Thermodynamic analysis of the selective carbothermic reduction of electric arc furnace dust

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Abstract

Electric arc furnace (EAF) dust, which is produced as a result of the melting of automobile scrap in an electric arc furnace, contains considerable amounts of zinc and lead, which are of significant economic value. Typically, the other major components are iron oxide and calcium oxide with minor amounts of other metal oxides. In this research, a detailed thermodynamic study of the pyrometallurgical processing of the dust, using carbon as a reducing agent was performed. The SOLGASMIX solver of Outokumpu HSC Chemistry® 5.1 was used to calculate the equilibrium composition under reducing conditions. The control input dust composition was as follows (in mass percent): 8.100% CaO, 8.250% $2CaO \cdot SiO_2$, 11.200% $CaCO_3$, 8.830% $CaO \cdot Fe_2O_3$, 7.840% Fe_3O_4, 3.770% PbO, 38.150% $ZnFe_2O_4$ and 13.860% ZnO.

Selective reduction and separation of both the zinc and the lead as metallic vapours, from the iron, in oxide form, was examined. The separation of the zinc or the lead from the iron, was defined quantitatively in terms of the selectivity factor ($\log \beta$) as follows.

for zinc $\beta_{Zn/Fe} = \dfrac{X_{Zn_g}}{X_{Fe_m}} \dfrac{Y_{Fe_o}}{Y_{Zn_o}}$

for lead $\beta_{Pb/Fe} = \dfrac{X_{Pb_g}}{X_{Fe_m}} \dfrac{Y_{Fe_o}}{Y_{Pb_{o+l}}}$

where the subscript symbols refer to the metal being present in gaseous (g), metallic solid (m), solid oxide (o) or metallic liquid (l) form, respectively. The standard calculations were performed for one hundred grams of dust at atmospheric pressure. The variables investigated were as follows; temperature in the range of 1273–1873 K, reactant ratio (i.e. moles of carbon per gram of dust), dust composition, addition of inert gas and reduced total pressure. The calculated values were in reasonable agreement with those from previously published studies and also industrial results.
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1. Introduction

When automobile scrap is remelted in an electric arc furnace (EAF) about one to two percent of the charge is converted into a dust, which is commonly referred to as electric arc furnace dust. The heterogeneous chemical composition of the scrap leads to a dust with a multitude of elements. In addition, the dust formation mechanisms are multifaceted and thus the dust has a complex mineralogy. Typically, these dusts are classified as hazardous wastes because of the relatively small amounts of leachable hexavalent chromium, cadmium and lead. However, they do contain substantial amounts of non-ferrous metals, such as zinc oxide and lead oxide, as well as iron oxide. Normally, the major mineralogical components are zinc ferrite ($ZnO \cdot Fe_2O_3$), magnetite (Fe_3O_4), zincite (ZnO) and lime (CaO), while the lead primarily occurs in relatively small amounts as lead oxide (PbO). Minor amounts of sulphates, sulphides and chlorides can also be present but, in general, over ninety percent of the dust is comprised of oxide species.

Dust treatment options may be classified as metal recovery for recycling such as the pyrometallurgical and/or hydrometallurgical processes, chemical stabilization, vitrification or direct recycling back to the EAF [1–6]. The most successful metal recovery technologies are the pyrometallurgical or high

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temperature metal recovery (HTMR) processes in which the non-ferrous metal oxides are reduced and simultaneously, these metals are volatilised and separated from the iron, using solid carbonaceous reducing agents. The recovery of the non-ferrous metals is economically attractive but the recovery of the iron, which is present at concentrations less than one-half that of the feed to a blast furnace is usually not economic. Furthermore, the reduction of the iron oxide to metallic iron is highly endothermic and also consumes a large amount of the reducing agent. Therefore, the selective recovery of the non-ferrous metals is a typical approach utilized in metal recovery and recycling. Condensation of the non-ferrous metals in metallic form is problematic and therefore, they are usually condensed as a crude mixed oxide [7]. The iron oxide and the other components are collected in the form of an iron-rich slag, which if it is inert and non-hazardous, can be utilized as a component of construction materials or disposed of as a non-hazardous waste.

