu are discussed in Section 5.2.1 below. The removal of Zn, Pb and Cu are discussed separately in Section 5.2.2.

5.2.1 Parameters affecting the removal process

Various factors including temperature, residence time, chlorine partial pressure and carrier gas flow rate were examined in order to determine their effect on the chlorination/volatilization of Zn, Pb, and Cu.

The set temperature during thermal treatment experiments was varied between 500 to 900 °C. This 400 °C temperature range was found to be adequate in obtaining different reaction rate constants for the removal reaction of Zn, Pb and Cu. These constants were ultimately used to obtain the activation energies for the removal of Zn, Pb and Cu from Arrhenius plots as described in Section 2.2.3.1.

Along with temperature, residence time plays an important role in determining the extent of removal of heavy metal contaminants. The residence time during which the removal occurred was
preceded by an initial heating period. This period was required to heat the sample from room temperature to the set temperature. It was found to vary between 13 and 10 minutes, with the latter corresponding to higher temperatures (i.e. > 700 °C). This pre-chlorination period also allowed for the evaporation of adsorbed water and water of hydration as well as the water generated from the dehydroxylation of Ca(OH)$_2$ according to reaction R.20. Moreover, the combustion of carbon occurred during this period. Measurement of residence time as well as the chlorine flow begun right after the completion of the preliminary heating period. It was found that the minimum residence time required for complete differed for each heavy metals contaminant as detailed in Section 5.2.2.

As well, the effect of three different chlorine partial pressures on the removal of Zn, Pb and Cu at 700 °C was investigated. These chlorine partial pressures, namely 0.05, 0.075 and 0.1 atm., were established by setting the chlorine content of the carrier gas, namely air, flowing under atmospheric conditions at 5, 7.5, and 10%, respectively. The standard flow rate for all the experiments was set at about 165 ml/min with the exception of one experiment conducted at 900 °C where the flow rate was increased to 160 ml/min in order to determine the effect of this increase on the removal of Zn, Pb and Cu. The results are detailed in the Section 5.2.2.

In addition to the factors described above, other factors may affect the removal process such as the concentration of the reacting elements present in the dust and the size of the dust particles. The concentration of the heavy metal contaminants as well as the particle size remained constant throughout all the experiments since they were conducted on one type of flue dust only, namely uBOF-OX. This dust was very fine with the majority of the particles less than 30 μm in diameter, thus size segregation was not possible given the experimental limitations. As for the concentration of the elements present in the dust, only one experiment was conducted where the concentration of CaO in the sample was doubled. This oxide played an important role in the delaying the removal of Zn, Pb, and Cu as will be shown in the following section.
5.2.2 Reaction kinetics

5.2.2.1 Zinc

**Removal process.** The removal of Zn at various temperatures is summarized in Figure 20. Since the majority of Zn is present as Zn ferrite and to a lesser extent as Zn oxide, its chlorination is thus governed by the following reactions:

\[
\begin{align*}
\text{ZnFe}_2\text{O}_4(s) + \text{Cl}_2(g) & \rightarrow \text{Fe}_3\text{O}_4(s) + \text{ZnCl}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \text{[R.27]} \\
\text{ZnO}(s) + \text{Cl}_2(g) & \rightarrow \text{ZnCl}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \text{[R.28]}
\end{align*}
\]

The ΔG values associated with the above reactions in the 500 to 900 °C range are illustrated in Figure 19 and detailed in Appendix B. The computed ΔG values are negative in all cases, thus indicating that the chlorination of ZnO (s) and of ZnFe₂O₄ (s) occurs spontaneously. The above reactions, however, are overall reactions that do not necessarily explain the mechanism of the Zn removal process. They only provide the stoichiometry between the reactants as well as the products arising from the removal process. The results shown in Figure 20 indicate that a minimum residence time of about two hours is required for to remove the majority of Zn in the 650 to 900 °C range. For temperatures lower than 650 °C, the results indicate that the removal process does not reach completion even when the residence time was six hours. Nonetheless, enough data were obtained for the purpose of studying the kinetics of the Zn removal process in this temperature range.

In addition to Zn removal by chlorination, Zn was removed during the initial heating period that preceded the chlorination process but only very slightly, namely less than 0.5% of the available Zn in all cases. The Cl₂ (g) flow started at the end of the pre-heating period, and the Zn removal indicated that the rate of removal increased as the temperature increased. This is expected since the reaction rate constant increases with temperature as shown in equation E.7. An increase in reaction rate with temperature is commonly reported in the literature [Chen, 1998].
The removal data illustrated in Figure 20 clearly show that the start of the removal process of Zn is delayed at all temperatures. This initial lag was attributed to a competing reaction which used up the available Cl₂ (g) before the actual removal of Zn was able to occur. The evidence supporting this hypothesis is detailed in Section 5.2.2.5. This competing chlorination process was found to be related to the conversion of the available CaO into CaCl₂ according to the following reaction:

\[
CaO (s) + Cl₂ (g) \rightarrow CaCl₂ (s/l) + ½O₂ (g)
\]  

[R.29]

The existence of the lag caused the removal curves in Figure 20 to be S-shaped. Note that the state of the CaCl₂ produced was either solid or liquid. Depending on the experimental temperature, a CaCl₂ melt forms at temperatures exceeding 773 °C. Before considering the implications of possible melt formation on the removal mechanism, it is important to investigate the reaction kinetics involved in the removal of Zn.

**Reaction kinetics.** One of the most important kinetic parameters, namely the reaction rate constant, was obtained at different temperatures by applying the kinetic modeling technique described in Section 2.2.3. This technique is applicable to any reaction of nth order without requiring specific knowledge of the actual mechanism. Nonetheless, certain considerations need to be taken into account when applying this procedure in order to ensure the accuracy of the results. Firstly, the modeling procedure in this case did not take into account the initial lag period which is separate from the actual removal process. Therefore, only those data points related to the removal of Zn starting at the end of the lag period were used for kinetic modeling. Secondly, most of the removal of Zn in the 700 °C to 900 °C occurred in a relatively small time interval that did not exceed one hour as indicated in Figure 20. After that, additional Zn removal did not level off; it rather continued at a much slower but steady rate. Such behaviour was originally attributed to a second removal process initiating when the first and main Zn removal process ended. This hypothesis was rejected after close examination of the slopes of the proposed second removal process: These slopes were found to be independent of
temperature as illustrated in Figure 21. If the proposed second removal process actually occurred, then the rate of Zn removal with time should have increased as temperature increased. The data illustrated in Figure 21 show otherwise, even a decrease in slope between 700 and 900 °C. It was then assumed that the additional slow removal of zinc after the main removal period had finished was due to the tendency of the residual Zn to partition between the phases present in the mixture and the ambient Cl₂/air atmosphere, eventually leading to a steady state. This assumption was then used to predict the final overall extent of Zn removal and to adjust the experimental data accordingly as explained in Appendix C.

Once the above considerations were taken into account, the kinetic modeling based on the Zn removal data showed that the removal process changes from first order in the 500 to 650 °C range to second order in the 700 to 900 °C as indicated in Table 6. This change in reaction order implies a change in mechanism possibly caused by a change in nature of the reacting environment. One reason for the change in the reaction mechanism is attributed to the possibility of melt formation at 700 °C and above. Experimental observations support the possibility of melt formation since sintering of the residues particles was found to occur at 700 °C and above. Furthermore, consideration of the pertinent phase diagrams illustrated in Figures 22 to 25 indicate that a eutectic mixture containing CaCl₂, MgCl₂, NaCl, KCl, and the chlorides of other elements including Fe and Mn can depress the melting point of CaCl₂ by about 54 °C and cause melting to start as low as 720 °C. The details of the calculations used to determine the CaCl₂ melting point depression are detailed in Appendix D. This procedure is only approximate since each element was considered separately because no multi-component phase diagram was found in the literature that accurately describes the examined complex system. The formation of eutectic mixtures containing chlorides has been investigated in previous studies. Il'yasov et. al. [1962] reported that a binary system consisting of Na₂Cl₂-PbCl₂ has a eutectic at 410 °C, 16.5% Na₂Cl₂ and that in the case of Na₂Cl₂-CdCl₂, a eutectic forms even at a lower temperature of 392 °C, 29% Na₂Cl₂.
Activation energy. The likely change in mechanism of Zn removal was also reflected by the change in the activation energy (Ea) values corresponding to the 500 to 650 °C and 700 to 900 °C. Before considering the Ea values, it is important to consider the reaction rate constants which were used to obtain Ea. The values of the rate constants for each temperature were derived from the first and second order kinetic fitting procedure described in Section 2.2.3. The empirical rate constants were used to model the removal of Zn as shown in Figures 26 and 27.

The accuracy of the estimated reaction rate constants was verified by conducting duplicated experiments at 700 and 800 °C. The rate constants obtained in the case of 700 °C were virtually identical as indicated in Table 5. In contrast, the rate constants obtained in the case of the two experiments conducted at 800 °C were 0.216 and 0.162 L²/mol²s, a 33% difference. The former value was subsequently used since it resulted in a better fitting of the experimental data. The accuracy of the rate constants could be improved by repeating more experiments at every temperature in order to obtain average values for the rate constants and to identify any possible outlier. In this study, only duplicate experiments were conducted at chosen temperatures due to time constraints.

Nonetheless, the most appropriate value of the rate constants obtained at different temperatures (i.e. the ones giving the best fitting of the experimental data) was used to generate the Arrhenius plots shown in Figures 28 and 29. Statistical tests detailed in Appendix E were used to estimate the uncertainty in the values of the Ea derived from the slope of the Arrhenius plots (Table 7) as well as the validity of the linear regression model used to obtain the Ea. The Ea for the 500 to 650 °C and 700 to 900 °C range was estimated at 118 (± 17) and 71 (± 148) kJ/mol, respectively. Note that the large uncertainty associated with the latter Ea is due to the low number of experimental data point. More importantly, the large difference in Ea between the low and the high temperature range suggests either a change in mechanism or a change in the rate determining step as indicated in the following section.
Rate determining step. In addition to the difference in Ea values between the low and the high temperature range, the values obtained for Ea in both temperature ranges were relatively high. This indicates that the rate determining step is chemically controlled rather than physically controlled (i.e. diffusion or mass transfer control) since diffusion control is mostly associated with Ea values under 50 kJ/mol as mentioned in Section 2.2.3.1. Note that the high uncertainty in the Ea corresponding to the 700 to 900 °C, namely 71 (± 148) kJ/mol, indicates that the rate controlling step may be physically controlled.

The possibility of mass transfer control of ZnCl₂ from the melt to the gaseous phase was eliminated by conducting duplicate experiments at 900 °C using a 50% higher carrier gas flow rate while keeping all other factors constant. It was found that the higher flow rate did not significantly affect the reaction rate constant (see Table 5). In other words, if the rate determining step were controlled by the evaporation of ZnCl₂ from the melt into the gaseous phase, then increasing the carrier gas flow rate would increase the rate of Zn removal. The experimental data show that the rate of Zn removal was not affected by the higher flow rate.

Furthermore, virtually identical rate constants were obtained from experiments where Cl₂ (g) partial pressure was varied between 0.05, 0.075, and 0.1 atm. At 700 °C while keeping all other factors constant (Table 5). This confirmed that the reaction order with respect to Cl₂ (g) is zero for chlorine partial pressure greater than 0.05 atm. and that the mass transfer of Cl₂ (g) from the gaseous phase to the reacting mixture is not controlling the rate determining step. Therefore, only diffusion control may govern the rate determining step above 700 °C.

Shrinking core model. The possibility that the rate determining step is controlled by mass transfer or by diffusion was eliminated when the shrinking core model was used to model the removal of Zn in the 500 to 650 °C range where the overall removal reaction is first order. When the equations governing the shrinking core model detailed in Section 2.2.3.2 were applied to the experimental data, it was found that the chemical control fit was superior to the fit obtained from the diffusion and mass
Figure 19: Delta(G) versus Temperature for the chlorination of the oxides of Pb, Cu, and Zn (including zinc ferrite)
Figure 20: Zn removal as a function of temperature. All experiments conducted in 5% Cl₂/air mixture flowing at 110 ml/min.

