



Thermodynamic analysis of the selective chlorination of electric arc furnace dust

C.A. Pickles*

Department of Mining Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6

ARTICLE INFO

Article history:

Received 19 August 2008

Received in revised form 29 October 2008

Accepted 30 November 2008

Available online 6 December 2008

Keywords:

Electric arc furnace

Dust

Thermodynamics

Selective

Chlorination

ABSTRACT

The remelting of automobile scrap in an electric arc furnace (EAF) results in the production of a dust, which contains high concentrations of the oxides of zinc, iron, calcium and other metals. Typically, the lead and zinc are of commercial value, while the other metals are not worth recovering. At the present time, EAF dusts are treated in high temperature Waelz rotary kiln-type processes, where the lead and zinc oxides are selectively reduced and simultaneously reoxidized and a crude zinc oxide is produced. Another alternative processing route is selective chlorination, in which the non-ferrous metals are preferentially chlorinated to their gaseous chlorides and in this manner separated from the iron. In the present research, a detailed thermodynamic analysis of this chlorination process has been performed and the following factors were investigated; temperature, amount of chlorine, lime content, silica content, presence of an inert gas and the oxygen potential. High lead and zinc recoveries as gaseous chlorides could be achieved but some of the iron oxide was also chlorinated. Additionally, the calcium oxide in the dust consumes chlorine, but this can be minimized by adding silica, which results in the formation of stable calcium silicates. The optimum conditions were determined for a typical dust composition. The selectivities achieved with chlorination were lower than those for reduction, as reported in the literature, but there are other advantages such as the potential recovery of copper.

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1. Introduction

In most countries, electric arc furnace (EAF) dust is considered to be a hazardous waste because of the presence of lead, cadmium, chromium and zinc. It is generated when automobile scrap is remelted in an electric arc furnace and about 10–20 kg are generated per ton of steel produced. The dust formation mechanism is relatively complex but it is believed that the dust forms as a result of the following processes: (i) the vaporization of elements and the formation of droplets in the vicinity of the arc and the oxygen jet, (ii) the formation of droplets as a result of the bursting of carbon monoxide gas bubbles at the slag–gas interface, (iii) the entrainment of low density furnace additives such as carbon and lime, and (iv) possibly the bursting of slag droplets that have been ejected into the furnace atmosphere [1]. As a result of the presence of numerous elements in the scrap and the dust formation mechanism, the dust is chemically, physically and mineralogically complex. Furthermore, the properties of each dust are site-specific since they depend upon the scrap composition and the furnace operating practice. Considerable research effort has been devoted to characterizing the dusts from steel plants in various countries [2–9]. The major elements present in the dust are usually zinc, iron

and calcium. Numerous other elements are found in low concentrations such as lead, silicon, aluminium, manganese, magnesium, chromium, nickel, copper and cadmium. Most of these elements are found in combination with oxygen but there can also be chlorides, fluorides, sulphates and sulphides. Typically, the zinc is found as zincite (ZnO), zinc ferrite or franklinite (ZnFe_2O_4), zinc chloride (ZnCl_2) and diiron zinc tetraoxide (Fe_2ZnO_4). The rest of the iron may be present as hematite (Fe_2O_3), magnetite (Fe_3O_4) or in combination with lime (CaO) as calcium ferrites or with silica as iron silicates. The lead is typically found as lead oxide (PbO) and lead chloride (PbCl_2). The amounts of zinc and lead in the dust are of economic value, while the iron is usually not worth recovering.

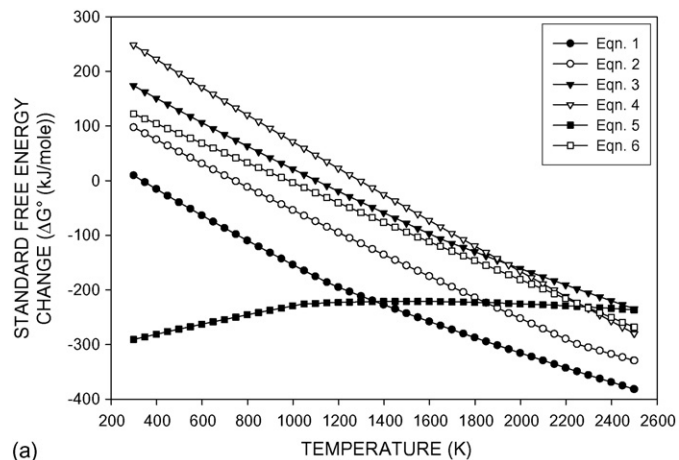
There are two major methods for treating the dust: recycling for metals recovery or stabilization for landfilling [10–18]. Numerous metal recovery processes have been developed that utilize either pyrometallurgical, hydrometallurgical or hybrid pyro-hydro techniques. However, only the pyrometallurgical or High Temperature Metals Recovery (HTMR) processes have achieved commercial success and this is mainly limited to variations of the Waelz rotary kiln process [19–25]. The dust is reacted with carbonaceous material and the zinc and lead oxides are reduced to metallic form and simultaneously vaporize, as well as any metal chlorides and fluorides. The non-ferrous metal oxides can be selectively reduced and the iron can be maintained in oxide form or the iron oxide can be reduced to metallic iron, if the price of iron is sufficiently high. Selective

* Tel.: +1 613 533 2759; fax: +1 613 533 6597.

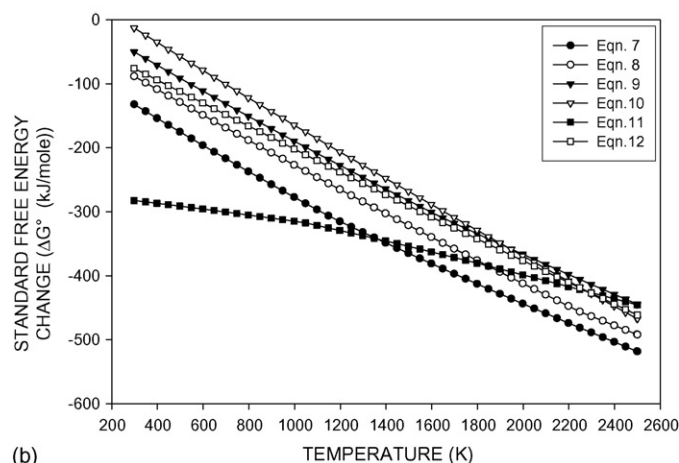
E-mail address: pickles-c@mine.queensu.ca.

reduction is based on the lower stabilities of the non-ferrous metal oxides in comparison to iron oxide (FeO) and is achieved by limiting the temperature and the amount of the reducing agent. Also, the boiling point of zinc is lower than the operating temperature of the HTMR process, while the vapour pressure of lead is sufficiently high, such that it concentrates with the zinc in the vapour phase. In general, the recovery of the non-ferrous metals in metallic form is usually not feasible and therefore they are recovered in oxidized form. This crude zinc oxide typically contains most of the zinc, the lead, the halides and small amounts of other species. The calcium oxide, silica, alumina and other unreduced oxides are collected as an oxide residue or clinker.

Although numerous reducing agents have been proposed for EAF dust, such as various carbonaceous materials [26–29], carbon monoxide [30–36], hydrogen [37–41], methane [42] and metallic iron [43–50], the favoured reducing agent is coal. In addition, the combustion of the coal can provide a significant amount of energy for the endothermic reduction reactions. The major disadvantage of coal is the presence of impurities such as sulphur, which can concentrate in the oxide residue or in any metallic iron, which may have been reduced. Also, if metallic iron is produced then it will contain considerable carbon, which is considered as an impurity if the iron is to be utilized as a feed for steelmaking. Additionally, the oxidation of carbon results in the production of carbon dioxide, which is a greenhouse gas. There are numerous other impurities in the dust and these will distribute themselves between the crude zinc oxide, the oxide residue and any metallic iron that is formed.



(a)



(b)

Fig. 1. Standard free energy changes of the (a) chlorination and (b) carbochlorination reactions.

Table 1

Species considered in the equilibrium calculations for the dust. The species that were considered in the pure oxide mixture calculations are shown in bold.