1.1. Selective reduction

In pyrometallurgical extraction, one method of metal separation from a metal oxide mixture is based on the specific selective reduction of one or more of the metal oxides, which are relatively unstable. Typically, this is achieved by controlling the temperature and/or the composition of the reducing atmosphere, that is, the reduction potential. Then, the reduced metal oxides can be collected in a separate phase such as a liquid or a gas. In the case of EAF dust, the non-ferrous metal oxides, such as those of zinc and lead, are less stable than iron oxide and, in addition, these metals have boiling points of 1180 and 2022 K, respectively, which are lower than that of iron (3134 K) and therefore selective reduction and separation via the gas phase should be feasible [8].
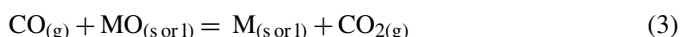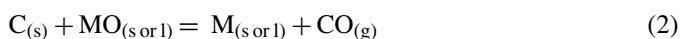
As mentioned previously, the majority of the pyrometallurgical processes for the recovery of metals from EAF dust utilize solid carbonaceous reducing agents. The overall reaction for the reduction of a solid metal oxide (MO) by solid carbon (C) to produce metal (M) is as follows:

$$C_{(s)} + 2MO_{(s \, or \, l)} = 2M_{(s \, or \, l)} + CO_{2(g)} \tag{1}$$
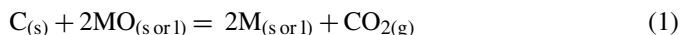
This solid–solid or solid–liquid direct reduction reaction depends on diffusion in the solid or liquid state and therefore, for this reaction to occur to any great extent there has to be intimate contact between the metal oxide and the solid carbon. In addition, the formation of an intermediate oxide or metal product layer between the two reactants is a barrier to further reaction. For relatively unstable metal oxides, such as lead oxide and zinc oxide, the minimum thermodynamic reduction temperature is relatively low and thus the diffusion rates in both the solid and liquid states are low. On the other hand, for more stable metal oxides such as wustite (FeO), the minimum thermodynamic reduction temperature is high and thus the diffusion rates are relatively high.

It is well known that the carbothermic reduction of metal oxides also involves carbon monoxide and the actual reduction process can occur in two stages as follows:

$$C_{(s)} + MO_{(s \, or \, l)} = M_{(s \, or \, l)} + CO_{(g)} \tag{2}$$

$$CO_{(g)} + MO_{(s \, or \, l)} = M_{(s \, or \, l)} + CO_{2(g)} \tag{3}$$

Carbon monoxide can be regenerated by the highly endothermic Boudouard reaction as follows:

$$C + CO_{2(g)} = 2CO_{(g)} \tag{4}$$

The indirect reduction of a metal oxide by carbon monoxide is a gas–solid reaction (Eq. (3)) and is more kinetically favourable than the solid–solid or solid–liquid reduction reactions (Eq. (2)) [9]. Accordingly, the reduction of metal oxides by solid carbonaceous reducing agents involves reduction both by solid carbon and by carbon monoxide. For relatively low stability metal oxides, the indirect reduction reaction (Eq. (3)) predominates, while for stable metal oxides the direct reduction reaction (Eq. (2)) prevails. In the case of EAF dust, it would be expected that indirect reduction would prevail not only for the reduction of the zinc and lead oxides, but also for the reduction of hematite (Fe_2O_3) to magnetite (Fe_3O_4) and the reduction of magnetite (Fe_3O_4) to wustite (FeO). However, the reduction of wustite to metallic iron would be expected to be mainly due to direct reduction. Therefore, promoting indirect reduction, which as mentioned previously, is achieved by controlling the reducing potential in the system, can facilitate the selective reduction of EAF dust.