Figure 21: Same graph as above with emphasis placed on the 50 to 100% Zn removal zone.
Figure 22: System CaCl₂-KCl

Figure 23: System CaCl₂-MgCl₂

Figure 24: System CaCl₂-NaCl

Figure 25: System CaCl₂-MnCl₂

[Source: Levin, 1964]
Figure 26. First order modeling of Zn removal in the 500 to 650 °C range
Symbols = experimental data, Lines = calculated (kinetic model)

Figure 27. Second order modeling of Zn removal in the 700 to 900 °C range
Symbols = experimental data, Lines = calculated (kinetic model)
Figure 28. Activation energy of Zn removal in the 500 to 650 °C range
Symbols = calculated (k values), Lines = best fit

Figure 29. Activation energy of Zn removal in the 700 to 900 °C range
Symbols = calculated (k values), Lines = best fit
Figure 30. Shrinking core modeling of Zn removal in the 500 to 650 °C range
Symbols = experimental data, Lines = calculated (Chemical Control)
transfer control model (see Appendix C). The good agreement between the chemical control version of the shrinking core model and the experimental data is shown in Figure 30. The rejection of the diffusion control rate determining step indicates that fluid film resistance and ash layer diffusion control are negligible compared to the chemical resistance. This is in agreement with the conclusion derived from the values of $E_A$ mentioned above for the 500 to 650 °C range, that is the rate determining step is chemically controlled. Nonetheless, the first order simple kinetic model is still preferred over the shrinking core model since the latter tends to over-estimate the removal of Zn at high removal. Additional experimentation using particles of different size is required to validate the accuracy of the shrinking core model.

5.2.2.2 Lead

**Removal process.** The removal of Pb at various temperatures is illustrated in Figure 31. Unlike Zn, no specific reactant was associated with the removal of Pb which was not linked to a specific compound since its low concentration was beyond the detection limit of XRD. Nonetheless, Pb was most likely present in its oxide form due to the highly oxidizing conditions above the BOF vessel where the dust particles were formed. If this is the case, then PbO would react with Cl$_2$(g) as follows:

$$\text{PbO}(s) + \text{Cl}_2(g) \rightarrow \text{PbCl}_2(g) + \frac{1}{2}\text{O}_2(g)$$  \hspace{1cm} [R.30]

This is a reasonable assumption since the $\Delta G^\circ$ and the $\Delta G$ of the above reaction are always negative in the 500 to 900 °C range as shown in Figure 2 and Figure 19, thus indicating that the reaction is favorable and spontaneous in this temperature range.

The Pb removal data obtained at different temperatures are illustrated in Figure 31. The amount of Pb removed during the initial heating period that preceded the removal process was found to be negligible in most cases, namely less than 0.5% of the available Pb. The only exception was
noted in the case of 900 °C where a significant amount (16%) of the original Pb present in the sample volatilized prior to the start of chlorination. This probably occurred due to the reaction of some of the Pb with the chlorides initially present in the sample. At the end of the initial heating period, Cl₂(g) was introduced into the system causing the removal of Pb to occur. The removal data indicated that the rate of reaction increased as the temperature increased. Similar to Zn removal, complete Pb removal was not accomplished in the 500 to 650 °C range even when residence time was six hours. Nonetheless, sufficient data were obtained in this range in order to study the kinetics of Pb removal. Temperatures exceeding 700 °C caused the Pb removal to reach completion in about an hour. The results indicate that the rate of Pb removal is higher than that of Zn at all temperatures. This is not readily explainable since the vapour pressure of ZnCl₂ is a hundred times greater than that of PbCl₂ in the 500 to 900 °C.

It was noted that in this case, similar to the Zn removal case, a lag period occurred prior to the initiation of the removal process, thus causing the removal curves illustrated in Figure 31 to be S-shaped. The delay was attributed to the chlorination of the available CaO in a competing chlorination process as mentioned above (see Section 5.2.2.5). This lag period, however, was on average shorter than that of Zn. It was even non-existent at 900 °C, thus illustrating the readiness of Pb (or PbO) to be chlorinated and volatilized compared to Zn.

**Reaction kinetics.** In addition to investigating the lag process and the rate of Pb removal, the experimental data were used to investigate the associated reaction kinetics. Amongst the important kinetic parameters, the reaction rate constants were obtained at different temperatures by applying the kinetic modeling technique described in Section 2.2.3. Similar to the case of Zn removal, the modeling procedure did not take into account the initial lag period. Therefore, only those data points related to the removal of Pb starting at the end of the lag period were used for kinetic modeling. Unlike the case of Zn, the data in Figure 31 show that the removal of Pb in the 650 °C to 900 °C reached completion shortly after one hour and subsequently leveled off near 100%. No continual slow
and steady removal of Pb occurred after most of the Pb was volatilized. This indicated that, unlike Zn, all of the Pb was removed without the tendency to establish a possible steady state condition between Pb, the other phases present in the melt, and the ambient Cl₂/air atmosphere. It was therefore unnecessary to include all the modifications used in the case of Zn during the modeling of Pb removal.

The kinetic modeling applied to the Pb removal data showed that the removal process changes from second order in the 500 to 650 °C range to first order in the 700 to 900 °C range as shown in Table 6. A shift in reaction order was also noted in the case of Zn, but in the reverse order, i.e. from first to second order. This shift in reaction rate order implies a change in mechanism caused by a change in the nature of the reacting environment. This change was associated with the of melt formation at 700 °C as mentioned earlier.

In addition to estimating the reaction rate order, the values of the rate constants for Pb removal at different temperatures were derived from the first and second order kinetic fitting procedure described in Section 2.2.3.1. These values were used along with the estimated reaction rate orders to model the removal of Pb as illustrated in Figures 32 and 33. Note that the model is not satisfactory in the case of 900 °C. This is the case mainly because the removal of Pb at 900 °C occurred so rapidly that not enough data points necessary for accurate kinetic modeling were collected in the range where the majority of Pb removal occurred. Below 900 °C, the precision in the computed rate constants was verified by conducting duplicate experiments at 700 and 800 °C. The rate constants obtained for 700 °C were in very good agreement, namely 0.047 and 0.050 L.s⁻¹ (see Table 5). In contrast, the rate constants obtained in the case of the two experiments conducted at 800 °C were 0.053 and 0.083 L²/mol².s, a 57% difference. The latter value was subsequently used since it resulted in a better fitting of the data. The lack in precision when estimating the rate constant at 800 °C was also noted in the case of Zn above. Complete reproducibility is unlikely due to the complexity of the uBOF-OX.
**Activation energy.** The rate constants obtained at different temperatures were used to calculate the Ea for Pb removal. The effect of the inaccuracies mentioned above is apparent by the scatter of data in the Arrhenius plots illustrated in Figures 34 and 35. Appropriate statistical analysis included in Appendix E was used to estimate the uncertainty in the Ea’s values derived from the slope of the Arrhenius plots. The change in mechanism of Pb removal was reflected by the change in the Ea values between the 500 to 650 °C and 700 to 900 °C temperature ranges where Ea values were 172 (± 38) and 57 (± 41) kJ/mol, respectively (Table 7). The large difference in Ea values obtained for the two temperature ranges is clearly indicative of a change of mechanism due to melt formation as described above. Unlike the case of Zn where the difference in Ea values was 66%, the Ea of Pb removal decreased by a factor of three between the 500 to 650 °C and the 600 to 900 °C range, thus indicating that Pb removal is more temperature sensitive than Zn removal.

**Rate determining step.** The high value of Ea in the 500 to 650 °C range (172 kJ/mol) indicates that the rate determining step for Pb removal is chemically controlled. This is not as conclusive in the 700 to 900 °C range due to the much lower Ea (57kJ/mol) and to the high uncertainty (± 41 kJ/mol). Moreover, the possibility of mass transfer control of PbCl₂ from the melt to the gaseous phase was not eliminated by conducting duplicate experiment at 900 °C using a 50% higher carrier gas flow rate while keeping all other factors constant since the rapid removal of Pb at this temperature prevents acquisition of sufficient experimental data. Similar to Zn, virtually identical rate constants were obtained from triplicate experiments where Cl₂ (g) partial pressure was varied between 0.05, 0.075, and 0.1 atm. while keeping all other factors constant (Table 5). This confirmed that the reaction order with respect to Cl₂ (g) is zero for chlorine partial pressure greater than 0.05 atm.

Similarly, The rate constants for the low and high carrier gas flow rate agreed within 5%, thus eliminating the possibility of mass transfer control associated with evaporation of PbCl₂. This only leaves the possibility of diffusion control above 700 °C.
Figure 31: Pb removal as a function of temperature. All experiments conducted in 5% Cl₂/air mixture flowing at 110 ml/min.
Figure 32. Second order modeling of Pb removal in the 500 to 650 °C range
Symbols = experimental data, Lines = calculated (kinetic model)

Figure 33. First order modeling of Pb removal in the 700 to 900 °C range
Symbols = experimental data, Lines = calculated (kinetic model)
Figure 34. Activation energy of Pb removal in the 500 to 650 °C range
Symbols = calculated (k values), Lines = best fit

Figure 35. Activation energy of Pb removal in the 700 to 900 °C range
Symbols = calculated (k values), Lines = best fit
Shrinking core model. Further investigation revealed that, unlike the case of Zn, neither the chemical control nor the physical control version of the shrinking core model was applicable to the removal of Pb. The non-conformity with the shrinking core model indicates that Pb is not confined to a spherical arrangement but is rather distributed among particles either in the form of surface deposits or inclusions. The experimental data were insufficient to further investigate the nature and distribution of Pb species, especially that Pb is present only as a minor element (0.06 wt.%) in the uBOF-OX flue dust.

5.2.2.3 Copper

Removal process. The removal of Cu at various temperatures is summarized in Figure 36. Similar to Pb, no specific reactant was associated with the chlorination of Cu since it was not linked to a specific compound mainly because its low concentration in the uBOF-OX was beyond the detection limit of XRD. Nonetheless, Cu was most likely present in its oxide form due to the highly oxidizing conditions above the BOF vessel where the dust particles were formed. If this is the case, then CuO would react with Cl₂ (g) as follows:

\[ \text{CuO} (s) + \text{Cl}_2(g) \rightarrow \text{CuCl}_2(g) + \frac{1}{2}\text{O}_2(g) \]  \[ \text{R.31} \]

Also similar to the case of Zn and Pb, the ΔG° and the ΔG of the above reaction are always negative in the 500 to 900 °C range as indicated in Figure 19, thus indicating that the reaction is favorable and spontaneous in this temperature range. Unlike the two other cases, it was found that the removal of Cu did not reach completion at any temperature even when the residence time was six hours as shown in Figure 36. However, similar to the case of Zn and Pb removal at lower temperatures, enough data were obtained in order to study the reaction kinetics of Cu removal for the 600 to 900 °C range. This was not the case for 500 and 550 °C where conversion was less than 15%
and the data thus unsuitable for kinetic modeling. Such low rate of conversion indicates that, unlike Pb, Cu does not chlorinate readily. The amount of Cu removed during the initial heating period that proceeded the chlorination process varied between 0.5 and 5% regardless of temperature. This initial volatilization is possibly caused by the reaction of some of the Cu initially present in the sample with the chlorides available in the flue dust. The initial removal values were subtracted from the data used in the kinetic modeling of the Cu removal process. Cu removal data also indicate that the rate of reaction increases as the temperature increases. As well, a lag period caused by the competing CaO chlorination process occurred prior to the initiation of Cu removal, thus causing the removal curves to be S-shaped as illustrated in Figure 36.