Gases	Oxides	Oxides	Chlorides	Elements
Al	Al ₂ O ₃	2CaO·SiO ₂	AlCl ₃	Al
Al ₂	Al ₂ O ₃ ·SiO ₂ (A)	3CaO·SiO ₂	Al ₂ Cl ₆	Ca
AlCl	Al ₂ O ₃ ·2SiO ₂	3CaO·2SiO ₂	CaCl ₂	Fe
AlCl ₂	3Al ₂ O ₃ ·2SiO ₂	CaSiO ₃	FeCl₂	Pb
AlCl ₃	Al ₂ SiO ₅	Ca ₂ SiO ₄ (L)	FeCl₃	Si
Al ₂ Cl ₄	CaAl ₂ O ₄	Ca ₃ SiO ₅	PbCl₂	Zn
Al ₂ Cl ₆	CaAl ₁₂ O ₁₉	Ca ₃ Si ₂ O ₇	ZnCl₂	C
AlO	Ca ₂ Al ₂ O ₅	Ca ₃ Si ₂ O ₇ ·2CaCO ₃		
AlO ₂	CaAl ₂ SiO ₆	2Ca ₂ SiO ₄ ·CaCO ₃		
Al ₂ O	CaAl ₂ Si ₂ O ₈	FeAl ₂ O ₄		
CO	Ca ₂ Al ₂ SiO ₇	Fe ₂ Al ₄ Si ₅ O ₁₈		
CO ₂	Ca ₃ Al ₂ Si ₃ O ₁₂	Fe ₃ Al ₂ Si ₃ O ₁₂		
O₂	Ca ₃ (Al ₂ Si ₂ O ₈) ₃ ·CaCO ₃	FeCO₃		
Ca	CaCO ₃	FeO		
CaO	CaFe ₃ O ₅	Fe₂O₃		
CaCl	CaFe ₅ O ₇	Fe₃O₄		
CaCl ₂	(CaFe) _{0.5} SiO ₃	FeO·SiO ₂		
Cl₂	CaFeSiO ₄	2FeO·SiO ₂		
Fe	CaFe(SiO ₃) ₂	FeSiO ₃		
Fe₂	Ca ₃ Fe ₂ Si ₃ O ₁₂	Fe ₂ SiO ₄ (B)		
FeCl	CaO	Fe₂ZnO₄		
FeCl₂	CaO·Al ₂ O ₃	PbCO₃		
FeCl₃	CaO·2Al ₂ O ₃	PbO		
Fe₂Cl₄	CaO·6Al ₂ O ₃	PbO₂		
Fe₂Cl₆	2CaO·Al ₂ O ₃	Pb₂O₃		
FeO	3CaO·Al ₂ O ₃	Pb₃O₄		
Pb	12CaO·7Al ₂ O ₃	PbO·PbCO ₃		
Pb₂	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	2PbO·PbCO ₃		
PbCl₂	CaO·Al ₂ O ₃ ·SiO ₂	SiO ₂		
PbCl₃	CaO·Al ₂ O ₃ ·2SiO ₂	ZnCO₃		
PbCl₄	2CaO·Al ₂ O ₂ ·SiO ₂	ZnFe₂O₄		
PbO	2CaO·Al ₂ O ₃ ·8SiO ₂	ZnO		
Si	3CaO·Al ₂ O ₃ ·3SiO ₂	ZnO·Al ₂ O ₃		
SiCl	CaO·Fe ₂ O ₃	ZnSiO ₃		
SiCl ₂	2CaO·Fe ₂ O ₃	Zn ₂ SiO ₄		
SiCl ₃				
SiCl ₄				
SiO				
Zn				
ZnCl₂				
Zn₂Cl₄				
ZnO				

2. Thermodynamics of chlorination reactions

An alternative method for pyrometallurgical treatment of EAF dust is to utilize chlorine as a reagent to selectively chlorinate both the lead and the zinc and separate them from the iron, which remains in oxide form. The potential advantages of selective chlorination include separation of the non-ferrous metals from the iron, the elimination of carbon as a contaminant of any metallic iron product, the chlorine reagent can be recycled, there are no greenhouse gas emissions due to carbon dioxide and finally other elements such as copper can be recovered. In a manner similar to selective reduction, selective chlorination is achieved by limiting the temperature and/or the amount of the chlorinating agent. In the present research, a detailed thermodynamic study was performed on the chlorination of EAF dust.

There is very little information in the literature on the chlorination of EAF dust. Wang et al. performed a thermodynamic study of the reaction of EAF dust with ferrous chloride (FeCl₂) and showed that the lead, zinc, cadmium and copper oxides can be converted into gaseous chlorides in the temperature range of 873 to 1173 K [51]. The removal efficiency of zinc was in the range of 96–98%, but this decreased above about 1223 K. For dusts with high calcium oxide contents, it was found that the addition of silica improved the removal efficiency of the non-ferrous metals. Matsuura and Tsukihashi performed a study of the chlorination kinetics of a mix-

ture of zinc oxide, zinc ferrite, lead oxide and hematite using an Ar–O₂–Cl₂ gas mixture in the temperature range of 1023–1273 K [52]. They concluded that selective chlorination and evaporation of the lead and zinc was possible and a high degree of selectivity could be achieved. On the other hand, Lee and Song utilized waste polyvinyl chloride (PVC) as a source of chlorine [53]. Rapid heating rates resulted in ferrous chloride acting as the chlorine provider to the zinc and the lead. About 96% of the zinc and 97% of the lead were recovered at 1073 K. The residue contained about 41% iron and 21% carbon.

In the presence of sufficient chlorine, the chlorination reactions for lead, zinc, iron, calcium oxide and zinc ferrite would be as follows:

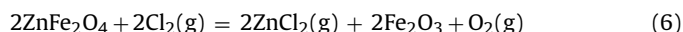
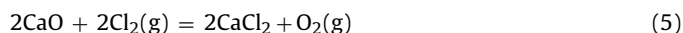
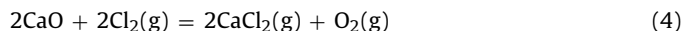
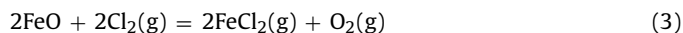
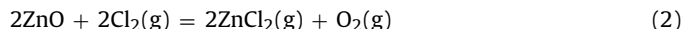
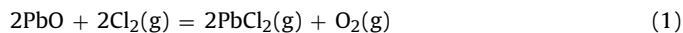
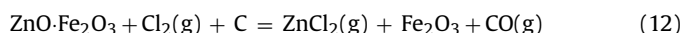
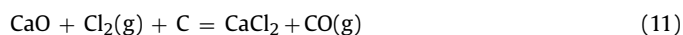
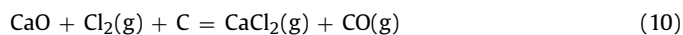
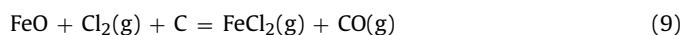
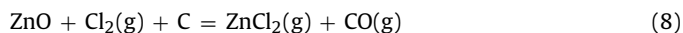
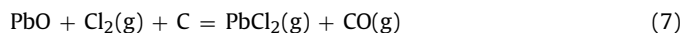


Fig. 1(a) shows the standard free energy changes for these six reactions as a function of temperature. It can be seen that gaseous lead chloride is more stable than gaseous zinc chloride, which in turn is more stable than ferrous chloride. Therefore, separation of the lead and zinc as gaseous chlorides from the iron oxide in the dust should

be feasible. Gaseous calcium chloride is stable at high temperatures, while condensed calcium chloride is stable across the whole temperature range. Therefore, it would be expected that some of the calcium oxide in the dust would be converted to calcium chloride and thus consume chlorine. Also, the chlorination of zinc ferrite to zinc chloride and hematite is thermodynamically feasible at high temperatures.

The chlorination reactions can be made more favourable by the addition of carbon as follows:



The standard free energy changes for these carbochlorination reactions are shown in Fig. 1(b) and by comparing these data with Fig. 1(a) it can be seen that these reactions have much lower free energies than the chlorination reactions. This is due to the formation of carbon monoxide gas, which is stable at high temperatures. However, the relative positions of the lines remain the same and therefore the separation of the lead and the zinc from the iron is again feasible. The formation of condensed calcium chloride is substantially enhanced by the presence of carbon and furthermore

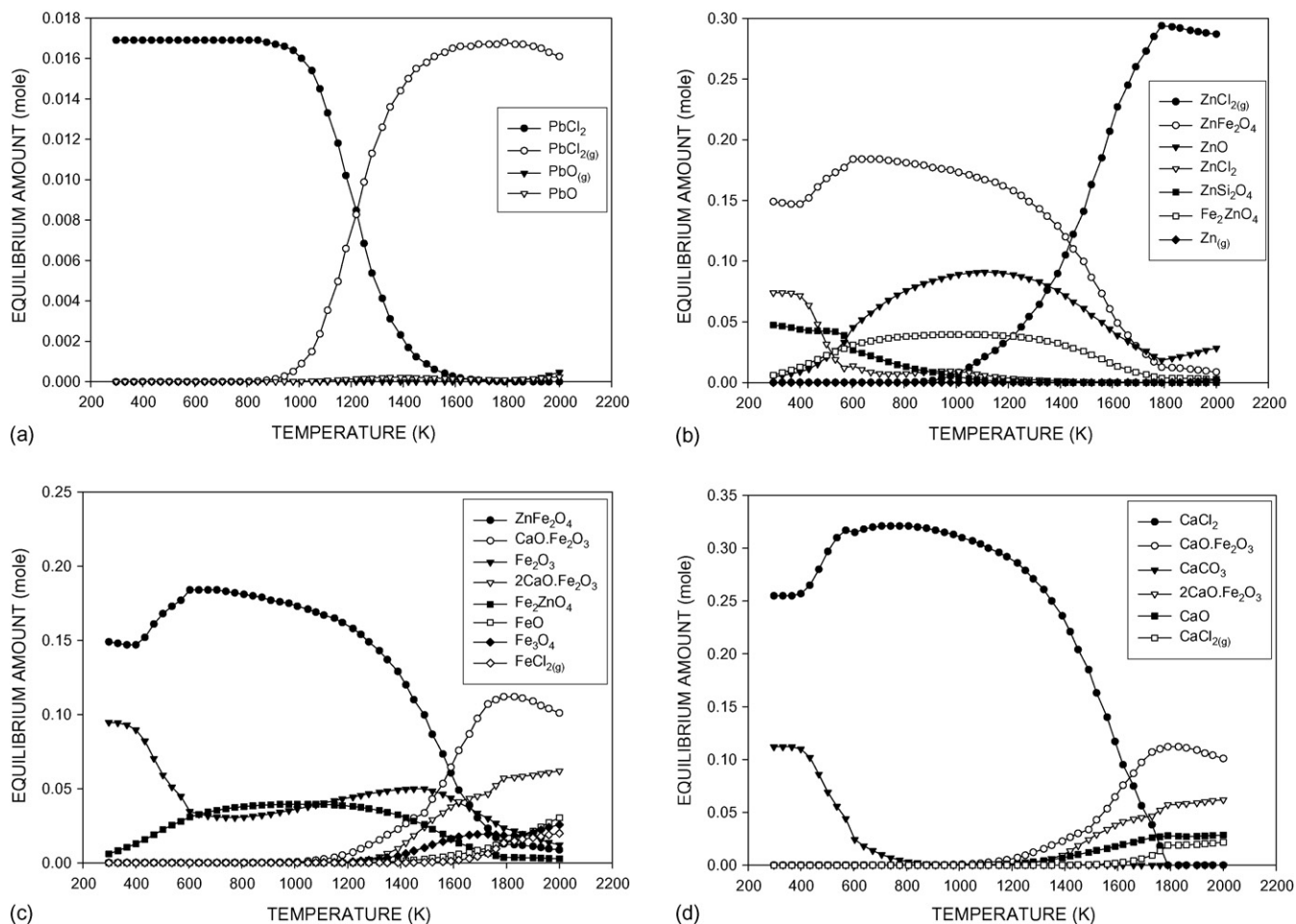


Fig. 2. Equilibrium amounts of (a) lead-, (b) zinc-, (c) iron- and (d) calcium-containing species as a function of temperature for a reactant ratio of 0.345 mol/100 g.