As a first approximation, the thermodynamics of the selective reduction of the iron oxide and the zinc and lead oxides in the EAF dust can be evaluated by considering the following carbothermic reduction reactions:
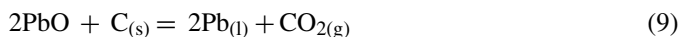
$$6Fe_2O_3 + C_{(s)} = 4Fe_3O_4 + CO_{2(g)} \tag{5}$$

$$2Fe_3O_4 + C_{(s)} = 6FeO + CO_{2(g)} \tag{6}$$

$$2FeO + C_{(s)} = 2Fe + CO_{2(g)} \tag{7}$$

$$2ZnO + C_{(s)} = 2Zn_{(g)} + CO_{2(g)} \tag{8}$$

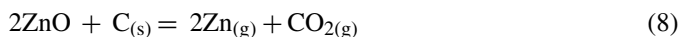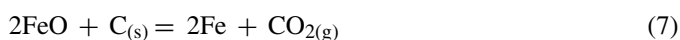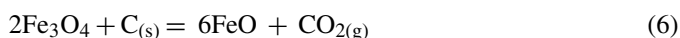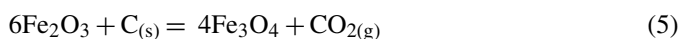$$2PbO + C_{(s)} = 2Pb_{(l)} + CO_{2(g)} \tag{9}$$

Fig. 1 shows the standard free energy changes for these reactions in the temperature range of 1273–1873 K. As mentioned previously, lead has a relatively high boiling point of 2022 K and thus for the purposes of these calculations, the lead was considered to be in the condensed state as liquid (l). The standard free energy changes for the reduction of hematite to magnetite (Eq. (5)) and magnetite to wustite (Eq. (6)) are both negative over the temperature range of interest. Since lead oxide is a relatively unstable oxide, then the reduction of lead oxide (Eq. (9)) occurs relatively easily. Of considerable interest, is the intersection of the lines for the reduction of wustite (Eq. (7)) and the reduction of zinc oxide (Eq. (8)). Below about 1480 K, wustite is less stable than zinc oxide while above this temperature, zinc oxide is less stable than wustite. Thus, above 1480 K it should be feasible to reduce the zinc oxide to zinc vapour, while the iron is maintained in oxide form.
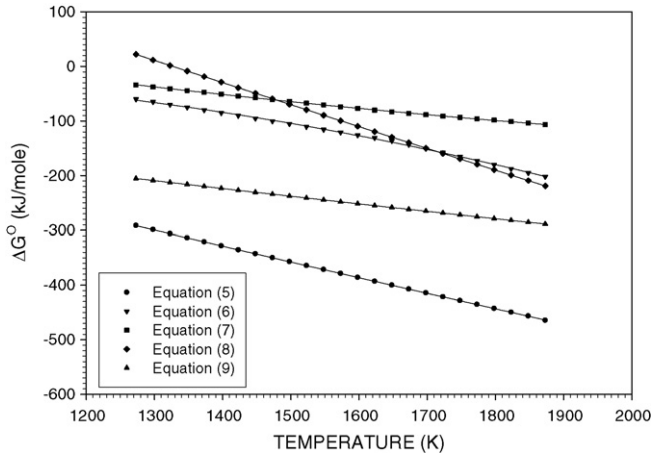
Fig. 1. Standard free energy changes for the reduction of hematite to magnetite (Eq. (5)), magnetite to wustite (Eq. (6)), wustite to metallic iron (Eq. (7)), zinc oxide to zinc vapour (Eq. (8)) and lead oxide to liquid lead (Eq. (9)) by carbon in the temperature range of 1273–1873 K.

The degree of separation of one metal from another can be quantified by utilizing the selectivity factor (β). This concept is adapted from the work by Varteressian and Fenske on solvent extraction [10] and the application of this approach for the reduction of EAF dust by carbon monoxide has been detailed in a previous publication [11]. The separation of one metal (A) from another metal (B) can be described by the selectivity factor (β) as follows:

$$\beta_{A/B} = \frac{X_A}{X_B} \frac{Y_B}{Y_A} \qquad (10)$$

where X and Y are the concentrations of the two metals, A and B, respectively, in the two different phases, that is, the gas phase and the condensed phases. The selectivity factor often varies between ten and one hundred and therefore it is often more convenient to determine $\log \beta$, which typically ranges between one and ten.