**Reaction kinetics.** The experimental data were used to investigate the reaction kinetics of the Cu removal process. The same kinetic modeling procedure that provided the order of reaction and reaction rate constants for Zn and Pb was applied to the Cu removal data obtained after the initial heating period had finished. No adjustments were required here since, unlike the case of Zn, the data do not support the possibility of a steady state condition being established at high reaction conversion. The estimated reaction rate order for each temperature were used along with the estimated rate constants to model the Cu removal process as shown in Figures 37 and 38. The results obtained through the aforementioned modeling procedure showed that Cu behaved similarly to Pb in that a change from second to first order kinetics occurred above 700 °C (see Table 6). This shift in reaction rate order implies a change in mechanism caused by a change in nature of the reacting environment due to melt formation at 700 °C and above as explained above.

Note that the agreement between the experimental and the computed values in the case of 600 °C is poor compared to that of 650 °C as illustrated in Figure 37. Furthermore, it was found that the fraction removed at 625 °C (13.4%) was lower than that of 600 °C (33.2%). This is contrary to theoretical expectations which predict an increase in conversion as temperature increases. A similar discrepancy was also noticed for some experiments conducted at the same temperature. For example,
when the experiment conducted at 800 °C was repeated, the Cu removal dropped from 73% to less than 10% while the behaviour of the other elements remained constant. This lack of reproducibility was attributed to the complexity inherent with industrial samples. More specifically, the Cu removal data suggest that Cu is possibly present in different forms other than the one described in reaction R.31 above, some less reactive than others (e.g. silicates, etc.). Therefore, it is likely that some of the dust samples may contain a higher fraction of the non-reactive Cu species, thus leading to unexpectedly low conversion. For example, Figure 2 shows that the chlorination of Cu⁺² is less favourable than that of Cu⁺¹.

**Activation energy.** The Arrhenius plots shown in Figures 39 and 40 provided the Ea for Cu removal in the low and high temperature ranges. The results included in Table 7 indicate that the Ea increases from 50 kJ/mol in the 500 to 650 °C range to 56 (± 132) kJ/mol in the 700 to 900 °C range caused an. This is contrary to the case of Zn and Pb where the shift in reaction order between the mentioned temperature ranges caused a decrease in the Ea. Note that, in this case, the Ea values obtained for the 500 to 650 °C range and the 700 to 900 °C range were based on two and three data points, respectively. This reduces the reliability of the Ea values since a slight change in one of the rate constants (say from 0.0020 L²/mol²s to 0.0022 L²/mol²s) causes the Ea to change significantly (from 48 to 63 kJ/mol, a 31% increase). The available data indicate that the Ea values obtained for the 500 to 650 °C and the 700 to 900 °C range appear to be similar.

**Rate determining step.** Both of the Ea values reported above are about 50 kJ/mole, thus indicating that the rate determining step may be controlled either by chemical reaction or by diffusion due to the large uncertainty in the estimated Ea values. Furthermore, an experiment carried out at 900 °C using a higher flow rate revealed a dependence of the reaction rate constant on the flow rate of the carrier gas (see Appendix C). This dependence indicates that the mass transfer of CuCl₂ from the melt to the gaseous phase may constitute the rate determining step at higher temperatures. Even the values for the rate constants obtained from experiments where Cl₂ (g) partial pressure was varied between
0.05, 0.075, and 0.1 atm. while keeping all other factors constant were identical only in the first two cases (see Table 5). This suggests that the reaction order with respect to Cl₂ (\( w \)) is non-zero, thus indicating a removal mechanism for Cu that differs from that of Zn or Pb, with a possible diffusion controlled rate determining step. The possibility of additional diffusion control contribution to the rate determining step is illustrated below.

**Shrinking core model.** This model was applied to the Cu removal data in the 700 to 900 °C range where the reaction was found to be first order. The results illustrated in Figure 41 indicate that the chemical control model provides a very good fit of the data in the 700 to 800 °C range. This is in agreement with previous studies which concluded that the rate determining step of the chlorination of CuO from copper ore is controlled by chemical reaction under similar conditions of temperature and pressure [Brittan, 1971]. At 900 °C, however, both diffusion control and chemical control appear to be applicable as indicated in Figure 42. Taking this into consideration along with the fact that a higher carrier gas flow rate changed the reaction rate constant as explained above, the rate determining step for Cu removal at 900 °C remains inconclusive given the limited number of data points. Furthermore, the lack of complete reproducibility in the behaviour of Cu as explained above hinders the exact characterization of the rate determining step in this case.

### 5.2.2.4 Other elements

The removal of elements other than Zn, Pb, and Cu was negligible in all cases and at all temperatures. For example, the removal of Fe and Mn did not exceed 1% in all cases as confirmed by a mass balance on the residues obtained at the end of each thermal treatment experiment. More interesting is that the removal pattern of those two elements were very similar in virtually all cases. The Fe and Mn removal pattern appeared to be close to that of Cu removal, but no kinetic modeling of the data was undertaken due to the low extent of removal. Even the onset of removal occurring at the end of the delay period was virtually identical for both elements. Some of the removed Fe and Mn
Figure 36: Cu removal as a function of temperature. All experiments conducted in 5% Cl₂/air mixture flowing at 110 ml/min.
Figure 37. Second order modeling of Cu removal in the 500 to 650 °C range
Symbols = experimental data, Lines = calculated (kinetic model)

Figure 38. First order modeling of Cu removal in the 700 to 900 °C range
Symbols = experimental data, Lines = calculated (kinetic model)
Figure 39. Activation energy of Cu removal in the 500 to 650 °C range
Symbols = calculated (k values), Lines = best fit

Figure 40. Activation energy of Cu removal in the 700 to 900 °C range
Symbols = calculated (k values), Lines = best fit
Figure 41. Shrinking core modeling of Cu removal in the 700 to 800 °C range
Symbols = experimental data, Lines = calculated (Chemical Control)

Figure 42. Shrinking core modeling of Cu removal at 900 °C
Symbols = experimental data
Solid Lines = calculated (Chemical Control)
Dashed Lines = calculated (Diffusion Control)
Table 5. Reaction rate for the removal of Zn, Pb, Cu in low and high temperature intervals

<table>
<thead>
<tr>
<th>Variable</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Cl₂/air</td>
<td>Total flow</td>
<td>Temp.</td>
<td>k</td>
</tr>
<tr>
<td>5%</td>
<td>110 mL/min</td>
<td>700 °C</td>
<td>0.144</td>
</tr>
<tr>
<td>5%</td>
<td>110 mL/min</td>
<td>700 °C</td>
<td>0.143</td>
</tr>
<tr>
<td>7.5%</td>
<td>110 mL/min</td>
<td>700 °C</td>
<td>0.149</td>
</tr>
<tr>
<td>10%</td>
<td>110 mL/min</td>
<td>700 °C</td>
<td>0.144</td>
</tr>
<tr>
<td>5%</td>
<td>110 mL/min</td>
<td>900 °C</td>
<td>0.655</td>
</tr>
<tr>
<td>5%</td>
<td>188 mL/min</td>
<td>900 °C</td>
<td>0.687</td>
</tr>
</tbody>
</table>

Table 6. Reaction order for the removal of Zn, Pb, Cu in low and high temperature intervals

<table>
<thead>
<tr>
<th>Order of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
</tr>
<tr>
<td>500 - 650</td>
</tr>
<tr>
<td>700 - 900</td>
</tr>
</tbody>
</table>

Table 7. Activation energy of removal reaction for Zn, Pb, Cu in low and high temperature intervals

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Zn [kJ/mol]</th>
<th>Pb [kJ/mol]</th>
<th>Cu [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 - 650</td>
<td>118 +/- 17</td>
<td>172.0 +/- 38</td>
<td>56.0 +/- 132</td>
</tr>
<tr>
<td>700 - 900</td>
<td>71.0 +/- 148</td>
<td>57.0 +/- 41</td>
<td>50 *</td>
</tr>
</tbody>
</table>

* = No error estimate since figure obtained from 2 data points only
condensed on the upstream at the outlet nozzle forming Fe-Mn silicate crystals as illustrated in Plate 23.

In addition to the volatilization of Fe and Mn, the removal of Ca, Mg, Na and K exceeded predicted values. In other words, even a carrier gas saturated with the sparsely volatile chlorides of these elements would be unable to deliver the amounts that were detected leaving the system during the thermal treatment duration. For example, the total amount of CaCl₂ delivered over a period of four hours by a 110 mL/min carrier gas saturated with CaCl₂ at 900 °C (vapour pressure = 3.44 × 10⁻⁶ atm) would only be about 0.1 mg. The experimental results, however, indicate that a 3.2 mg of CaCl₂ was generated under similar conditions. The removal of these elements must therefore have been assisted by other volatile species that acted as carriers of the alkali and alkaline earth metals. These volatile species are most likely complex di-metal halides having relatively higher partial pressure compared to the simple chlorides. Literature studies confirm the formation of volatile gaseous complexes such as NaFeCl₄, MgFe₂Cl₈ and CaFe₂Cl₈ during similar operating conditions [Emmenger, 1977][Dewing, 1970].

5.2.2.5 Lag phenomenon

The residues collected at the end of each experiment were analyzed in order to better understand the removal process of the heavy metal contaminants from the uBOF-OX and to search for additional evidence of a mechanism change occurring at 700 °C. Such analysis was also aimed at understanding the lag process which preceded the removal of Zn, Pb, and Cu in all cases. This lag period is attributed to the chlorination of CaO available in the flue dust. The chlorination of CaO is more favourable than that of ZnO, PbO and CuO for T < 1100 °C as shown in Figure 2. A maximum lag time of about 25 minutes was estimated for a 5% Cl₂/air gaseous mixture flowing at 110 mL/min at room temperature and pressure to completely chlorinate a 3 g uBOF-OX sample containing 7.68% Ca. This differed from the experimentally determined lag time. In the case of Zn, for example, the
data illustrated in Figure 43 indicate that the lag time decreased as the temperature increased possibly because the competing chlorination of CaO occurred faster at higher temperatures. This effect is even more accentuated in the case of Pb whose chlorination is almost as favourable as that of CaO at 800 °C (see Figure 2), hence the elimination of the lag at high temperatures as indicated in Figure 44. In the case of Cu, the lag was not detected for temperatures lower than 700°C, most likely due to the high volatility of CuCl₂(g) which readily evaporated. At 700°C and above, the formation of a melt probably hindered the direct evaporation of CuCl₂(g), thus increasing the lag time as indicated in Figure 45.

The effect of CaO on the lag was further demonstrated by doubling the concentration of CaO in the flue dust sample prior to treatment at 700 °C. The results included in Figures 46 to 48 clearly show that the lag increases as the concentration of CaO.

Confirmation that the lag process is due to the conversion of CaO to CaCl₂ was qualitatively established by the measurement of a weight gain (7 to 10%) at the end of each experiment mostly due to the Cl₂(g) capture by CaO and to a lesser extent to the oxidation of magnetite to form hematite. The presence of soluble chlorides in the solid residues at the end of each experiment was also qualitatively confirmed by leaching the solid residues with de-ionized water and adding a few drops of concentrated AgNO₃(aq). The formation of a white solid precipitate (most likely AgCl(s)) confirmed that chlorides existed in the solid residues. This precipitate was virtually undetected when the procedure was repeated with untreated uBOF-OX, thus confirming that the thermal treatment process caused chlorine capture by the solid residues during the duration of the treatment.

The qualitative identification of the Cl₂(g) captured by CaO during the thermal treatment process was also assessed quantitatively. This was accomplished by analyzing the solution obtained after leaching the solid residues with de-ionized water for an extended period of time. ICP analysis was used in this case to determine the soluble cations and a specific ion electrode was used to measure the total chloride content of the solution. Once the cations were identified, the theoretical amount of chloride required to form their simple salts was estimated and compared with the actual
chloride present in the solution. The results shown in Figure 49 show a reasonable agreement between the measured chloride and the theoretical chloride required for the formation of salt of the main cations present in solution, namely CaCl₂, MnCl₂, MgCl₂, NaCl, KCl, and CuCl₂. This confirmed the conversion of the oxides of these cations into chlorides during the treatment process.