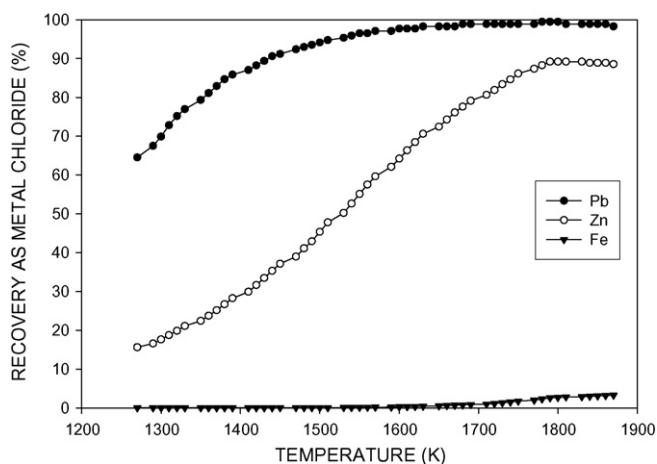


Fig. 3. Lead, zinc and iron recoveries as gaseous metal chloride as a function of temperature for a reactant ratio of 0.345 mol/100 g.

calcium chloride becomes significantly more stable than the lead, zinc and iron chlorides. Therefore, the consumption of chlorine by calcium oxide becomes even more favourable. Again, the zinc oxide in zinc ferrite can be selectively chlorinated to zinc chloride.

3. Equilibrium calculations

The dust was assumed to consist mainly of the oxides of zinc, lead, iron, calcium, silicon and aluminium. In addition, some oxygen and carbon were present as carbon dioxide in carbonates. The control dust composition was as follows (in mass percent): 1.344% C, 14.692% Ca, 27.920% Fe, 28.966% O, 3.500% Pb, 1.603% Si, 0.495% Al and 21.482% Zn. The following species were assumed to be present in the dust (in mass percent): 6.100% CaO, 8.250% 2CaO·SiO₂, 11.200% CaCO₃, 8.830% CaO·Fe₂O₃, 2.000% CaO·Al₂O₃·SiO₂, 7.840% Fe₃O₄, 3.770% PbO, 38.150% ZnFe₂O₄ and 13.860% ZnO. The control mass was 100 g and the total pressure was 1 bar. The amount of chlorine added in the control calculations was 0.345 mol, which was the stoichiometric amount as given by reactions (1), (2) and (6) for the chlorination of both the lead and the zinc oxide in the dust. The compositions of the products resulting from the reaction of the dust with chlorine were calculated using the SOLGASMIX equilibrium module of Outokumpu HSC Chemistry[®] 5.1 [54]. This module uses the Gibbs free energy minimization method to determine the multicomponent equilibrium in a heterogeneous system under the

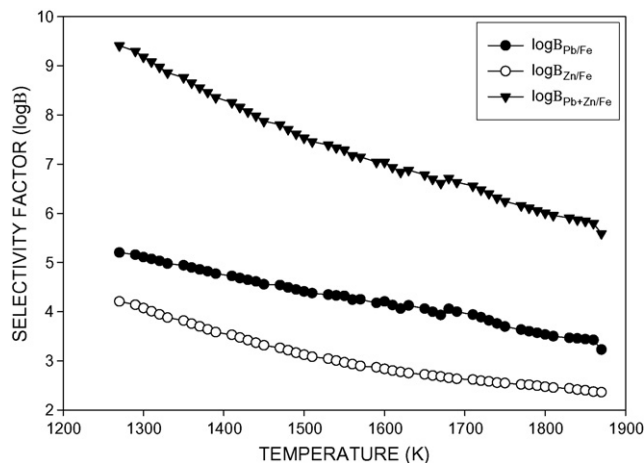


Fig. 4. Lead, zinc and combined lead plus zinc selectivity factors as a function of temperature for a reactant ratio of 0.345 mol/100 g.

constraints of fixed mass, constant pressure and constant temperature. Using lead, zinc, iron, calcium, silicon, aluminium, oxygen, carbon and chlorine as the input elements for the equilibrium module generated a list of 317 species. However, only a limited number of these are present under the equilibrium conditions of this study and these are shown in Table 1 together with those present in the original dust for a total of 126 species. As a result of the selective chlorination process, an iron oxide plus calcium oxide-rich residue is produced and the components in the residue were assumed to mix ideally. For comparison purposes, calculations were also performed for an oxide mixture consisting of only lead oxide, zinc oxide and zinc ferrite. The species considered in this analysis are shown in bold in Table 1 and the number of moles of these species was equivalent to those utilized for the dust and the amount of carbon dioxide was equivalent to that in the dust.

The quantitative parameters utilized in evaluating the chlorination process were as follows:

$$\text{Reaction ratio (RR}_r) = \frac{r \text{ (moles)}}{100 \text{ g dust}} \quad (13)$$

where r is the specific amount of chlorinating agent in moles.

$$\text{Metal recovery (R}_i, \%) = \frac{m_{i,\text{Cl}}}{m_{i,\text{O}}} \times 100 \quad (14)$$

where $m_{i,\text{Cl}}$ is the mass of metal i in chloride form (Cl) and $m_{i,\text{O}}$ is the original mass of i in oxide form (O). The selectivity factors for lead or zinc or the combined lead plus zinc factor were defined as follows:

- For the separation of lead:

$$\beta_{\text{Pb/Fe}} = \frac{X_{\text{PbCl}} Y_{\text{FeO}}}{X_{\text{FeCl}} Y_{\text{PbO}}} \quad (15)$$

- For the separation of zinc:

$$\beta_{\text{Zn/Fe}} = \frac{X_{\text{ZnCl}} Y_{\text{FeO}}}{X_{\text{FeCl}} Y_{\text{ZnO}}} \quad (16)$$

- For the separation of lead plus zinc:

$$\beta_{\text{Pb+Zn/Fe}} = \frac{X_{\text{PbCl}} Y_{\text{FeO}}}{X_{\text{FeCl}} Y_{\text{PbO}}} + \frac{X_{\text{ZnCl}} Y_{\text{FeO}}}{X_{\text{FeCl}} Y_{\text{ZnO}}} \quad (17)$$

where X and Y are the concentrations of the lead, zinc or iron in the chloride phase (Cl) or in the oxide phase (O), respectively. It is convenient to utilize $\log \beta$, which typically varies from 1 to 10.

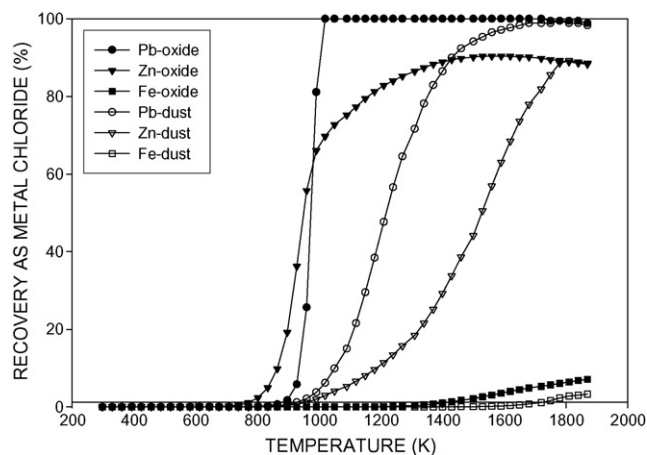


Fig. 5. Comparison of the lead, zinc and iron recoveries as metal chloride as a function of temperature for a lead-zinc-iron oxide mixture (oxide) and also for the EAF dust (dust). The stoichiometric amount of chlorine (0.345 mol) was utilized in the calculations.

4. Selective chlorination of lead and zinc in EAF dust

4.1. Effect of temperature

The effect of temperature in the range of 298 to 1998 K on the behaviours of the lead, zinc, iron and calcium-containing species are shown in Fig. 2(a), (b), (c) and (d), respectively. The reactant ratio of 0.345 mol/100 g was the stoichiometric amount as given by reactions (1), (2) and (6) for lead and zinc oxide. The behaviours of the lead-containing species are shown in Fig. 2(a) and the equilib-

rium maximum amount of lead chloride would be 0.017 mol. Lead chloride is stable across the whole temperature range and converts from the condensed to the gaseous state from about 900 to 1550 K, where a maximum value is reached. Thereafter, the amount remains essentially constant until about 1900 K and then decreases. Both condensed and gaseous lead monoxide begin to form above about 1000 K, and their amounts increase slowly with increasing temperature, as the conditions become slightly more oxidizing for lead.