For electric arc furnace dust, the selective reduction separation factor can be defined in terms of the degree of separation of one metal in gaseous form, for example, zinc or lead, from another metal in condensed form, for example, metallic iron, as follows:

for the separation of zinc from iron; $\beta_{Zn/Fe} = \dfrac{X_{Zn}}{X_{Fe}} \dfrac{Y_{Fe}}{Y_{Zn}}$ (11)

for the separation of lead from iron; $\beta_{Pb/Fe} = \dfrac{X_{Pb}}{X_{Fe}} \dfrac{Y_{Fe}}{Y_{Pb}}$ (12)

If the iron can be maintained in oxide form, then the selectivity factor for the separation of zinc from iron, as iron oxide, $\beta_{Zn/Fe}$ is defined as follows:

$$\beta_{Zn/Fe} = \frac{X_{Zn_g}}{X_{Fe_m}} \frac{Y_{Fe_o}}{Y_{Zn_o}} \qquad (13)$$

where the symbols g, m and o refer to the element being present in gaseous, metallic or oxide form, respectively. Similarly, the separation of lead from iron as iron oxide can be defined as follows:

$$\beta_{Pb/Fe} = \frac{X_{Pb_g}}{X_{Fe_m}} \frac{Y_{Fe_o}}{Y_{Pb_{o+l}}} \qquad (14)$$

As mentioned previously, lead has a relatively high boiling point of 2022 K and thus for the reduction temperature range of 1273–1873 K utilized in this study, the lead can be in the condensed state as liquid (l) in addition to being in the gaseous (g) or oxide form (o). Furthermore, it is of importance to maximize the separation of both zinc and lead from the iron and therefore the combined selectivity factor for both zinc plus lead can be defined as follows:

$$\beta_{(Zn+Pb/Fe)} = \beta_{Zn/Fe}\beta_{Pb/Fe} = \frac{X_{Zn_g}}{X_{Fe_m}} \frac{Y_{Fe_o}}{Y_{Zn}} \frac{X_{Pb_g}}{X_{Fe_m}} \frac{Y_{Fe_o}}{Y_{Pb_{o+l}}}$$

$$= \frac{X_{Zn_g}}{Y_{Zn_o}} \frac{X_{Pb_g}}{Y_{Pb_{o+l}}} \frac{Y_{Fe_o}^2}{Y_{Fe_m}^2} \qquad (15)$$

and therefore

$$\log \beta_{(Zn+Pb/Fe)} = \log \beta_{Zn/Fe} + \log \beta_{Pb/Fe} \qquad (16)$$

Similarly, the separation of gaseous lead from zinc oxide is of interest and can be defined as follows:

$$\beta_{Pb/Zn} = \frac{X_{Pb_g}}{X_{Zn_o}} \frac{Y_{Zn_g}}{Y_{Pb_{0+1}}} \qquad (17)$$

1.2. Equilibrium calculations

The equilibrium composition of the reaction products was calculated using the equilibrium module of Outokumpu HSC Chemistry® 5.1 [12]. The calculations were performed using the SOLGASMIX solver and the equilibrium composition was determined by the Gibbs free energy minimization method for isothermal, isobaric and fixed mass conditions. The standard dust composition utilized in the calculations was as follows (in mass percent): 1.344% C, 15.754% Ca, 27.920% Fe, 28.656% O, 3.500% Pb, 1.345% Si and 21.482% Zn. The following species were assumed to be present in the dust, with the indicated composition (in mass percent): 8.100% CaO, 8.250% 2CaO·SiO$_2$, 11.200% CaCO$_3$, 8.830% CaO·Fe$_2$O$_3$, 7.840% Fe$_3$O$_4$, 3.770% PbO, 38.150% ZnFe$_2$O$_4$ and 13.860% ZnO. The standard calculations were performed for one hundred grams of dust over the reduction temperature range of 1273–1873 K at atmospheric pressure (1 bar).