In addition to wet chemistry, x-ray diffraction analysis was used to investigate the change in mineralogy induced by the chlorination of the iron oxide fines. Figure 50 illustrates this change by comparing the diffractogram of uBOF-OX fines treated at 600 °C along with the diffractogram of an untreated uBOF-OX fines. The most noticeable change is a decrease of the magnetite main peak relative to that of the more oxidized hematite. This change is attributed to the presence of excess oxygen in the chlorinating atmosphere resulting in the partial oxidation of magnetite to hematite. The most important change is attributed to the disappearance of the CaO peak and the appearance of the CaCl₂ phase during the lag period observed for each thermal treatment experiment regardless of temperature. Other minor phases also present in the residues are probably chlorides of other cations as mentioned above. Similar patterns were obtained in the diffractograms obtained at higher temperatures with the location and the intensity of the detected peaks virtually identical to those peaks detected at 600 °C. One exception is the slight but consistent increase in hematite coupled by a decrease in magnetite as the temperature increased. The increase in temperature most likely caused an increase in the oxidation rate of Fe species without causing the reaction to become thermodynamically unfavorable.

5.2.2.6 Additional residue analysis

Further analysis of the residues included the hot aqua-regia digestion of solid samples obtained from the residues generated during experiments conducted at different temperatures. The digestions were done in duplicates in order to check for reproducibility of the data, and the results were found to be reproducible in all cases (± 10%). The undigested residues, mainly inert silicates,
were dried and weighed separately. The results illustrated in Figure 51 show an interesting pattern: The weight of the undigested residues remained unchanged for experiments conducted in the 500 to 650 °C range only to sharply increase for the experiments conducted in the 700 to 900 °C range. This represents more evidence that a change in the removal mechanism occurred at 700 °C. The increase in the amount of undigested residues was also investigated by analyzing the solution obtained at the end of the digestion. This analysis provided the concentration of the elements that were solubilized during the aqua-regia digestion. These concentrations were then used to estimate the amounts of the original oxides that were present in the sample residues. The difference between the weight of the original sample residues and the sum of the oxides was computed. This difference should actually correspond to the silicates present in the sample residues. The same pattern in the calculated and measured silicates was identified as illustrated in Figure 51, thus validating the change occurring in the residues obtained in the 500 to 650 °C and those obtained in the 700 to 900 °C range.

Further examination of the data revealed that the increase in the weight of the undigested residues was actually due to more Fe becoming entrapped in the silicate matrix starting at 700 °C. This is illustrated in Figure 52 which is basically a mass balance showing that the difference between the initial Fe content of the sample residues and the Fe solubilized by the aqua-regia solution becomes significant in the 700 to 900 °C. No such difference was noted in the case of Ca, Mg and Mn, thus indicating that the reaction of Fe with the silicates is responsible for the majority of the weight increase of the undigested fraction obtained after digestion of the residues in hot aqua-regia. This was confirmed by the EDX analysis conducted on this undigested fraction. The results show that the silicates obtained at 600 °C were mainly comprised of Si (>90%) as well as traces of Ca (up to 1.5%) and Fe (up to 4%), whereas the silicates obtained at 700 °C and above were comprised mainly of Fe (up to 90%) as well as Si (up to 35%) and minor amounts of Mg (up to 5%) and Ca (up to 2%). This difference in the chemical make-up of the residues constitutes another indication that a melt formed above 700 °C, thereby facilitating the transport of Fe into the silicates. Even the morphology
Figure 43. Lag as a function of Temperature (Zn removal)

Figure 44. Lag as a function of Temperature (Pb removal)

Figure 45. Lag as a function of Temperature (Cu removal)
Figure 46. Lag increase during Zn removal due to doubling of [CaO]

Figure 47. Lag increase during Pb removal due to doubling of [CaO]

Figure 48. Lag increase during Zn removal due to doubling of [CaO]
Figure 49. Actual Cl$_2$ present in a 1 g treated uBOF-OX sample compared to theoretical Cl$_2$ based on water soluble cations obtained from the treated sample (charge balance).

Figure 50. Diffractograms showing the main phases detected by XRD in untreated and treated uBOF-OX samples.
Figure 51. Measured undigested residues compared to theoretical undigested residues after hot aqua-regia digestion (uBOF-OX)

Figure 52. Comparison between actual and measured elemental mass for a 0.2 g sample of treated uBOF-OX digested with aqua-regia
Plate 23. Fe-Mn silicate deposit upstream
Plate 26. Undigested residues of uBOF-OX treated at 800 °C

Plate 27. Undigested residues of uBOF-OX treated at 900 °C
of the silicates obtained at different temperatures was not the same as illustrated in Plates 24 to 27. They show that the silicate spheres increase in size as the temperature increases.

5.2.3 Thermal treatment summary

The heavy metal contaminants including Zn, Pb and Cu were selectively removed from uBOF-OX by thermal chlorination under oxidizing conditions in the form of volatile heavy metal chlorides. The chlorination process that generates these chlorides was found to be best modeled as first order for Zn and as second order for Pb and Cu in the 500 to 650 °C range. These orders changed to second order for Zn and first order for Pb and Cu in the 700 to 900 °C range. Such shift in order between the low and high temperature range indicated a possible change in mechanism when the chlorination was conducted at 700 °C and above. The change in the chlorination mechanism is supported by the formation of a melt in the reacting mixture as low as 700 °C.

The orders of reaction were also used along with the reaction rate constants obtained at different temperatures to determine the Ea values for the removal of Zn, Pb and Cu. The Ea values for Zn and Pb decreased from 118 (± 17) and 172 (± 38) kJ/mol in the 500 to 650 °C range to 71 (± 148) and 57 (± 41) kJ/mol 700 to 900 °C range, respectively. This change in Ea is more evidence that the mechanism changes above 700 °C. The magnitude of Ea for Zn and Pb indicate that the rate determining step is chemically controlled in the 500 to 650 °C range. This was confirmed by the successful application of the shrinking core model (chemical control version) to the removal of Zn. The removal of Pb did not follow the shrinking core model. Accurate identification of the rate determining step for Zn and Pb in the 700 to 900 °C was not possible due to the high uncertainty in the estimated values of Ea's. High uncertainty was also associated with the Ea values of Cu removal, namely 56 (± 132) for 500 to 650 °C and 50 kJ/mol for 700 to 900 °C. Note that the latter Ea does not have an uncertainty estimate since the Ea value was estimated from two data points only. The identification of the Cu removal rate determining step is thus not conclusive.
An initial lag preceded the removal of all three elements in most of the cases. This lag was attributed to a competing chlorinating mechanism, namely the conversion of CaO to CaCl₂ as confirmed by the XRD analysis of the solid residues.

It is expected that the characterization study and the reaction kinetics investigation will ultimately facilitate and validate the design of a large thermal treatment unit capable of decontaminating the steelmaking flue dust.

6. CONCLUSIONS

1. The characterization indicates that the flue dust is an iron rich and complex material
2. In the case of BOF-OX, Zn is concentrated in the fine particles and can thus be separated by physical means. This is not the case for BOF-OG.
3. The removal of Zn, Pb and Cu was successfully achieved through thermal chlorination under oxidative conditions. The highest removal occurred at 900 °C in all cases.
4. A lag period due to the competing chlorination of preexisting CaO preceded the removal Zn, Pb and Cu. This lag varied from element to element.
5. The removal kinetics were best modeled as first order for Zn and as second order for Pb and Cu in the 500 to 650 °C range. These orders changed to second order for Zn and first order for Pb and Cu in the 700 to 900 °C range. This change in reaction order suggests a change in mechanism.
6. The formation of a melt at 700 °C and above was investigated and established.
7. The magnitude of the activation energy associated with the removal of Zn, Pb, and Cu indicate that the rate determining step is controlled by chemical reaction in all cases. More experimental data are needed in the 500 to 650 °C range to confirm the aforementioned conclusion.
7. RECOMMENDATIONS

1. Conduct more thermal treatment experiments in order to obtain more data to be used in validating the estimated activation energies for Zn and Pb in the 700 to 900 °C range. Repeat the same in the 500 to 650 °C range for the same purpose in the case of Cu.

2. Study the composition of the gaseous mixture at the outlet nozzle in order to identify the actual composition of the volatile chloride species generated during the thermal treatment process. This might be possibly achieved by attaching a high temperature GC at the outlet nozzle.

3. Consider pelletizing the flue dust samples prior to treatment in order to test the effect of sample size and shape of the reaction kinetics.

4. Selectively repeat the chlorination experiments described above under neutral conditions such as N₂ in order to examine the effect of O₂ suppression on the extent and kinetics of decontamination.

5. Examine the chlorination residues under SEM in order to determine any possible change in particle morphology induced by the treatment process.

6. Conduct chlorination experiments on BOF-OG for the purpose of testing the efficiency and kinetics of heavy metal contaminants removal on a different kind of steelmaking flue dust.

7. Conduct synthetic experiments to verify the empirical models used above. Vary the composition of the matrix in order to test the effect of each component on the kinetics and outcome of reaction. Examine the experimental data and postulate reaction mechanisms governing the chlorination process and attempt to verify mechanism experimentally.

8. Apply this method on other granular samples such soil contaminated with heavy metals.

9. Design a pilot plant scale operation, possibly a rotating kiln, to test the decontamination process on a larger quantity of flue dust containing heavy metal contaminants.
8. REFERENCES


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9. APPENDICES
Appendix A: Sedimentation Analysis

The Andreassen pipette illustrated in Figure 6 was used to investigate the particle size distribution of uBOF-OX with diameter less than 53 µm. When these dust particles undergo gravity sedimentation under laminar conditions, they experience three main forces (lift force is assumed negligible in this case):

\[ F_B = \text{Buoyancy force} \]
\[ F_D = \text{Drag force} \]
\[ F_s = \text{Gravity force} \]

- A force balance around the sedimenting particles yields:

\[ F_s = F_D + F_B \]
\[ \Rightarrow F_D = F_s - F_B \]
\[ \Rightarrow F_D = m_s g - m_L g \]
\[ \Rightarrow F_D = 4/3 \pi r^3 \rho_s g - 4/3 \pi r^3 \rho_L g \]
\[ \Rightarrow F_D = 4/3 \pi r^3 g (\rho_s - \rho_L) \]
\[ \Rightarrow F_D = \pi/6 d^3 g (\rho_s - \rho_L) \]

Where:

- \( m_s \) = Mass of solid particles
- \( m_L \) = Mass of liquid dispersant
- \( \rho_s \) = Density of solid particles
- \( \rho_L \) = Density of liquid dispersant
- \( d \) = Diameter of particles

- For a laminar regime, \( F_D \) is given by Stoke's formula:

\[ \Rightarrow F_D = 3 \pi \mu d v \]
\[ \Rightarrow F_D = \pi/6 d^3 g (\rho_s - \rho_L) \text{ from above} \]
\[ \Rightarrow 3 \pi \mu d v = \pi/6 d^3 g (\rho_s - \rho_L) \]
\[ \Rightarrow v = (d^2 g) (18\mu)^{-1} (\rho_s - \rho_L) \]
\[ h/t = \left( \frac{d^2 g}{18 \mu} \right) \left( \rho_s - \rho_L \right) \]

Where:

- \( v \) = Velocity of sedimenting solid particles
- \( h \) = Distance traveled by solid particles
- \( t \) = Time required to travel a distance \( h \)
- \( \mu \) = Viscosity of dispersant fluid

The above formula giving \( h/t \) is used to estimate the time \( t \) required for particles of diameter \( d \) to sediment a distance \( h \) which corresponds to the distance from the liquid meniscus to the sampling depth. Supposing that the particles are distributed according to a size distribution \( F(d) \), then after \( t \), all particles with diameter larger than \( d \), will have sedimented below the sampling depth as illustrated below. Meanwhile, the concentration of the smaller particles remains constant. The fraction of particles with diameter less than \( d \), can thus be determined by taking the ratio of the particle concentration, \( C \), (measured at \( t \)) over the initial concentration \( C_0 \). The ratio \( C/C_0 \) represent the percentage of particles below this diameter. By computing this ratio at different time intervals and plotting it against the particle diameter, one obtains a cumulative undersize distribution for the material.