For the zinc-containing species, as shown in Fig. 2(b), the major species at room temperature are zinc silicate, zinc ferrite and con-

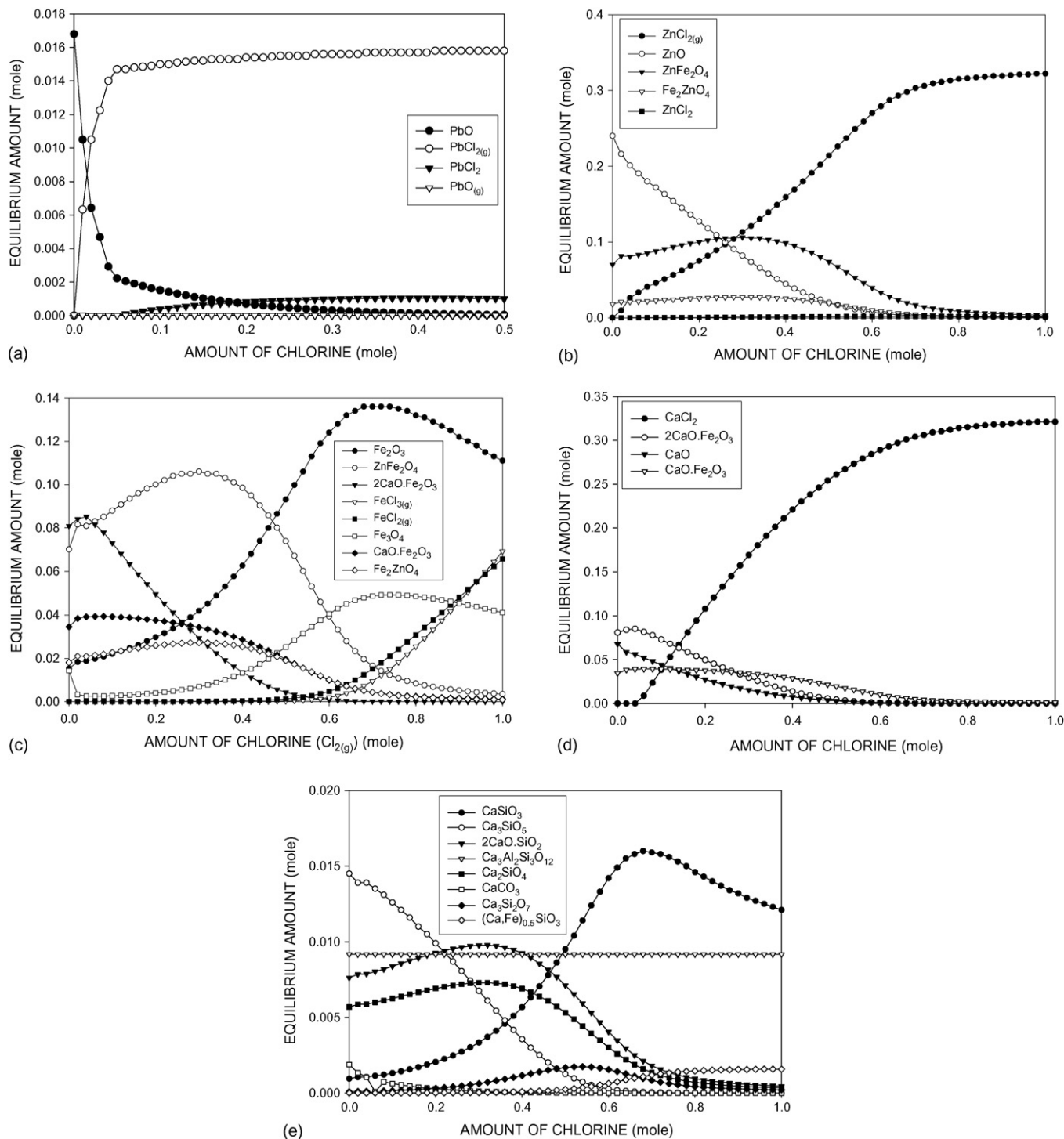


Fig. 6. Equilibrium amounts of (a) lead-containing species, (b) zinc-containing species, (c) iron-containing species, (d) calcium chloride, calcium oxide and the calcium ferrites, and (e) calcium carbonate and the calcium silicates as a function of the amount of chlorine for a temperature of 1473 K.

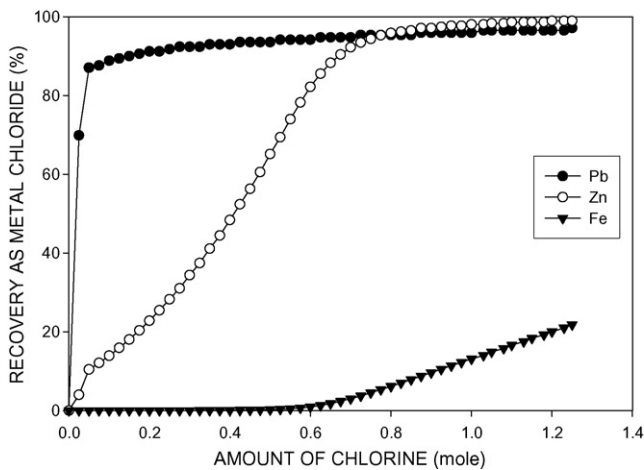


Fig. 7. Lead, zinc and iron recoveries as gaseous metal chloride as a function of the amount of chlorine for a temperature of 1473 K.

densified zinc chloride. The equilibrium maximum amount of zinc chloride would be 0.329 mol. With increasing temperature, the predominant species become diiron zinc tetraoxide, zincite and zinc ferrite. At about 900 K, gaseous zinc chloride begins to form in ever-increasing amounts and this consumes the other zinc-containing species and consequently their amounts continuously decrease. The amount of gaseous zinc chloride reaches a maximum value at about 1800 K, and then begins to decrease. Simultaneously, the amount of zinc oxide begins to increase, indicating that the conditions are becoming oxidizing with respect to zinc. Additionally, a small amount of gaseous metallic zinc is formed at these higher temperatures.

As shown in Fig. 2(c), the major iron-containing species at room temperature are zinc ferrite and hematite. The maximum equilibrium amount of iron chloride would be 0.5 mol. In the intermediate temperature range, these species continue to exist with increasing temperature, with hematite decreasing and zinc ferrite increasing and additionally diiron zinc tetraoxide begins to form. However, as the temperature increases above about 1000 K, their amounts are diminished by the sequential formation of monocalcium ferrite, dicalcium ferrite, magnetite, wustite and gaseous iron chloride. The amount of iron chloride becomes significant at the high end of the temperature range. As shown in Fig. 2(d), the major calcium-containing species at room temperature are condensed calcium chloride and calcium carbonate. As the temperature increases, the

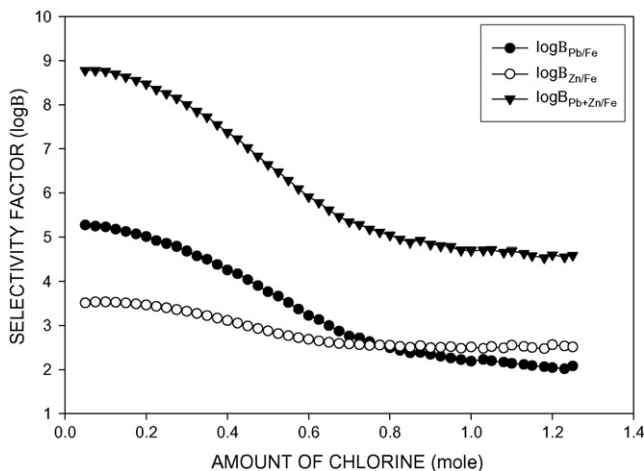


Fig. 8. Lead, zinc and combined lead plus zinc selectivity factors as a function of the amount of chlorine for a temperature of 1473 K.

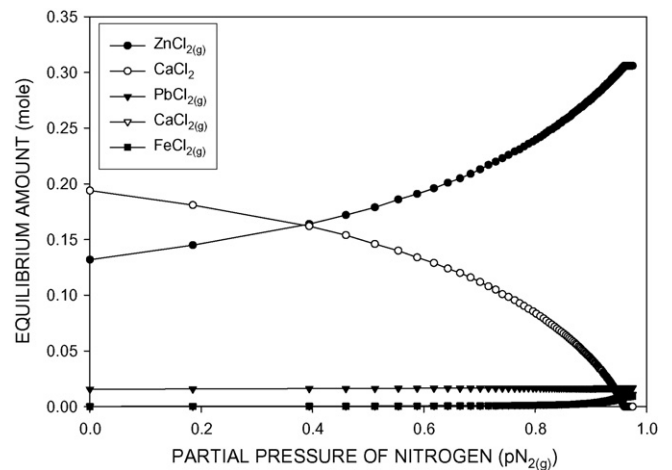


Fig. 9. Effect of partial pressure of nitrogen on the equilibrium amounts of lead, zinc, iron and calcium chlorides at 1473 K and a reactant ratio of 0.345 mol/100 g.

calcium carbonate is converted to calcium chloride, which predominates over the intermediate temperature range. As mentioned previously, at about 1000 K, monocalcium ferrite begins to form and as the temperature increases this is followed by dicalcium ferrite, calcium oxide and gaseous calcium chloride. Thus, some of the chlorine is consumed to form gaseous calcium chloride and the amount becomes significant at the higher end of the temperature range.