The input of the elements iron, zinc, lead, calcium, silicon and oxygen into the equilibrium module, generated a list of 129 possible species. Since, the majority of these species would be considered unstable, under the conditions of this study, then, only the thirty-one species shown in Table 1 were utilized as the input for the calculations. This list includes the species originally present in the dust plus those, which the equilibrium program predicted would be stable in significant amounts. Lead silicate compounds were not included, as they would neither be expected to be present in the original dust nor to form during pyrometallurgical processing. The lead silicates are extremely stable compounds and their presence would hinder the reduc-

Table 1
Species considered in the equilibrium calculations

Elements	Gases	Oxides
Fe	CO, CO_2	ZnO, PbO
Pb	O_2	CaO, $CaCO_3$
Zn	Pb, PbO	$2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$
C	Zn, ZnO	$CaSiO_3$, Ca_3SiO_5
	Fe, FeO	$CaO \cdot Fe_2O_3$, $2CaO \cdot Fe_2O_3$
		SiO_2, $2FeO \cdot SiO_2$
		FeO, Fe_3O_4, Fe_2O_3
		$ZnFe_2O_4$, $ZnSiO_4$, Fe_2ZnO_4

tion of the lead oxide and therefore the lead recovery would be unreasonably low over the reduction temperature range that was investigated. Carbon was incorporated as an input element in the calculations and also carbon monoxide and carbon dioxide were included as gaseous reduction reaction products. A number of liquid and solid solutions could possibly be formed over the reaction conditions in this study. For example, the reduction of zinc ferrite results in the production of magnetite, which could possibly back-react with any unreacted zinc ferrite to form a solid solution and therefore affect the reaction kinetics and the equilibrium composition of the reaction products [13]. However, even in this case, it has been shown that this should not hinder the reduction of the zinc ferrite in the solid solution [13–15]. Therefore, in this study, the formation of liquid and solid solutions was considered to have no significant effects on the equilibrium composition of the products of the reduction process.

A metallic iron recovery of zero in the selectivity factor equations would give rise to a selectivity factor of infinity. Moreover, when metallic iron is not produced under equilibrium conditions then the HSC program generates a default value of 1×10^{-36} moles for the amount of metallic iron. The utilization of this value in the calculations would result in values of about 36 for $\log \beta$, which would be unrealistic. In order to determine a more practical value for $\log \beta$, the lowest twenty-four values for the amount of metallic iron produced, from all the equilibrium calculations, were assigned sample numbers from one to twenty four in terms of decreasing amount of iron. A plot of the data gives a more realistic value of about 1×10^{-6} moles [11] and this value was utilized as the default value in the subsequent calculations.

The reactant to dust ratio or more simply the reactant ratio (RR_C) was defined as the number of moles of carbon utilized per one hundred grams of electric arc furnace dust. The metal recovery (R_i), where i represents Zn, Pb or Fe, under a certain set of conditions was defined as the amount of metal recovered from the corresponding metal oxide and was calculated as follows:

$$R_i = \left[\frac{m_{i,m}}{m_{i,o}} \right] 100\% \tag{18}$$

where $m_{i,m}$ is the mass of i in metallic form after reduction and $m_{i,o}$ is the original mass of i in oxide form. For both zinc and lead, the value utilized for the mass of metal after reduction was that in the gas phase only and any metal produced in the condensed states was not included in the recovery calculations. In the case

of iron, the amount of metal in the gas phase was negligible and only the amount in the condensed phases was utilized.

2. Equilibrium calculations

2.1. Reduction of the zinc and lead oxides in EAF dust

In order to understand the reduction of EAF dust by carbon, it is useful to consider the behaviour of the dust as a function of temperature in the absence of any reducing agent. This aspect has been discussed in a previous paper and therefore only a summary will be provide here [11]. The decomposition of the calcium carbonate to form calcium oxide and carbon dioxide, begins at about 1100 K and is essentially complete by about 1400 K. Both $CaO \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ are present in relatively high concentrations across the whole temperature range, but as the calcium carbonate begins to decompose, the $2CaO \cdot Fe_2O_3$ content begins to increase, reaches a maximum at about 1400 K and then decreases as more $CaO \cdot Fe_2O_3$ begins to form up to about 1750 K. The CaO content continues to increase up to this temperature and then more $2CaO \cdot Fe_2O_3$ begins to be produced and therefore the CaO content decreases. Both Ca_3SiO_5 and $2CaO \cdot SiO_2$ are present in significant amounts across the whole temperature range. Other species are present only in small amounts.