As mentioned above, this procedure was used to determine the particle size distribution of uBOF-OX with diameter less than 53 \( \mu \)m. The results are illustrated on the following pages. The necessary parameters and relevant data are presented in a tabular format.

[Chen, 1986]
Experiment #1: Cumulative size distribution of dehydrates uBOF-OX (volume basis)
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Experiment #2: Cumulative size distribution of dehydrates uBOF-OX (volume basis)
Appendix B. Thermodynamic Calculations

Consider the following reaction:

\[ \text{MO (s)} + \text{Cl}_2 (g) \rightarrow \text{MCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) \]

The \( \Delta G \) for the above reaction is determined at a given temperature from the following equation:

\[ \Delta G_T = \Delta G^\circ_T + RT \ln K_p \]

Where:

1. \( \Delta G^\circ_T \) is the standard Gibbs free energy at the given temperature:
   \[ \Delta G^\circ_T = \left[ \Delta G^\circ_T \right]_{\text{Prod cursed}} - \left[ \Delta G^\circ_T \right]_{\text{Reaction}} \] (Tabulated values obtained from Barin, 1995)

2. \( K_p \) is the reaction constant at the given temperature:
   \[ K_p = \frac{P_{\text{MCl}_2(g)} \times P_{\text{O}_2(g)}^{1/2}}{P_{\text{Cl}_2(g)} \times a_{\text{MO(s)}}} \]

   where \( P_i \) and \( a_i \) are the partial pressure and activity of element \( i \) respectively. \( P_i \) and \( a_i \) are estimated using the following equations:

   1) Ideal gas law: \( P_i = \frac{\dot{N}_i \cdot RT}{Q} \), where \( \dot{N}_i \) is the molar flow rate of element \( i \) and \( Q \) is the volumetric flow rate

   2) \( a_{\text{MO(s)}} \) is assumed to be equal to one

Thus \( \Delta G_T = \Delta G^\circ_T + RT \ln \left[ \frac{P_{\text{MCl}_2(g)} \times P_{\text{O}_2(g)}^{1/2}}{P_{\text{Cl}_2(g)}} \right] \)

Using the above procedure along with the experimental data, \( \Delta G_T \) values for Zn, Pb, and Cu were calculated as illustrated on the following pages.
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Note: Data obtained from the Ellingham diagram

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Note: ΔG° of ZnFe2O4 (s) chlorination at 1100 and 1200 K are extrapolated
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Data obtained from Barin, 1995
Appendix C: Reaction Kinetics

C.1 Rate equation

The empirical equations used to fit the removal data of Zn, Cu, and Pb are developed in this section. These equations were used to obtain important kinetic parameters such as reaction order and reaction rate constant for the following reaction:

\[ aA + bB \rightarrow \text{products} \]

- The rate of disappearance of A at constant volume is given by:

\[ \frac{dC_A}{dt} = k C_A^p C_B^q \]

Where \( p + q = n \) and \( n \) = overall reaction rate order and \( k \) is the reaction rate constant given by:

\[ k = k_0 e^{-\frac{E_a}{RT}} \]

Note that \( E_a \) is obtained from the slope of \( \ln(k) \) vs. \( 1/T \).

- Using one of the reactants in excess, say B:

\[ C_B >> C_A \]

\[ \Rightarrow -\frac{dC_A}{dt} = k' C_A^p \]

Where \( k' = k C_B^q \)

- Using fractional conversion:

\[ f_A = \frac{C_{A0} - C_A}{C_{A0}} \]

\[ \Rightarrow -\frac{dC_A}{dt} = C_{A0} \frac{df_A}{dt} \]

- Substituting in the rate equation:

\[ \Rightarrow C_{A0} \frac{df_A}{dt} = k' \left[ C_{A0} (1 - f_A)^p \right] \]
Evaluating the above integral gives the following rate equation:
\[-\ln(1 - f_A) = k''t\]

Case 1: \( p = 1 \)
Evaluating the above integral gives the following rate equation:
\[-\ln(1 - f_A) = k''t\]

Case 2: \( p \neq 1 \)
Evaluating the above integral gives the following rate equation:
\[\frac{1}{(p - 1)}[(1 - f_A)^{-p} - 1] = k''t\]

In order to determine the appropriate \( p \), different \( p \) values are chosen initially and the rate equations are used to plot the right hand-side versus time using experimental \( f_A \). The best value of \( p \) should produce a linear plot which slope is \( k'' \). Once \( k'' \) and \( p \) are determined, \( q \) can be determined from the experimental data obtained from duplicate experiments where only \( C_B \) is varied.

Experiment 1: \( k_1'' = k_1' C_{A_0}^{p-1} = k_1 C_{B_1} C_{A_0}^{p-1} = k_0 e \frac{-E_a}{RT} C_{B_1} C_{A_0}^{p-1} \)

Experiment 2: \( k_2'' = k_2' C_{A_0}^{p-1} = k_2 C_{B_2} C_{A_0}^{p-1} = k_0 e \frac{-E_a}{RT} C_{B_2} C_{A_0}^{p-1} \)

(Assuming that \( E_a \) and \( k_0 \) are independent of temperature)

\[ \frac{k_1''}{k_2''} = \left( \frac{C_{B_1}}{C_{B_2}} \right)^q \]

\[ \ln \left( \frac{k_1''}{k_2''} \right) = q \ln \left( \frac{C_{B_1}}{C_{B_2}} \right) \]
In the case of Zn, its removal in the 650 °C to 900 °C occurred largely in a relatively small time interval not exceeding one hour as indicated in Figure 20. After that, additional minor Zn removal did not level within the experimental duration; it rather continued at a much slower but steady rate as detailed in Section 5.2.2.1. This Zn removal pattern thus required the forecasting of the final extent of removal (or \( f_A \)) after which no more Zn is removed in order to only account for the reactive Zn fraction in the treated flue dust sample as detailed below. Forecasting \( f_A \) was achieved by using Euler's first order approximation:

\[
f_{A_{ini}} = f_{A_i} + \left( \frac{df_A}{dt} \right)_{i+1} \Delta t
\]

Where:

1. Initially \( f_{A_i} = f_A \) obtained at the end of the experiment, and subsequent values are given by \( f_{A_{ini}} = f_{A_i} \).
2. \( \Delta t \) is the time interval for each approximation (step size). It is chosen to be 60 minutes.
3. \( \left( \frac{df_A}{dt} \right)_{i+1} = \left( \frac{df_A}{dt} \right) + \left( \frac{d^2 f_A}{dt^2} \right) \Delta t \).

Where initially \( \left( \frac{df_A}{dt} \right) = \left( \frac{df_A}{dt} \right) \) obtained at the end of the experiment, and subsequent values are given by \( \left( \frac{df_A}{dt} \right) = \left( \frac{df_A}{dt} \right)_{i+1} \). As for \( \left( \frac{d^2 f_A}{dt^2} \right) \), it is a constant obtained from the data at the end of the experiment. Its value is about 0.6 in the 650 to 700 °C range.

The iteration process was conducted by incrementing \( \Delta t \) until the computed value of \( f_{A_{ini}} \) became constant or \( f_{A_{final}} \). This value was then used to adjust the experimental \( f_A \) values in order to accurately estimate the removal of Zn from the reactive Zn rather than the total Zn present in the sample. The following ratio was used for that purpose:

\[
f_{A_{final}} = \frac{f_A_{final}}{f_A_{ini}}
\]

- The procedures explained above were used to obtain \( k' \), \( p \), and \( q \) for Zn, Pb, and Cu, as illustrated on the following pages.
500 °C  1 atmosphere  5% Cl₂/sir  110 ml/min  uBOF-OX  Element removed : Zn

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**Zn volatilization kinetics : n < 1**

**Zn volatilization kinetics : n = 2**

**Zn volatilization kinetics : n = 3**

**Zn volatilization kinetics : n = 4**
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Zn volatilization kinetics: $n < 1$

Rate Equation: $y = 0.0018x - 0.0068$
$R^2 = 0.9999$

Zn volatilization kinetics: $n = 2$

Rate Equation: $y = 0.0023x - 0.1417$
$R^2 = 0.9993$

Zn volatilization kinetics: $n = 3$

Rate Equation: $y = 0.003x - 0.362$
$R^2 = 0.9999$

Zn volatilization kinetics: $n = 4$
600 °C 1 atmosphere 5% Cl2/air 110 ml/min uBOF-OX Element removed: Zn

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### Zn Volatilization Kinetics

- **n = 1**: $y = 0.5086 + 0.3164x$, $R^2 = 0.9984$
- **n = 2**: $y = 0.9172x - 1.5170$, $R^2 = 0.9272$
- **n = 3**: $y = 5.567x - 21.065$, $R^2 = 0.9583$
- **n = 4**: $y = 20.968x - 94.083$, $R^2 = 0.9727$
### Zn volatilization kinetics: $n < 1$

![Graph with rate equation $y = 0.0070x - 0.3433$ and $R^2 = 0.9963$.]

### Zn volatilization kinetics: $n = 2$

![Graph with rate equation $y = 0.0235x - 1.9071$ and $R^2 = 0.9748$.]

### Zn volatilization kinetics: $n = 3$

![Graph with rate equation.]

### Zn volatilization kinetics: $n = 4$

![Graph with rate equation.]

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625 °C, 1 atmosphere, 5% Cl₂/air, 110 ml/min, uBOF-OX, Element removed: Zn
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**Zn volatilization kinetics:**
- **n < 1**
- **n = 2**
- **n = 3**
- **n = 4**
### Table 1: Zn Volatilization Kinetics

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### Diagrams

**Zn Volatilization Kinetics: \( n = 1 \)**

**Zn Volatilization Kinetics: \( n = 2 \)**

**Zn Volatilization Kinetics: \( n = 3 \)**

**Zn Volatilization Kinetics: \( n = 4 \)**
### Table 1: Zn Volatilization Kinetics

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### Graphs

#### Zn Volatilization Kinetics: \( n < 1 \)

- Rate Equation: \( r = 0.14t \times 0.794 \)
  
- \( R^2 = 0.882 \)

#### Zn Volatilization Kinetics: \( n = 2 \)

- Rate Equation: \( r = 0.14t^2 \)

#### Zn Volatilization Kinetics: \( n = 3 \)

- Rate Equation: \( r = 0.14t^3 \)

#### Zn Volatilization Kinetics: \( n = 4 \)

- Rate Equation: \( r = 0.14t^4 \)
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## Diagrams

1. **Zn Volatilization Kinetics: \( n < 1 \)**
   - Rate Equation: \( y = 0.143x - 4.294 \), \( R^2 = 0.986 \)
   - Time [min]: 0 to 210
   - Rate Equation: 0.5 to 3.3

2. **Zn Volatilization Kinetics: \( n = 2 \)**
   - Rate Equation: \( y = 0.143x - 4.294 \), \( R^2 = 0.986 \)
   - Time [min]: 0 to 210
   - Rate Equation: 0.5 to 20.0

3. **Zn Volatilization Kinetics: \( n = 3 \)**
   - Time [min]: 0 to 210
   - Rate Equation: 0.5 to 200

4. **Zn Volatilization Kinetics: \( n = 4 \)**
   - Time [min]: 0 to 210
   - Rate Equation: 0.5 to 3000
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### Kinetic Models

- **n = 1**: 
  \[ \text{Rate} = k \times t \]

- **n = 2**: 
  \[ \text{Rate} = k \times t^2 \]

- **n = 3**: 
  \[ \text{Rate} = k \times t^3 \]

- **n = 4**: 
  \[ \text{Rate} = k \times t^4 \]
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**Zn volatilization kinetics:**

- **n = 1**
  - Rate Equation: \( f = k_t \cdot (\text{Time}) \)
  - Graph showing data points and the rate equation for different values of rate constant (\( k \)).

- **n = 2**
  - Rate Equation: \( f = k_t \cdot (\text{Time})^2 \)
  - Graph showing data points and the rate equation for different values of rate constant (\( k \)).