The effect of temperature on the recoveries of lead, zinc and iron in the temperature range of 1273–1873 K is shown in Fig. 3, for the control conditions. The lead recovery reached about 98% at about 1650 K, attained a maximum value of about 99.5% at about 1800 K and then decreased slightly. The zinc recovery reached a maximum value of about 90% at 1800 K, before decreasing slightly. Above about 1550 K, the formation of gaseous iron chloride became significant and this contributed to the decreased recoveries of the lead and zinc chlorides.

The selectivity factors for lead, zinc and lead plus zinc in the dust are shown as a function of temperature in Fig. 4. Despite a general trend of increasing recoveries of lead and zinc chlorides with increasing temperature, as discussed previously in Fig. 3, it can be seen that the selectivity factors decrease with increasing temperature. This decrease is mainly attributed to the formation of an increasing amount of gaseous iron chloride with increasing temperature. For both lead and zinc, the metal recoveries and the amount of gaseous iron chloride are low, at low temperatures and this low-

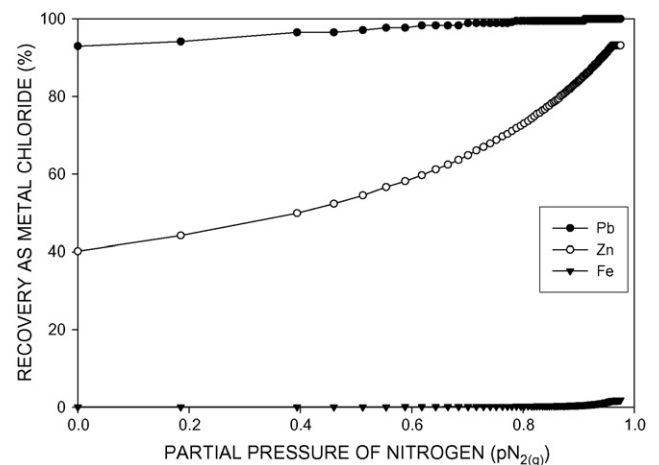


Fig. 10. Lead, zinc and iron recoveries as metal chloride as a function of the partial pressure of nitrogen at 1473 K and a reactant ratio of 0.345 mol/100 g.

ers the selectivity factors. Despite an increasing non-ferrous metal recovery with increasing temperature, the amount of gaseous iron chloride increases and this lowers the selectivity factors. Therefore, the lead plus zinc selectivity factors are low and follow a similar trend as the two individual non-ferrous metals. These results demonstrate the inherent difficulty of achieving high selectivities using chlorine gas as a reagent.

The temperatures for significant recoveries of lead and zinc reported in the above discussion are considerably higher than those reported in the literature [51,52]. Therefore, calculations were performed in order to compare the chlorination temperatures required for both the control dust composition and the metal oxide mixture and the results are shown in Fig. 5. The stoichiometric amount of chlorine (0.345 mol) was utilized. It can be seen that the temperatures required for the maximum lead and zinc recoveries are about 700 and 400 K lower, respectively, for the metal oxide mixture than for the actual EAF dust. The values for the metal oxide mixture are closer to those reported in the literature but still somewhat higher and this likely reflects differences in the thermodynamic data utilized, the calculation method and the conditions selected. However, it is clear that the recovery of the non-ferrous metal chlorides from EAF dust by a chlorination process is more difficult than would be predicted based on calculations for either the non-ferrous and ferrous metal oxides or even mixtures of these oxides.

4.2. Effect of chlorine gas

The effects of the amount of chlorine gas added on the behaviour of the lead, zinc, iron and calcium-containing species at 1473 K are shown in Fig. 6(a)–(e). As shown in Fig. 6(a), the amount of gaseous lead chloride initially increases rapidly

up to a chlorine addition of 0.05 mol and then increases very slowly. Correspondingly, the amount of condensed lead monoxide decreases rapidly and then more slowly. Gaseous lead monoxide is present only in very small amounts. The behaviour of the zinc-containing species is shown in Fig. 6(b) and it can be seen that the amount of gaseous zinc chloride increases with increasing chlorine and only begins to level off at a chlorine addition of about 0.8 mol, which is over twice the stoichiometric value. The amount of zincite continuously decreases as gaseous zinc chloride is formed, while the amount of diiron zinc tetraoxide remains relatively constant before decreasing at high chlorine amounts. On the other hand, the amount of zinc ferrite increases slightly at low chlorine amounts, reaching a maximum and then decreases after most of the zincite has been converted to gaseous zinc chloride. It is noteworthy that the complete conversion of the zinc oxide in the zinc ferrite to gaseous zinc chloride is difficult and requires excessive amounts of chlorine. The zinc ferrite requires higher chlorine amounts than diiron zinc tetraoxide to be fully converted to gaseous zinc chloride, which in turn requires more chlorine than zincite. This behaviour reflects the higher stability of zinc ferrite in comparison to diiron zinc tetraoxide, which in turn is more stable than zincite, with respect to reaction with chlorine gas. The amount of condensed zinc chloride remains relatively low across the whole chlorine addition range.

As shown in Fig. 6(c), the more complex iron-containing species are converted into simpler species as the amount of chlorine increases. Initially, the amount of dicalcium ferrite decreases rapidly and subsequently, the monocalcium ferrite. On the other hand, the amounts of zinc ferrite and diiron zinc tetraoxide increase somewhat but then proceed to decrease. With increasing chlorine, the amounts of hematite and magnetite increase but ultimately at high chlorine amounts these two iron oxides are converted

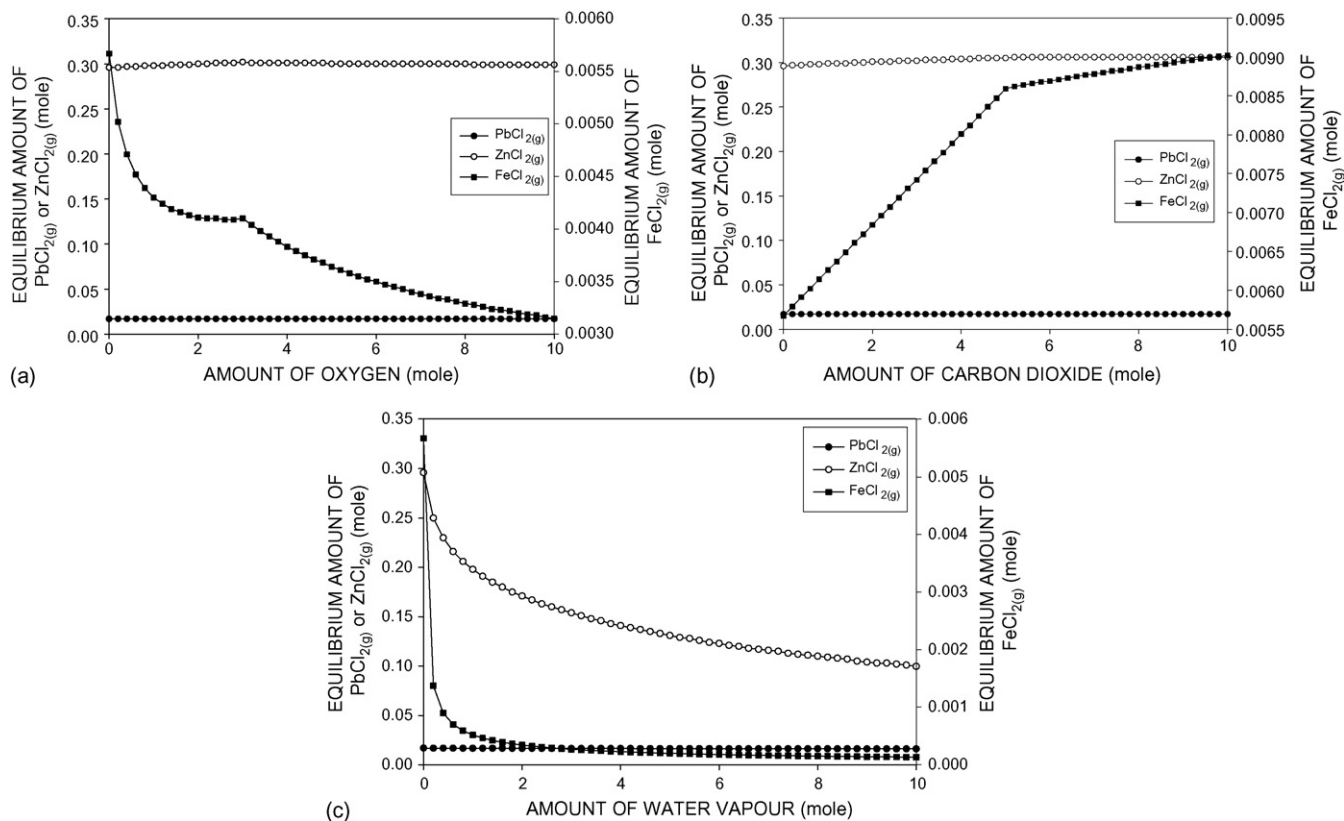


Fig. 11. Equilibrium amounts of lead, zinc and iron chlorides as a function of the amount of (a) oxygen, (b) carbon dioxide and (c) water vapour. The reactant ratio was 0.345 mol/100 g, the temperature was 1473 K and the amount of nitrogen was 10 mol.

to gaseous ferrous and ferric chlorides and thus the amounts of the oxides decrease. Ferrous chloride forms more readily and predominates over ferric chloride except at high chlorine additions. The amounts of condensed ferrous and ferric chlorides were very small. Fig. 6(d) shows that the decrease in the amounts of calcium oxide and the calcium ferrites with increasing chlorine is due to their conversion to condensed calcium chloride, which is highly favourable because of the high stability of calcium chloride. Additionally, the amounts of calcium oxide decrease. Fig. 6(e) shows the behaviour of the calcium silicates. At 1473 K the amount of calcium carbonate is very small. As the amount of chlorine increases, the silicates with the highest amount of lime are converted into the silicates with lower lime contents. The amount of tricalcium silicate (Ca_3SiO_5) decreases rapidly with increasing chlorine and as a result the amounts of calcium orthosilicate ($2\text{CaO}\cdot\text{SiO}_2$), dicalcium orthosilicate (Ca_2SiO_4), calcium silicate ($\text{Ca}_3\text{Si}_2\text{O}_7$) and calcium metasilicate (CaSiO_3) increase at low chlorine amounts but eventually decrease as the amount of chlorine increases. At high chlorine amounts CaSiO_3 predominates. The amount of grossularite ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) remained constant and the amount of clinohedenbergite ($(\text{CaFe})_{0.5}\text{SiO}_3$) was relatively low but increased at high chlorine levels.