As the temperature increases, zinc ferrite becomes less stable and decomposes to zinc oxide and iron oxide according to the following reaction:

$$ZnO \cdot Fe_2O_3 = ZnO + Fe_2O_3 \tag{19}$$
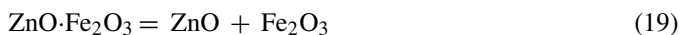
Thus, the amounts of zinc oxide and iron oxide increase with increasing temperature, but some of the iron oxide can combine with the CaO to form the calcium ferrites. However, in general, the amounts of the three uncombined iron oxides increase with temperature with the amount of FeO becoming more significant above about 1500 K.

The stabilities of all the oxides in the system increase with decreasing temperature and since there is a limited amount of oxygen available, then there is insufficient oxygen to maintain the least stable metal oxide, PbO. Thus, metallic liquid lead is formed at temperatures below about 800 K and at room temperature there is only a small amount of lead oxide. On the other hand, at extremely high temperatures, both PbO(g) and also some lead vapour begin to form and this again decreases the equilibrium amount of condensed lead oxide.

For the standard dust composition, the stoichiometric amount of carbon for the complete reduction of both the zinc oxide (as zincite and zinc ferrite) and the lead oxide, according to Eq. (8) and (9), respectively, would be 0.173 mol or a reactant ratio of 0.00173 mol/g. Therefore, this stoichiometric value was utilized to examine the behaviour of the various components in the dust under reducing conditions. Fig. 2 shows the behaviour of the calcium, calcium–iron, calcium–silicon, iron–silicon and silicon-containing oxide species. Again, as for the case of no carbon addition, the major change with increasing temperature is the decomposition of calcium carbonate at about 1000 K. In con-
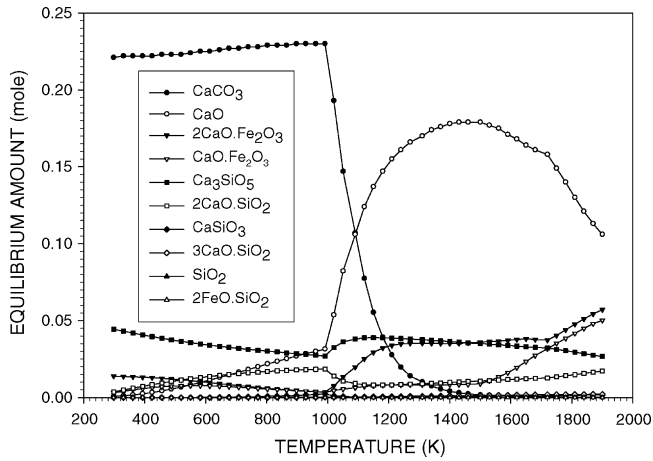
Fig. 2. Equilibrium amounts of the calcium, calcium–iron, calcium–silicon, ironsilicon and silicon-containing oxide species as a function of temperature in the presence of 0.173 mol of carbon as a reducing agent.

trast to the results without a carbon addition, the calcium ferrites ($CaO·Fe_2O_3$ and $2CaO·Fe_2O_3$) are not stable at temperatures below about 1000 K, but above this temperature their stability increases particularly above about 1500 K and this results in a decrease in the equilibrium amount of free CaO. On the other hand, the calcium silicates (Ca_3SiO_5 and $2CaO·SiO_2$) are not significantly affected by the presence of carbon and they remain stable over the whole temperature range.