- **n = 3**
  - Rate Equation: \( f = k_t \cdot (\text{Time})^3 \)
  - Graph showing data points and the rate equation for different values of rate constant (\( k \)).

- **n = 4**
  - Rate Equation: \( f = k_t \cdot (\text{Time})^4 \)
  - Graph showing data points and the rate equation for different values of rate constant (\( k \)).

**Notes:**
- The experiments were conducted at 800°C, under 1 atmosphere, with 5% Cl₂/sir, and 110 ml/min, using uBOF-OX.
- Elements removed: Zn.
### Table 1: Experimental Data

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### Graphs

- **Zn volatilization kinetics: n = 1**
- **Zn volatilization kinetics: n = 2**
- **Zn volatilization kinetics: n = 3**
- **Zn volatilization kinetics: n = 4**
### Zn volatilization kinetics, $n = 1$, 500 °C

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### Zn volatilization kinetics, $n = 1$, 550 °C

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### Zn Volatilization Kinetics: $n = 1$, $650^\circ C$

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![Graph of Zn volatilization kinetics, $n = 1$, 625° C](image1.png)

![Graph of Zn volatilization kinetics, $n = 1$, 650° C](image2.png)
### Zn volatilization kinetics, \( n = 2 \), 700°C a

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### Zn volatilization kinetics, \( n = 2 \), 700°C b

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### Zn Volatilization Kinetics

**n = 1**

- Initial rate: 0.000
- Rate constant: k = 0.015

**n = 2**

- Initial rate: 0.000
- Rate constant: k = 0.015

**n = 3**

- Initial rate: 0.000
- Rate constant: k = 0.015

**n = 4**

- Initial rate: 0.000
- Rate constant: k = 0.015
### Zn Volatilization Kinetics

#### $\text{Temp.: } 700 ^\circ \text{C}$

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#### Graphs

1. **Zn Volatilization Kinetics: $n < 1$**
   - Rate Equation
   - Time (min)
   - Rate (

2. **Zn Volatilization Kinetics: $n = 2$**
   - Rate Equation
   - Time (min)
   - Rate (min)
   - $n = 0.146 \times 1.712$
   - $R^2 = 0.806$

3. **Zn Volatilization Kinetics: $n = 3$**
   - Rate Equation
   - Time (min)
   - Rate (min)

4. **Zn Volatilization Kinetics: $n = 4$**
   - Rate Equation
   - Time (min)
   - Rate (min)
### 7.6% Cl₂

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### Zn Volatilization Kinetics

- **n < 1**
- **n = 2**
- **n = 3**
- **n = 4**

### Rate Equation

For each curve, the rate equation and corresponding data points are shown. The plots illustrate the change in Zn concentration over time, with different rate equations applied to model the process.
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Zn volatilization kinetics, n = 2, 900 °C

![Graph showing Zn volatilization kinetics](image-url)
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**Pb volatilization kinetics: n = 1**

\[ y = 0.0018x + 0.640, \quad R^2 = 0.899 \]

**Pb volatilization kinetics: n = 2**

\[ y = 0.0018x + 0.670, \quad R^2 = 0.899 \]

**Pb volatilization kinetics: n = 3**

**Pb volatilization kinetics: n = 4**
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**Pb volatilization kinetics:**

- **n < 1**
- **n = 0.00571 - 0.1802**
- **R² = 0.9991**

- **n = 4**
- **n = 0.0013 x 0.623**
- **R² = 0.9992**

**Rate Equation**

- **Time (min)**
- **Rate Equation**
- **Pb volatilization kinetics**
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**Pb volatilization kinetics:**

- **n = 0, 0.5, 1**
  - Rate Equation:
    - $y = 0.013x - 0.026$
    - $R^2 = 0.880$

- **n = 2**
  - Rate Equation:
    - $y = 0.036x - 0.977$
    - $R^2 = 0.885$

- **n = 3**
  - Rate Equation:

- **n = 4**
  - Rate Equation:
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**Pb volatilization kinetics:**

- **n = 1**
  
  \[ y = 0.018t - 0.431 \]
  
  \[ R^2 = 0.977 \]

- **n = 2**
  
  \[ y = 0.072t^2 - 3.180 \]
  
  \[ R^2 = 0.986 \]

- **n = 3**
  
- **n = 4**
**650 °C**  
1 atmosphere  
5% Cl/air  
110 ml/min  
UBOF-OX  
Element removed: Pb

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**Pb volatilization kinetics:**

- **n = 1**
  - Rate Equation: \( y = 0.047x - 0.016 \)
  - \( R^2 = 0.983 \)

- **n = 2**
  - Rate Equation: \( y = 0.983x + 25.814 \)
  - \( R^2 = 0.974 \)

- **n = 3**
  - Rate Equation

- **n = 4**
  - Rate Equation
**700 °C, Trial #2**

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**Pb volatilization kinetics:**

1. $n = 1$

![Graph with $n = 1$](image1.png)

2. $n = 2$

![Graph with $n = 2$](image2.png)

3. $n = 3$

![Graph with $n = 3$](image3.png)

4. $n = 4$

![Graph with $n = 4$](image4.png)
800 °C, Trial #1  1 atmosphere  5% Cl₂/air  110 ml/min  uBOF-OX  Element removed :  Pb

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**Pb volatilization kinetics : n = 1**

- y = 0.033x - 0.738
- R² = 0.988

**Pb volatilization kinetics : n = 2**

- y = 1.104x - 48.757
- R² = 0.846

**Pb volatilization kinetics : n = 3**

**Pb volatilization kinetics : n = 4**
800 °C, Trial #2  1 atmosphere  5% Cl/air  110 ml/min  uBOF-OX  Element removed:  Pb

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**Pb volatilization kinetics:**
- **n = 0.5**
- **n = 0.999**
- **n = 1.0**
- **n = 2.0**
### Lead Volatilization Kinetics

**900 °C** 1 atmosphere  5% Cl/air  110 ml/min  uBOF-OX  Element removed:  Pb

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#### Pb Volatilization Kinetics: $n = 1$

#### Pb Volatilization Kinetics: $n = 2$

#### Pb Volatilization Kinetics: $n = 3$

#### Pb Volatilization Kinetics: $n = 4$
### Pb Volatilization Kinetics, 500 °C

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**Table 1: Pb Volatilization Kinetics, 700 °C, Trial 1**

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**Diagram 1:** Pb volatilization kinetics, 700 °C, trial 1

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**Table 2: Pb Volatilization Kinetics, 700 °C, Trial 2**

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**Diagram 2:** Pb volatilization kinetics, 700 °C, trial 2

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**Legend:** Pb = Lead; mm = minutes; ml = milliliters
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### Table: Pb volatilization kinetics, 800 °C, trial1

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Pb volatilization kinetics : \( n = 1 \)

\[ y = 0.094x - 0.520 \]
\[ R^2 = 0.944 \]

Pb volatilization kinetics : \( n = 2 \)

Pb volatilization kinetics : \( n = 3 \)

Pb volatilization kinetics : \( n = 4 \)
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**Pb volatilization kinetics: \( n < 1 \)**

**Pb volatilization kinetics: \( n = 2 \)**

**Pb volatilization kinetics: \( n = 3 \)**

**Pb volatilization kinetics: \( n = 4 \)**
### 5% Cl₂, 1.5x flow 186 mL/min

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### Pb volatilization kinetics, n = 1, 800 °C

- Time (min)
- % Volatilization

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**Cu volatilization kinetics:**

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- **n = 2**
- **n = 3**
- **n = 4**
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**Cu volatilization kinetics:**
- $n = 1$
- $n = 2$
- $n = 3$
- $n = 4$
### Cu Volatilization Characteristics

- **Temperature:** 625 °C
- **Atmosphere:** 1 atmosphere
- **Cl in air:** 5%
- **Flue gas flow rate:** 110 ml/min
- **BoF-CX**

#### Element Removed: Cu

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#### Figures:

- **Cu Volatilization kinetics:**
  - **n = 0, 0.5, 1**
  - **n = 2**
  - **n = 3**
  - **n = 4**

These figures illustrate the rate equation over time for different values of n, showing the trend of Cu volatilization under various conditions.
650 °C  1 atmosphere  5% CI/air  110 ml/min  uBOF-OX  Element removed: Cu

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**Cu volatilization kinetics: n = 0, 0.5, 1**

- Plot 1: Rate Equation vs. Time [min]
- Plot 2: Rate Equation vs. Time [min]

**Cu volatilization kinetics: n = 2**

- Plot 3: Rate Equation vs. Time [min]
- Plot 4: Rate Equation vs. Time [min]
### Cu Volatilization Kinetics

#### $n = 0, 0.5, 1$

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#### $n = 2$

#### $n = 3$
### Cu Volatilization Kinetics

**80°C, Trial #2**  
1 atmosphere  
5% Cl/air  
110 mL/min  
uoBOF-OX  
Element removed: Cu

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**Cu volatilization kinetics:**  
$n = 0, 0.5, 1$

**Cu volatilization kinetics:**  
$n = 2$

**Cu volatilization kinetics:**  
$n = 3$
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Cu volatilization kinetics: $n = 0, 0.5, 1$

Cu volatilization kinetics: $n = 2$

Cu volatilization kinetics: $n = 3$

Cu volatilization kinetics: $n = 4$
Temp.: 800 °C  Trial # 2  Data is way below expectation, namely conversion is < 10%  Cu

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**Cu volatilization kinetics:**

- $n = 0, 0.5, 1$  
  
  \[ y = 2.0(1 - e^{-0.411t}) \]
  
  \[ R^2 = 0.9974 \]

- $n = 2$  
  
  \[ y = 0.0442t - 2.7498 \]
  
  \[ R^2 = 0.9974 \]

- $n = 3$  
  
  \[ y = 0.123t - 3.4567 \]
  
  \[ R^2 = 0.9974 \]

- $n = 4$  
  
  \[ y = 0.214t - 4.5678 \]
  
  \[ R^2 = 0.9974 \]
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**Cu volatilization kinetics, 700 °C, trial 1**

**Cu volatilization kinetics, 700 °C, trial 2**
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| 30         | 1.2%       | 60        | 23.7%     |
| 40         | 0.9%       | 90        | 33.3%     |
| 50         | 1.4%       | 120       | 41.7%     |
| 60         | 2.7%       | 180       | 55.5%     |
| 75         | 5.6%       | 240       | 66.0%     |

**Cu volatilization kinetics, 800 °C, trial 1**

![Graph](image1)

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| 30         | 6.7%       | 60        | 23.7%     |
| 40         | 8.8%       | 90        | 33.3%     |
| 50         | 13.9%      | 120       | 41.7%     |
| 60         | 19.5%      | 180       | 55.5%     |
| 80         | 35.4%      | 240       | 66.0%     |

**Cu volatilization kinetics, 900 °C**

![Graph](image2)
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**Cu volatization kinetics:**

- \( n = 0, 0.6 \)
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- \( n = 2 \)
- \( n = 3 \)
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**Cu volatilization kinetics:** $n = 0, 0.5$
### 7.6% Cu

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Cu volatilization kinetics: $n = 0, 0.5, 1$

Cu volatilization kinetics: $n = 2$

Cu volatilization kinetics: $n = 3$

Cu volatilization kinetics: $n = 4$
8% Cu

High flow rate = 166 mL/min

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Cu volatilization kinetics, n = 1, 900 °C

% Volatilization vs. Time [min]
C.2 Shrinking core model

The overview of the shrinking core model has been provided in Section 2.2.3.2 where the development of the main equations governing this model have been presented. Recall equations E.13 and E.14:

\[ 1 - \frac{2}{3} f_A - (1-f_A)^{2/3} = \alpha \, t \quad \text{(diffusion control)} \quad \text{[E.13]} \]
\[ 1 - (1-f_A)^{1/3} = \alpha \, t \quad \text{(chemical control)} \quad \text{[E.14]} \]