Fig. 7 shows the effect of chlorine on the metal recoveries for the temperature of 1473 K. At low chlorine additions, the non-ferrous metal recoveries are relatively low and the amount of iron is low, while at high chlorine additions the non-ferrous metal recoveries increase but the amount of gaseous iron chloride also increases. High lead recoveries approaching 100% were easily achieved, but similar recoveries for zinc required excessive amounts of chlorine. Fig. 8 shows the effect of chlorine on the selectivity factors for the temperature of 1473 K. In a manner similar to temperature, the selectivity factors are low and decrease with increasing chlorine addition. At high chlorine values the selectivity becomes essentially independent of the chlorine addition. In a manner similar to the effect of temperature, these results illustrate the difficulty of achieving high selectivities when using pure chlorine as a reagent.

4.3. Effect of inert gas

According to reactions (1)–(3) and (6), the formation of the gaseous lead, zinc and iron chlorides should be favoured by the presence of an unreactive or inert gas such as nitrogen or argon. Also, the formation of gaseous calcium chloride, according to reaction (4), would be promoted, while the formation of condensed calcium chloride according to reaction (5) would be hindered. Fig. 9 shows the equilibrium amounts of these species as a function of the partial pressure of the nitrogen for the stoichiometric condition and a temperature of 1473 K and Fig. 10 shows the metal recoveries. It can be seen that the amount of zinc chloride vapour increased significantly with increasing nitrogen partial pressure and reached a constant value at very high nitrogen partial pressures. Conversely, the amount of condensed calcium chloride decreased dramatically and completely disappeared at very high pressures. The amount of lead chloride vapour increased only slightly, since in the absence of nitrogen the amount was close to the maximum. The amounts of calcium chloride and ferrous chloride vapours increased slowly at low nitrogen partial pressures and then more rapidly at higher pressures, but their amounts remained relatively low. In terms of metal recovery, the lead recovery was high at 92% in the absence of nitrogen, increased slowly with increasing nitrogen and reached 100% at high nitrogen partial pressures. For the case of zinc, the recovery was about 40% in the absence of nitrogen and increased continuously to a maximum value of about 93% at high nitrogen partial pressures. The iron recovery achieved a value of about 2% at high nitrogen partial pressures.

The levelling off of the zinc recovery corresponded to a nitrogen addition of 10 mol and this value was utilized in subsequent calculations.

4.4. Effect of oxidizing gas

A more accurate control of the oxygen potential in the system could be utilized to maintain the iron as iron oxide rather than being chlorinated to iron chloride. Fig. 11(a), (b) and (c) show the effects of oxygen, carbon dioxide and water vapour, respectively, on the amounts of gaseous lead, zinc and iron chlorides. The temperature was 1473 K, the reactant ratio was 0.345 mol/100 g and the nitrogen addition was 10 mol. For the case of oxygen it can be seen that the amount of iron chloride initially decreases dramatically with increasing oxygen and then more slowly. On the other hand, the amount of gaseous zinc chloride increases slightly at low oxygen additions levels off and then decreases slightly at high chlorine additions, while the amount of lead chloride remains unaffected. At 10 mol of oxygen, the amount of zinc chloride had only decreased slightly, while the amount of iron chloride was very low and therefore this value was used in the subsequent calculations. Conversely, the addition of carbon dioxide (Fig. 11(b)) favours the formation of an increased amount of iron chloride. The amount of zinc chloride increased slightly while the amount of lead chloride remained essentially unchanged. For the case of water vapour (Fig. 11(c)), there is an initial very rapid drop in the amount of iron chloride to very low levels but the amount of zinc chloride also drops quite rapidly. At higher moisture additions, the amount of zinc chloride continues to decrease. The amount of lead chloride decreases slightly with increasing

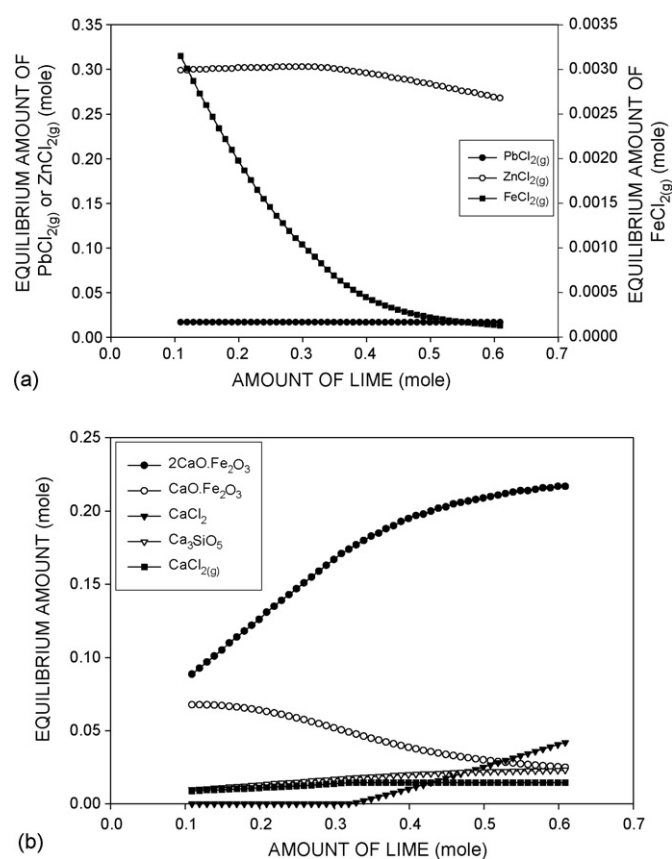


Fig. 12. Equilibrium amounts of (a) lead, zinc and iron chlorides, and (b) the calcium-containing species as a function of the amount of lime. The temperature was 1473 K, the reactant ratio was 0.345 mol/100 g and the amounts of nitrogen and oxygen were 10 mol.

moisture additions. Therefore, with regards to oxidizing agents, oxygen is superior in terms of maintaining a high zinc recovery but also permitting a reduction in the amount of gaseous iron chloride.

4.5. Effect of calcium oxide

An increasing amount of calcium oxide would be expected to result in an increasing amount of calcium ferrites and therefore a reduction in the amount of gaseous iron chloride. On the other hand, more calcium oxide could favour the formation of additional calcium chloride and thus increase the consumption of chlorine gas. Fig. 12(a) and (b) shows the effects of lime on the amounts of gaseous lead, zinc and iron chlorides and the calcium-containing species, respectively. The temperature was 1473 K, the reactant ratio was 0.345 mol/100 g and 10 mol of both oxygen and nitrogen were utilized. The amount of gaseous lead chloride is unchanged but the amount of zinc chloride increases slightly to a maximum at a lime addition of about 0.3 mol before decreasing. On the other hand, the amount of iron chloride initially decreases rapidly and then more slowly and approaches very low equilibrium amounts. As shown in Fig. 12(b), the amount of dicalcium ferrite ($2\text{CaO}\cdot\text{Fe}_2\text{O}_3$) increases dramatically with increasing lime addition, at the expense of monocalcium ferrite ($\text{CaO}\cdot\text{Fe}_2\text{O}_3$). The amount of condensed calcium chloride remains constant below a lime addition of 0.35 mol but then increases sharply. On the other hand, the amount of gaseous calcium chloride increased only slightly with increasing lime content. Thus, for a lime content of about 0.3 mol, the amount of gaseous lead chloride is unchanged, the amount of zinc chloride

increases slightly and the amount of iron chloride is reduced by about 70%.

4.6. Effect of silica

As discussed previously, some of the calcium oxide in the dust is converted to either condensed calcium chloride or gaseous calcium chloride and this consumes chlorine. The stabilization of this calcium oxide as calcium silicate should minimize the amount of lime that is converted. Fig. 13(a) and (b) shows the effect of silica on the amounts of calcium chloride and the calcium silicates, respectively. The temperature was 1473 K, the reactant ratio was 0.345 mol/100 g, the nitrogen and oxygen amounts were both 10 mol and the control dust composition was utilized. Initially, the amount of gaseous calcium chloride decreases rapidly and subsequently more slowly at high silica additions. The amount of condensed calcium chloride is very small. Correspondingly, the amounts of the calcium silicates increase with increasing silica, as shown in Fig. 13(b). In general, the calcium silicates with higher lime contents are replaced by those with a higher silica content as the amount of silica increases. Therefore, the amount of calcium metasilicate (CaSiO_3) increases dramatically with increasing silica and predominates at high silica levels. Also, the amount of $(\text{CaFe})_{0.5}\text{SiO}_3$ increases at high silica levels. Fig. 13(c) shows the effect of silica on the amounts of zinc, lead and iron chlorides. The amount of lead chloride remains essentially constant and the amount of zinc chloride decreases only slightly. However, the amount of iron chloride shows a significant increase with silica addition, before decreasing slightly and levelling off at high silica additions.