The behaviour of the zinc, zinc–iron, zinc–silicon and iron-containing oxide species under reducing conditions are shown in Fig. 3 and these can be compared with the results in the absence of any reducing agent. In the presence of carbon, the equilibrium amount of zinc ferrite is relatively low and the amount of FeO increases dramatically up to about 1100 K and then decreases as the calcium ferrites become more stable. The amount of magnetite decreases up to about 1100 K and then remains relatively constant. Above about 1200 K, the zinc oxide is reduced to elemental zinc vapour, which forms in ever-increasing amounts. However, complete reduction of the zinc oxide is not achieved
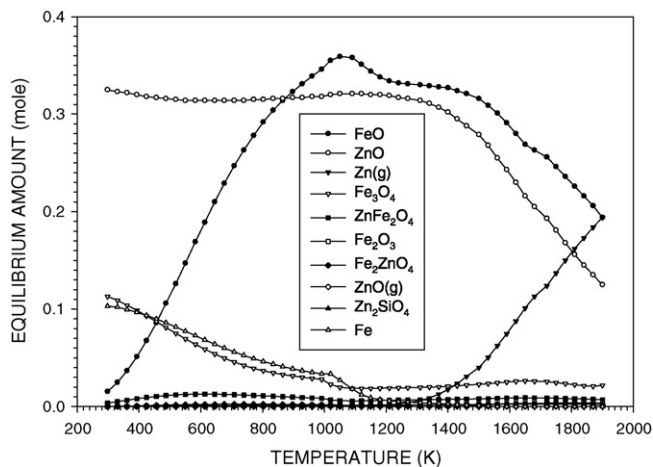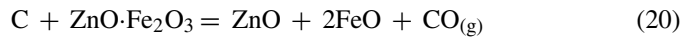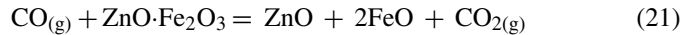
since the amount of carbon added (i.e. the stoichiometric amount for zinc oxide and lead oxide) is insufficient and some carbon is utilized for the reduction of the iron oxides.

In the presence of carbon, the following reactions are facilitated:

$$C + ZnO·Fe_2O_3 = ZnO + 2FeO + CO_{(g)} \qquad (20)$$

and

$$CO_{(g)} + ZnO·Fe_2O_3 = ZnO + 2FeO + CO_{2(g)} \qquad (21)$$

The standard-free energy changes for these two reactions are shown in Fig. 4. For comparison purposes, the standard-free energy change for the thermal decomposition of zinc ferrite in the absence of a reducing agent (Eq. (19)) is also included and it can be seen that this reaction is not favourable across the whole temperature range. Otherwise, it can be seen that under reducing conditions, Eq. (21) is favourable at temperatures above about 525 K, while Eq. (20) becomes even more favourable at temperatures above about 925 K. Consequently, under reducing conditions, these reactions promote both the decomposition of the zinc ferrite and the formation of FeO. Also included in Fig. 3, is the amount of metallic iron and it can be seen that at low temperatures, it is present in substantial quantities but its concentration decreases with increasing temperature and becomes negligible above 1150 K.

The behaviours of the lead-containing species are shown in Fig. 5 and these can be contrasted with those in the absence of a reducing agent. With a carbon addition, elemental lead is stable essentially across the whole temperature range, with liquid lead predominating at lower temperatures and lead vapour at higher temperatures. At about 1100 K some condensed lead oxide begins to form and eventually some lead oxide vapour.

Since the standard EAF dust composition includes carbon dioxide in the form of calcium carbonate, it is of interest to investigate the effect of the carbonaceous reducing agent on the behaviour of the carbon-containing species as shown in Fig. 6. The standard dust composition contains a relatively large amount of calcium carbonate (11.2%) and it can be seen in