Where \( f_A \) is the fractional conversion of A, \( t \) is time, and \( \alpha \) is a proportionality constant that is directly proportional to the size of particle and inversely proportional to the fluid film mass transfer coefficient, the ash layer diffusion coefficient, and the reaction rate constant at the solid reactant surface as shown below:

\[
\frac{1}{\alpha} = \frac{RaC_{20}}{C_{20} \left( \frac{1}{3k_{m1}} + \frac{1}{ak_sC_{20}} + \frac{R}{6D_{w1}} \right)}
\]

The terms used in the above equation are defined in Section 2.2.3.2. Equations E.13 and E.14 were used to verify whether the removal of Zn, Pb and Cu followed the shrinking core model. This was accomplished by plotting the left hand-side of equations E.13 and E.14 versus time and checking the linearity of the plot to determine whether diffusion or chemical control apply to the removal of the aforementioned elements. \( \alpha \) is obtained from the slope of the linear plot and used to draw the calculated removal versus the actual removal of Zn, Pb, and Cu. The results of this procedure are included on the following pages.
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- 10: 0.00 0.0000
- 20: 0.02 0.0000
- 30: 0.07 0.0000
- 45: 0.41 0.0000
- 60: 1.53 0.0001
- 75: 2.64 0.0002
- 90: 4.25 0.0006
- 105: 5.54 0.0010
- 120: 6.76 0.0016
- 140: 8.00 0.0022
- 160: 9.42 0.0031
- 180: 10.68 0.0040
- 210: 12.51 0.0055
- 240: 14.35 0.0073
- 300: 17.65 0.0116
- 360: 20.95 0.0162

S.C.M.: Temp: Element:

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| t - actual [min]| f - actual | Equation |}

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- 20: 0.09 0.0000
- 30: 0.14 0.0000
- 45: 0.31 0.0000
- 60: 0.94 0.0000
- 75: 3.09 0.0003
- 90: 6.24 0.0013
- 105: 9.32 0.0030
- 120: 11.91 0.0050
- 140: 15.33 0.0084
- 165: 18.33 0.0122
- 180: 20.43 0.0154
- 210: 24.69 0.0229
- 240: 29.01 0.0324
- 300: 36.23 0.0528
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**ADJUSTED**
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### Graph 1

**Zn volatilization kinetics, 500 °C**

- Time [min]
- % Volatilized

### Graph 2

**Zn volatilization kinetics, 550 °C**

- Time [min]
- % Volatilized
### Zn volatilization kinetics, 600 °C

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### Zn volatilization kinetics, 625 °C

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**Modeling Pb Volat. Kinetics, 800 °C, trial 1**

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### Modeling Cu Volat. Kinetics, 700 °C, trial1

![Graph 1](image1)

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### Graph 1: Cu Volatilization Kinetics, 700 °C, trial 1

- Equation: \( y = 0.00087x - 0.02319 \)
- \( R^2 = 0.99539 \)

### Table 2: Cu Volatilization Kinetics, 700 °C, trial 2

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- \( R^2 = 0.99643 \)
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![Graph](image1.png)

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**Cu volatilization kinetics, 700a °C**

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Appendix D. Melting point depression

Determining the melting point depression of CaCl₂ requires knowing the concentration of chloride species that were present in the reacting mixture during chlorination at 700 °C. These concentrations were determined by water-leaching the solid residues obtained at the end of the chlorination treatment and analyzing the cations in the filtrate using ICP. A charge balance using chloride ions was then conducted based on the measured cation concentrations. The results were as follows:

\[
\begin{align*}
\text{KCl} & = 1.2 \text{ mol}\% \\
\text{MgCl}_2 & = 10.9 \text{ mol}\% \\
\text{NaCl} & = 2.3 \text{ mol}\% \\
\text{MnCl}_2 + \text{FeCl}_3 & = 1.7 \text{ mol}\%
\end{align*}
\]

The contribution of each of the chlorides towards the melting point depression of CaCl₂ was obtained from the phase diagram of each binary chloride mixture (shown on the following page) by drawing a line from the onset of temperature depression where the mole fraction of CaCl₂ is 100%. The following values were obtained from the slope of each line:

\[
\begin{align*}
\text{KCl} & = 4.7 \text{ °C/mol}\% \\
\text{MgCl}_2 & = 2.8 \text{ °C/mol}\% \\
\text{NaCl} & = 7.6 \text{ °C/mol}\% \\
\text{MnCl}_2 & = 2.6 \text{ °C/mol}\%
\end{align*}
\]

It was assumed that the melting point depression due the presence of FeCl₃ was the same as the one caused by the presence of MnCl₂. Using the above data, the CaCl₂ melting point depression was thus given by:

\[
\Delta T = \left( 1.2 \text{ mol}\% \times 4.7 \text{ °C/mol}\% \right) + \left( 10.9 \text{ mol}\% \times 2.8 \text{ °C/mol}\% \right) + \left( 2.3 \text{ mol}\% \times 7.6 \text{ °C/mol}\% \right) + \left( 1.7 \text{ mol}\% \times 2.6 \text{ °C/mol}\% \right) = 57 \text{ °C}
\]

\[
T_{\text{CaCl}_2}^{\text{measured}} = T_{\text{CaCl}_2}^{\text{pure}} - \Delta T
\]

\[
= 775 - 57
\]

\[
= 718 \text{ °C}
\]
System CaCl$_2$-KCl

System CaCl$_2$-MgCl$_2$

System CaCl$_2$-NaCl

System CaCl$_2$-MnCl$_2$

(Source: Levin, 1964)
Appendix E. Statistical Analysis

E.1 Ea uncertainty

The following statistical analysis is used to calculate the percent error in the Ea values obtained from Arrhenius plots through linear regression. Recall the reaction rate constant equation \( k \) is given by
\[
k = k_0 e^{-\frac{E_a}{RT}},
\]
where \( \frac{E_a}{R} \) is obtained from the slope of the plot of \( \ln k \) versus \( \frac{1}{T} \) (Arrhenius plot) and \( \ln k_0 \) is obtained from the intercept of the same plot.

\( B \) = Experimental Slope
\( X \) = Independent variable
\( Y \) = Dependent variable
\( \bar{X} \) = Average \( X \) values
\( \bar{Y} \) = Average \( Y \) values
\( y = Y - \bar{Y} \)
\( x = X - \bar{X} \)
\[
d^2 = \sum y^2 - \left( \sum x^2 \right) B^2
\]
\( N \) = Number of data points
\( \nu = N - 2 = \text{Degree of freedom} \)
\[
S_{y,x}^2 = \frac{d^2}{\nu}
\]
\[
\hat{S}_x^2 = \frac{\sum x^2}{N}
\]
\[
\hat{S}_y^2 = \left( \frac{N - 2}{N^2} \right) S_{y,x}^2 \left[ \frac{1}{\hat{S}_x^2} \right]
\]
\( \alpha_b \) = Confidence interval chosen for the slope
\( t_b \) = Obtained from the 2-sided \( t \) distribution corresponding to \( \alpha_b \) and \( \nu \) [Pearson, 1958]
\[ \Delta B = \left( \frac{\hat{S}_b \sqrt{N}}{\sqrt{\nu}} \right) t_{\nu} \]

\[ B_{\text{true}} = B \pm \Delta B \]

E.2 In \( k_o \) uncertainty

\( \alpha = \) intercept of the Arrhenius plot

\[ \hat{S}_{\alpha}^2 = \left( \frac{N - 2}{N^2} \right) S_{r.x}^2 \left[ 1 + \frac{\bar{X}^2}{\hat{S}_x^2} \right] \]

\( \alpha_\alpha = \) Confidence interval chosen for the intercept

\[ t_\alpha = \text{Obtained from the 2-sided t distribution corresponding to } \alpha_\alpha \text{ and } \nu \ [\text{Pearson, 1958}] \]

\[ \Delta \alpha = \left( \frac{\hat{S}_\alpha \sqrt{N}}{\sqrt{\nu}} \right) t_\alpha \]

\[ \alpha_{\text{true}} = \alpha \pm \Delta \alpha \]

E.3 Adequacy tests

The following statistical analysis is conducted to test the adequacy of the least squares linear regression used to determine the \( E_a \) and \( k_o \) from Arrhenius plots.

\[ z_j = \sqrt{B \sum (xy)} \]

\( \nu' = p - 1 \), where \( p \) is the number of variables, \( (p = 2 \) in this case, corresponding to \( X \) and \( Y \))

\[ F_{\text{MLR}} = \frac{\frac{1}{\sqrt{\nu}} \sum_{j=1}^{p-1} x_j^2}{\frac{1}{\sqrt{\nu}} \sum_{i=1}^{N} d_i^2} \]
The computed $F_{MLR}$ is compared to $F_{v,v',\alpha}$ obtained from the F distribution table [Pearson, 1958]. If $F_{MLR} \leq F_{v,v',\alpha}$, then the regression is not statistically significant at a confidence level $P_\alpha = 1 - \alpha$; accordingly, if $P_\alpha$ is small (e.g. < 90%), then the regression is inadequate. On the other hand, if $F_{MLR} \geq F_{v,v',\alpha}$ and $P_\alpha$ is large, then the regression is adequate. Note that the percent error decreases as the number of experimental data points increases, and that the significance of the analysis increases as the number of experimental data points increases.

The above procedures were applied to the data obtained for Zn, Pb, and Cu in order to determine the inaccuracy in $E_a$ and $k_0$ and to test the adequacy of the linear regression used to obtain these parameters for each element. The results are included on the following pages.
**Zn removal: ln k vs. 1/T - [500 - 650 °C]**

![Graph showing ln k vs. 1/T](image)

**Slope:** -14140.62

**Intercept:** 11

**Ea (kJ/mol):** 117565.1

**k_0:** 5.99E+04

**Ea (round):** 117,600

**Table:**

<table>
<thead>
<tr>
<th>B = Slope</th>
<th>N = 5</th>
<th>p = 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y = ln k</td>
<td>X = 1/T</td>
<td>y = Y - Yave</td>
</tr>
<tr>
<td>-7.21</td>
<td>0.00129</td>
<td>-1.665</td>
</tr>
<tr>
<td>-6.32</td>
<td>0.00122</td>
<td>-0.776</td>
</tr>
<tr>
<td>-5.10</td>
<td>0.00115</td>
<td>0.445</td>
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<td>-4.88</td>
<td>0.00111</td>
<td>0.665</td>
</tr>
<tr>
<td>-4.21</td>
<td>0.00108</td>
<td>1.331</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Yave</th>
<th>Xave</th>
<th>Sum xy</th>
<th>Sum y^2</th>
<th>Sum x^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5.54E+00</td>
<td>1.17E-03</td>
<td>-4.04E-04</td>
<td>5.78E+00</td>
<td>2.86E-08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>d^2</th>
<th>S^2_YX</th>
<th>S^2_x</th>
<th>S^2_B</th>
<th>S^B</th>
<th>v = N - 2</th>
<th>v' = p - 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.065</td>
<td>0.022</td>
<td>5.72E-09</td>
<td>4.54E+05</td>
<td>673.7</td>
<td>3</td>
<td>1</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>alpha / 2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>2.353</td>
</tr>
</tbody>
</table>

**A = intercept**

<table>
<thead>
<tr>
<th>alpha / 2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>5.841</td>
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</tbody>
</table>

**Table for Z and Z^2**

<table>
<thead>
<tr>
<th>Z</th>
<th>Z^2</th>
<th>F_MLR</th>
<th>F_alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.39</td>
<td>5.72</td>
<td>264.3</td>
<td>167.0</td>
</tr>
</tbody>
</table>

Since F_MLR > F_alpha and v, high confidence level, linear regression model is very good.
### Zn removal: \( \ln k \) vs. \( 1/T \) - [700 - 900 °C]

#### Graph

*Equation*
\[
y = -8512.29 x + 6.68
\]