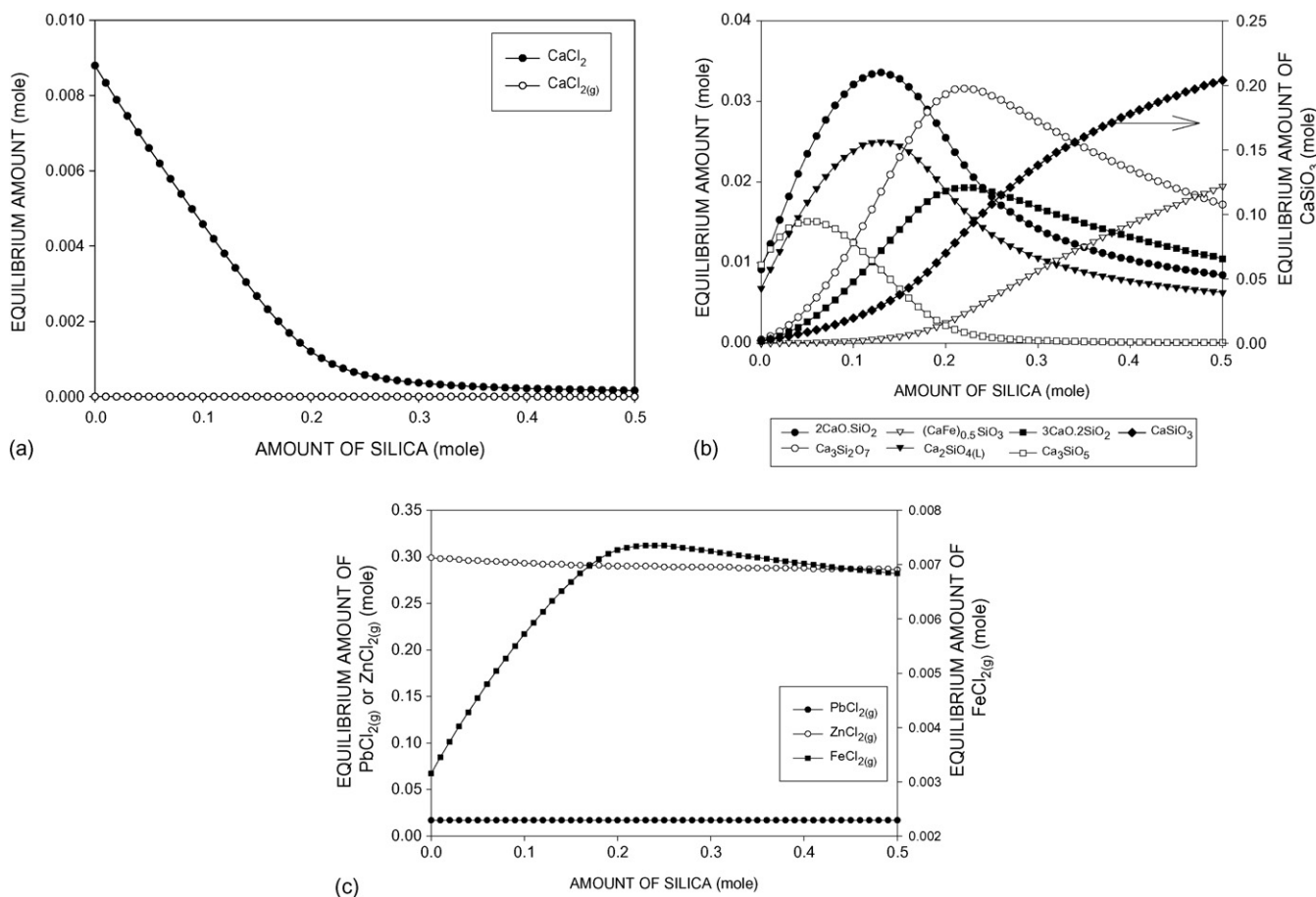


Fig. 13. Equilibrium amounts of (a) condensed and gaseous calcium chloride, (b) calcium silicates and (c) gaseous lead, zinc and iron chlorides as a function of the amount of silica. The temperature was 1473 K, the reactant ratio was 0.345 mol/g and the amounts of nitrogen and oxygen were 10 mol.

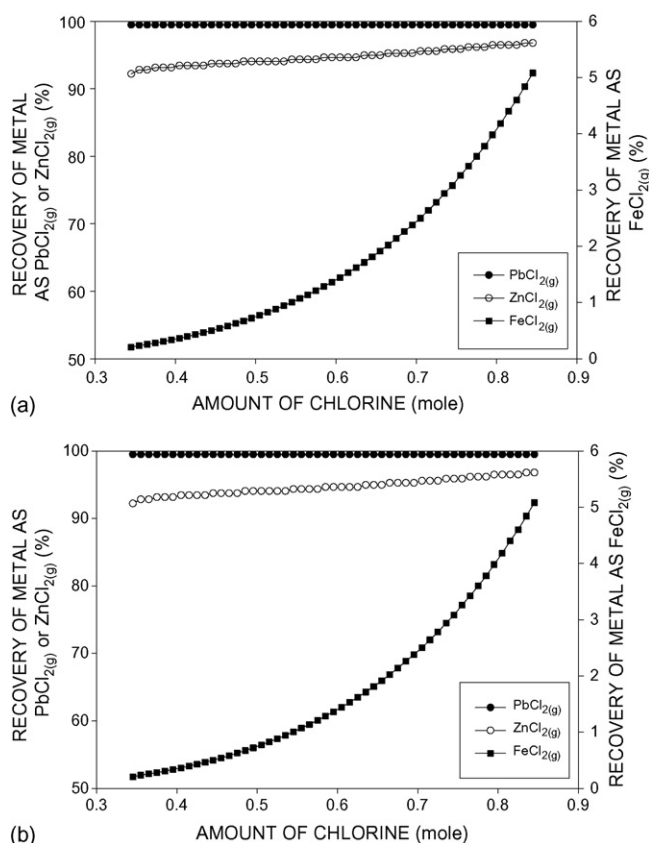


Fig. 14. Lead, zinc and iron recoveries as gaseous metal chlorides as a function of (a) temperature and (b) amount of chlorine for the optimum conditions.

5. Optimization of chlorination conditions

Based on the above discussion it would be expected that the optimum conditions for selective chlorination would be achieved by controlling the following factors: temperature, amount of chlorine, nitrogen partial pressure, oxygen partial pressure and the amounts of lime and silica. Fig. 14(a) shows the effect of temperature on the lead, zinc and iron recoveries for a reactant ratio of 0.345 mol/100 g, nitrogen and oxygen additions of 10 mol and a calcium oxide amount of 0.3 mol. It can be seen that the recovery of zinc chloride vapour reaches a maximum value of about 92% at 1480 K. Above this temperature, the recovery decreases due to the formation of zinc vapour. The lead chloride recovery remains close to 100% until about 1600 K and then begins to decrease due to the formation of lead vapour. The recovery of gaseous iron chloride is low at low temperatures but increases continuously with temperature. Thus, the optimum temperature for the maximum recovery of lead and zinc and also relatively low amounts of gaseous iron chloride would be about 1480 K. The effect of chlorine addition to the stoichiometric reactant ratio of 0.345 mol/100 g is shown in Fig. 14(b) and it can be seen that the lead recovery remains essentially independent of the amount of chlorine, while the zinc recovery shows marginal improvement. A doubling of the amount of chlorine only improves the zinc recovery by about 4%. On the other hand, the amount of gaseous iron chloride increases rapidly with the amount of chlorine.

Fig. 15(a) and (b) shows the selectivity factors as a function of temperature and chlorine addition, respectively. Again the selectivity factors for lead are high at low temperatures because of the high recoveries and low amounts of iron chloride vapours. But the amount of iron chloride increases with temperature and ultimately the recovery of gaseous lead chloride decreases and thus the selec-

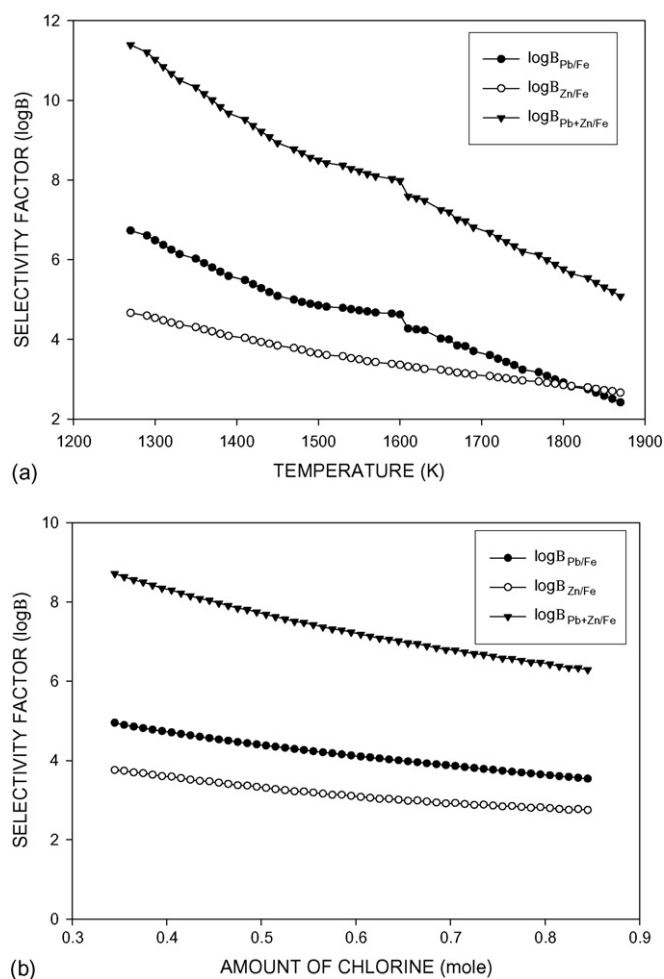


Fig. 15. Lead, zinc and combined lead plus zinc selectivity factors as a function of (a) temperature and (b) the amount of chlorine for the optimum conditions.

tivity factors decrease. For zinc, the recoveries are lower than for lead and thus the selectivity factors are lower, but in a manner similar to lead, they decrease with increasing temperature. With regards to the effect of chlorine, as shown in Fig. 15(b), the selectivity factors for both lead and zinc decrease with increasing chlorine despite the fact that the lead recovery remains close to 100% and the zinc recovery increases with chlorine. The decrease in selectivity is due to the rapidly increasing rate of formation of iron chloride.

6. Behaviour of other non-ferrous metals

There are a number of other non-ferrous metals in the dust and these will distribute themselves between the gaseous chloride, the oxide residue and any condensed chloride phase that forms. Two important non-ferrous metal impurities are cadmium and copper. The additional species utilized in the equilibrium calculations are given in Table 2 and the cadmium and copper contents of the dust were 0.089% and 0.894%, respectively. The amounts of the other components were adjusted to keep the total amount of dust equal to 100%. The optimum conditions were utilized with a chlorine addition of 0.4 mol. Cadmium would be expected to behave like zinc and the various cadmium-containing species are shown as a function of temperature in Fig. 16. The maximum equilibrium amount of gaseous cadmium dichloride would be 0.001 mol. It can be seen that at high temperatures the majority of the cadmium is present as cadmium dichloride vapour with the amount reaching a maximum value at a temperature of about 1500 K. Subsequently, an increasing

Table 2
Additional species utilized in the equilibrium calculations for cadmium and copper.

Gases	Chlorides	Oxides	Elements
Cd	CdCl ₂	CdO	Cd
CdCl	CuCl	CuO	Cu
CdCl ₂	CuCl ₂	Cu ₂ O	
Cd ₂ Cl ₄			
CdO			
Cu			
Cu ₂			
CuCl ₂			
Cu ₂ Cl ₄			
Cu ₃ Cl ₃			
Cu ₄ Cl ₄			
Cu ₅ Cl ₅			
CuO			

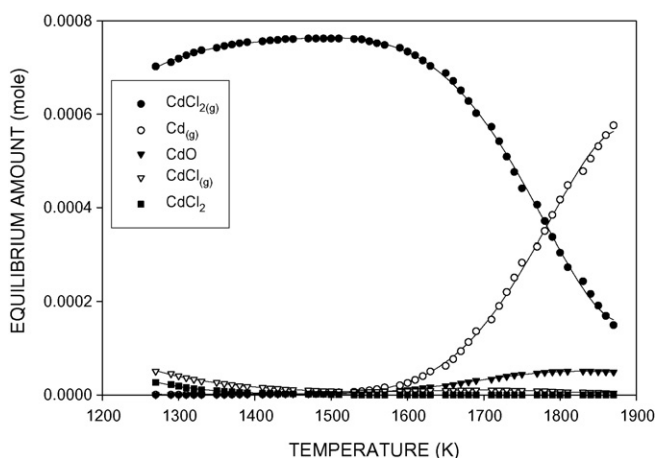


Fig. 16. Equilibrium amounts of cadmium-containing species as a function of temperature for the optimum conditions.

amount of cadmium vapour forms and this reduces the amount of gaseous chloride.

Since copper is generally considered to be a detrimental impurity element in steel, then its presence in the dust lowers the value of the oxide residue or any metallic iron product, resulting from the processing of the dust. There is currently no viable method to recover the copper from the dust or from the oxide residue or from any metallic iron product or ultimately any iron or steel produced using these materials as a part of the feed. Typically, the copper impurity problem is resolved by diluting the copper-containing iron with another source of iron units with a much lower copper content. Gaseous copper dichloride would be expected to be stable and therefore there is some potential to separate it from the iron. Fig. 17 shows the equilibrium distribution of the predominant copper-containing species in the chlorination process as a function of temperature. The maximum equilibrium amount of gaseous cupric chloride would be 0.013 mol. It can be seen that at high temperatures the amount of gaseous cupric chloride reaches a maximum value at about 1550 K and subsequently decreases as the amount of cuprous oxide increases. Therefore, it is possible to separate the majority of the copper from the iron, which remains as an oxide in the residue.

7. Comparison of chlorination with reduction

Fig. 18 compares the combined selectivity factors for the reduction of the dust under similar conditions by various reducing agents, as published in the literature [29,30,39,43,55], with those for chlorination. For the reducing agents, the selectivity factors increase with temperature but conversely for chlorination they decrease with

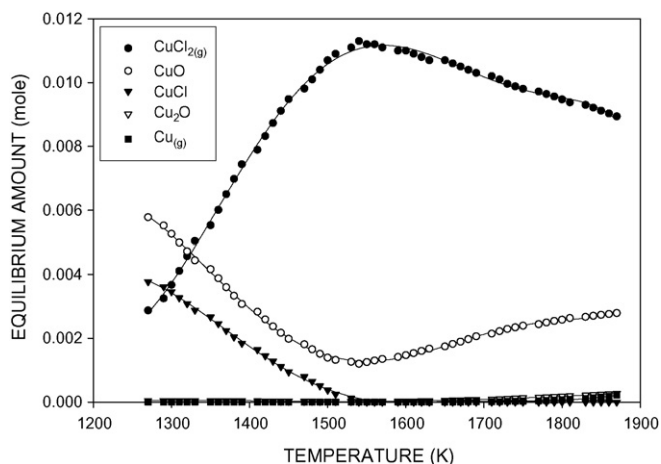


Fig. 17. Equilibrium amounts of copper-containing species as a function of temperature for the optimum conditions.

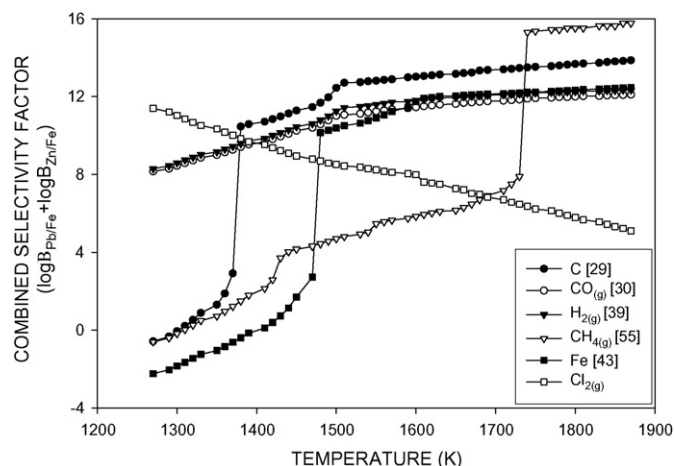


Fig. 18. Comparison of the combined lead plus zinc selectivity factors for chlorination with the results for various reducing agents as described in the literature.

temperature. The discontinuities in the plots for carbon, methane and iron are attributed to the presence of metallic iron, which temporarily exists as an intermediate equilibrium species, but is ultimately consumed during the reduction of zinc oxide as the temperature increases. It can be seen that at the lower temperatures, the combined selectivity factors for chlorination are higher than for reduction, but under these conditions the zinc recovery is very low. For chlorination, at the optimum temperature for zinc recovery of about 1473 K and a lead recovery of almost 100%, the selectivity factor is lower than that of the reducing agents. Additionally, the maximum selectivities for chlorination were lower than for reduction. This lower selectivity for chlorination is attributed to both the inability to convert all of the zinc oxide to gaseous zinc chloride and also to the increasing stability of gaseous iron chloride as the temperature increases.

8. Conclusions

A thermodynamic analysis of the selective chlorination of the lead and zinc in a typical electric arc furnace dust was performed using the SOLGASMIX equilibrium module of Outokumpu HSC Chemistry® 5.1. The equilibrium amounts of the various species resulting from the reaction of the dust with chlorine gas were determined. Both the lead and zinc could be chlorinated to their respective gaseous chlorides and only a small amount of iron oxide

was converted to gaseous iron chloride. The calcium in the dust consumed chlorine and the reaction product was mainly condensed calcium chloride rather than gaseous calcium chloride. The addition of silica resulted in the formation of stable calcium silicates and this minimized the formation of calcium chloride. On the other hand, the formation of some calcium chloride reduced the amount of iron chloride. The presence of an unreactive gas, such as nitrogen, enhanced the recovery of the non-ferrous metals. Also, by adding some oxygen, the stability of iron oxide was promoted and this reduced the conversion of iron oxide to gaseous iron chloride. Utilizing these various factors, the optimum chlorination conditions were determined for the dust utilized in this study. Additionally, other non-ferrous metals, such as copper, could be chlorinated and recovered as gaseous chlorides. However, the combined lead plus zinc selectivities achieved with chlorination, were lower than those reported in the literature for various reducing agents. This is mainly attributed to the difficulty of achieving zinc recoveries approaching 100% and also the relative ease of formation of gaseous iron chloride.

Acknowledgement

The author would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for support of this research.

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