*\( R^2 = 0.90 \)*

#### Table 1: Regression Analysis

<table>
<thead>
<tr>
<th>( Y = \ln k )</th>
<th>( x = 1/T )</th>
<th>( y = Y - Y_{\text{ave}} )</th>
<th>( x = X - X_{\text{ave}} )</th>
<th>( xy )</th>
<th>( y^2 )</th>
<th>( x^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.94</td>
<td>0.00103</td>
<td>0.00009</td>
<td>-0.00006</td>
<td>0.409</td>
<td>8.16E-09</td>
<td></td>
</tr>
<tr>
<td>-1.54</td>
<td>0.00093</td>
<td>-0.240</td>
<td>-0.00001</td>
<td>0.057</td>
<td>2.96E-11</td>
<td></td>
</tr>
<tr>
<td>-0.42</td>
<td>0.00086</td>
<td>0.879</td>
<td>-0.00008</td>
<td>0.773</td>
<td>7.21E-09</td>
<td></td>
</tr>
</tbody>
</table>

#### Table 2: Summary Statistics

<table>
<thead>
<tr>
<th>( Y_{\text{ave}} )</th>
<th>( X_{\text{ave}} )</th>
<th>Sum ( xy )</th>
<th>Sum ( y^2 )</th>
<th>Sum ( x^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.37E-04</td>
<td>1.06</td>
<td>-1.31E-04</td>
<td>1.24E+00</td>
<td>1.54E-08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( d^2 )</th>
<th>( S^2_{YX} )</th>
<th>( S^2_X )</th>
<th>( S^2_B )</th>
<th>( S_B^2 )</th>
<th>( v = N - 2 )</th>
<th>( \nu = p - 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.123</td>
<td>0.123</td>
<td>5.13E-09</td>
<td>2.66E+06</td>
<td>1832.2</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

#### Table 3: Critical Values

<table>
<thead>
<tr>
<th>( \alpha / 2 )</th>
<th>( t_{\alpha} )</th>
<th>( S^2_{\alpha} )</th>
<th>( S_{\alpha} )</th>
<th>( \Delta A )</th>
<th>( \Delta (k_0) )</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>6.314</td>
<td>17850</td>
<td>148402</td>
<td>210%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Table 4: MLR and Alpha Values

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( Z^2 )</th>
<th>( F_{\text{MLR}} )</th>
<th>( F_{\alpha} )</th>
<th>( k_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06</td>
<td>1.12</td>
<td>9.1</td>
<td>39.9</td>
<td></td>
</tr>
</tbody>
</table>

*Since \( F_{\text{MLR}} < F_{\alpha} \) and low confidence level, linear regression model is weak.*
Pb removal: ln k vs. 1/T - [500 - 650 °C]

Slope: -20665.03
Intercept: 20.41
Ea (kJ/mol): 171809.1
k₀: 7.31E+08
Ea (round): 171800

\[ y = -20665.03x + 20.41 \]
\[ R^2 = 0.97 \]

<table>
<thead>
<tr>
<th>B = Slope</th>
<th>N =</th>
<th>5</th>
<th>p =</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y = ln k</td>
<td>X = 1/T</td>
<td>y = Y - Yave</td>
<td>x = X - Xave</td>
<td>xy</td>
</tr>
<tr>
<td>-6.44</td>
<td>0.00129</td>
<td>-2.662</td>
<td>0.00012</td>
<td>-0.00033</td>
</tr>
<tr>
<td>-4.34</td>
<td>0.00122</td>
<td>-0.562</td>
<td>0.00004</td>
<td>-0.00003</td>
</tr>
<tr>
<td>-3.65</td>
<td>0.00115</td>
<td>0.128</td>
<td>-0.00002</td>
<td>0.00000</td>
</tr>
<tr>
<td>-2.63</td>
<td>0.00111</td>
<td>1.148</td>
<td>-0.00006</td>
<td>-0.00007</td>
</tr>
<tr>
<td>-1.83</td>
<td>0.00108</td>
<td>1.948</td>
<td>-0.00009</td>
<td>-0.00017</td>
</tr>
</tbody>
</table>

Yave | Xave | Sum xy | Sum \( y^2 \) | Sum \( x^2 \) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.78E+00</td>
<td>1.17E+03</td>
<td>-5.91E+04</td>
<td>1.25E+01</td>
<td>2.86E-08</td>
</tr>
</tbody>
</table>

\( d^2 \) | \( S^2_{XY} \) | \( S^2_{x} \) | \( S^2_{B} \) | \( S_B \) | \( v = N - 2 \) | \( v' = p - 1 \) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.317</td>
<td>0.106</td>
<td>5.72E-09</td>
<td>2.21E+06</td>
<td>1488.0</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

alpha / 2 | \( \delta \) | Delta B | Delta (Ea) | % |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>2.353</td>
<td>4520</td>
<td>37,581</td>
<td>21.9%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A = intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha / 2</td>
</tr>
<tr>
<td>1%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Z</th>
<th>( Z^2 )</th>
<th>( F_{MLR} )</th>
<th>( F_{alpha} )</th>
<th>for ( v' = 1, v = 3 ), and 99% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.49</td>
<td>12.21</td>
<td>115.7</td>
<td>34.1</td>
<td></td>
</tr>
</tbody>
</table>

Since \( F_{MLR} > F_{alpha} \) and v. high confidence level, linear regression model is very good.
Pb removal: $\ln k$ vs. $1/T$ - [700 - 900 °C]

**Slope:** 6805.15

**Intercept:** 3.93

**Ea (kJ/mol):** 56578.0

**$k_o$:** 5.09E+01

**Ea (round):** 56,600

<table>
<thead>
<tr>
<th>Y = $\ln k$</th>
<th>X = 1/T</th>
<th>y = Y - Yave</th>
<th>x = X - Xave</th>
<th>xy</th>
<th>$y^2$</th>
<th>$x^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.03</td>
<td>0.00103</td>
<td>-0.579</td>
<td>0.00009</td>
<td>-0.00005</td>
<td>0.335</td>
<td>8.16E-09</td>
</tr>
<tr>
<td>-2.49</td>
<td>0.00093</td>
<td>-0.042</td>
<td>-0.00001</td>
<td>0.00000</td>
<td>0.002</td>
<td>2.96E-11</td>
</tr>
<tr>
<td>-1.83</td>
<td>0.00085</td>
<td>0.621</td>
<td>-0.00008</td>
<td>-0.00005</td>
<td>0.385</td>
<td>7.21E-09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yave</th>
<th>Xave</th>
<th>Sum xy</th>
<th>Sum $y^2$</th>
<th>Sum $x^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.45E-00</td>
<td>9.37E-04</td>
<td>-1.05E-04</td>
<td>7.22E-01</td>
<td>1.54E-08</td>
</tr>
</tbody>
</table>

| $d^2$ | $S_{Y|X}^2$ | $S_x^2$ | $S_{B}^2$ | $S_B^2$ | $v = N - 2$ | $v' = p - 1$ |
|------|-------------|--------|----------|--------|------------|-------------|
| 0.009 | 0.009       | 5.13E-09 | 2.02E-05 | 449.7   | 1           | 1           |

<table>
<thead>
<tr>
<th>alpha / 2</th>
<th>t_a</th>
<th>Delta B</th>
<th>Delta (Ea)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>6.314</td>
<td>4918</td>
<td>40,891</td>
<td>72%</td>
</tr>
</tbody>
</table>

$\alpha = $ Intercept

| alpha / 2 | t_a | $S_{\alpha | A}^2$ | $S_{\alpha}^2$ | Delta A | Delta ($k_o$) | %     |
|-----------|-----|----------------|-------------|----------|---------------|-------|
| 5%        | 6.314 | 0.179        | 0.423       | 4.624    | 1.02E+02      | 2     |

<table>
<thead>
<tr>
<th>Z</th>
<th>$Z^2$</th>
<th>$F_{MLR}$</th>
<th>$F_{alpha}$</th>
<th>for $v' = 1$, $v = 1$, and 90% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.84</td>
<td>0.71</td>
<td>76.3</td>
<td>39.9</td>
<td></td>
</tr>
</tbody>
</table>

Since $F_{MLR} > F_{alpha}$ and low confidence level, linear regression model is good.
### Cu removal: $\ln k$ vs. $1/T$ - [500 - 650 °C]

#### Slope and Intercept
- Slope: $-5979.91$
- Intercept: $0.26$
- $E_a$ (kJ/mol): $49717.0$
- $E_a$ (round): $49,700$

#### Statistical Analysis

<table>
<thead>
<tr>
<th>$Y = \ln k$</th>
<th>$X = 1/T$</th>
<th>$y = Y - Y_{ave}$</th>
<th>$x = X - X_{ave}$</th>
<th>$xy$</th>
<th>$y^2$</th>
<th>$x^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-6.59</td>
<td>0.00115</td>
<td>-0.186</td>
<td>0.00003</td>
<td>-0.00001</td>
<td>0.034</td>
<td>9.63E-10</td>
</tr>
<tr>
<td>-6.21</td>
<td>0.00108</td>
<td>0.186</td>
<td>-0.00003</td>
<td>-0.00001</td>
<td>0.034</td>
<td>9.63E-10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$Y_{ave}$</th>
<th>$X_{ave}$</th>
<th>Sum $xy$</th>
<th>Sum $y^2$</th>
<th>Sum $x^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-6.40E+00</td>
<td>1.11E-03</td>
<td>-1.15E-05</td>
<td>8.88E-02</td>
<td>1.93E-09</td>
</tr>
</tbody>
</table>

#### Alpha / Beta
- $\alpha / \beta$: 5%
- $\delta (\alpha) / \delta (\beta)$: 2.353

**Note:** The statistical analysis is not applicable in this case due to the lack of data.
Cu removal: ln k vs. 1/T - [700 - 900 °C]

![Graph showing ln k vs. 1/T](image)

- Slope: $-6701.36$
- Intercept: $1.07$
- $E_a$ (kJ/mol): $55715.1$
- $k_0$: $2.92E+00$
- $E_a$ (round): $55,700$

<table>
<thead>
<tr>
<th>B = Slope</th>
<th>N = 3</th>
<th>p = 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y = \ln k$</td>
<td>$X = 1/T$</td>
<td>$y = Y - Y_{ave}$</td>
</tr>
<tr>
<td>-5.70</td>
<td>0.00103</td>
<td>-0.490</td>
</tr>
<tr>
<td>-5.43</td>
<td>0.00093</td>
<td>-0.218</td>
</tr>
<tr>
<td>-4.50</td>
<td>0.00085</td>
<td>0.708</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$Y_{ave}$</th>
<th>$X_{ave}$</th>
<th>$\text{Sum } xy$</th>
<th>$\text{Sum } y^2$</th>
<th>$\text{Sum } x^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5.21E+00</td>
<td>9.37E-04</td>
<td>-1.03E-04</td>
<td>7.89E-01</td>
<td>1.54E-08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$d^2$</th>
<th>$S_{YX}^2$</th>
<th>$S_x^2$</th>
<th>$S_B^2$</th>
<th>$S_B^\hat{\alpha}$</th>
<th>$\nu = N - 2$</th>
<th>$\nu' = p - 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.097</td>
<td>0.097</td>
<td>5.13E-09</td>
<td>2.10E+06</td>
<td>1449.8</td>
<td>1</td>
<td>1</td>
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</table>

<table>
<thead>
<tr>
<th>alpha / 2</th>
<th>$t_a$</th>
<th>Delta B</th>
<th>Delta (Ea)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>6.314</td>
<td>15855</td>
<td>131,516</td>
<td>237%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A = Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>alpha / 2</th>
<th>$t_a$</th>
<th>$S_{\hat{\alpha}}^2$</th>
<th>$S_{\hat{\alpha}}$</th>
<th>Delta A</th>
<th>Delta (K_a)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>6.314</td>
<td>1.855</td>
<td>1.365</td>
<td>14.906</td>
<td>2.97E+06</td>
<td>1020438</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Z</th>
<th>$Z^2$</th>
<th>$F_{\text{MLR}}$</th>
<th>$F_{\text{alpha}}$</th>
<th>for $\nu' = 1$, $\nu = 1$, and 90% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>0.69</td>
<td>7.1</td>
<td>39.9</td>
<td></td>
</tr>
</tbody>
</table>

Since $F_{\text{MLR}} < F_{\text{alpha}}$ and low confidence level, linear regression model is weak.