Fig. 3. Equilibrium amounts of the zinc, zinc–iron, zinc–silicon and iron-containing oxide species as a function of temperature in the presence of 0.173 mol of carbon as a reducing agent.
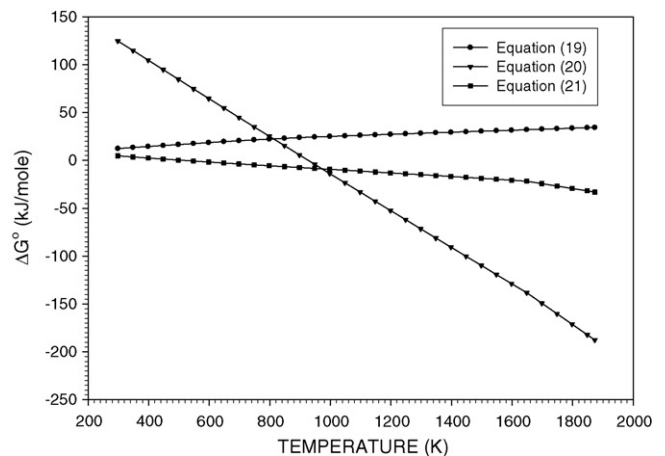

Fig. 4. Standard free energy changes for the decomposition of zinc ferrite (Eq. (19)), reaction of zinc ferrite with carbon (Eq. (20)) and reaction of zinc ferrite with carbon monoxide (Eq. (21)) in the temperature range of 1273–1873 K.
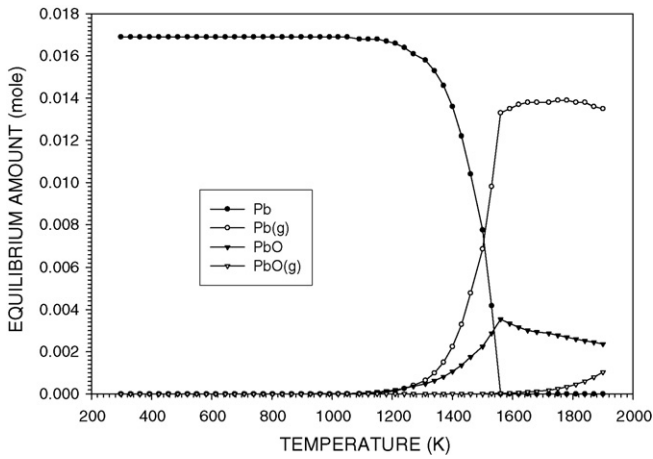
Fig. 5. Equilibrium amounts of the lead-containing species as a function of temperature in the presence of 0.173 mol of carbon as a reducing agent.

Fig. 6 that the major decrease in the elemental carbon concentration occurs when the calcium carbonate begins to decompose at about 1000 K. Above this temperature, both the carbon monoxide and the carbon dioxide concentrations increase, with carbon monoxide increasing more rapidly than carbon dioxide. These results indicate that at about 1000 K, carbon is reacting with the carbon dioxide, which results in the production of carbon monoxide according to the Boudouard reaction (Eq. (4)). At about 1250 K, the carbon monoxide content reaches a maximum and then decreases, while the corresponding carbon dioxide content continues to increase as the zinc oxide is reduced by carbon monoxide according to Eq. (3). Thus, the thermodynamic calculations demonstrate that indirect reduction predominates over direct reduction for zinc oxide.

2.2. Selective reduction of EAF dust by carbon

The zinc recoveries as a function of the reactant ratio and the temperature with carbon as a reducing agent, are shown in the three-dimensional mesh plot in Fig. 7. High zinc recoveries can be realized at relatively low temperatures and low reac-

Fig. 7. Zinc recovery (R_{Zn}) as a function of the reactant ratio (RR_C) and temperature.

tant ratios. For example, zinc recoveries of over ninety percent were achieved at reactant ratios of about 0.005 mol/g and temperatures of about 1633 K. However, to achieve zinc recoveries of ninety eight percent, much higher temperatures and reactant ratios are required, for example, 1663 K and a reactant ratio of 0.01 mol/g. Since the reduction of hematite to magnetite (Eq. (5)) and magnetite to wustite (Eq. (6)) and eventually wustite to metallic iron (Eq. (7)) are thermodynamically favourable, then these reactions will also consume some carbon. Furthermore, as both the temperature and the reactant ratio increase, this results in the generation of an increased amount of carbon monoxide and
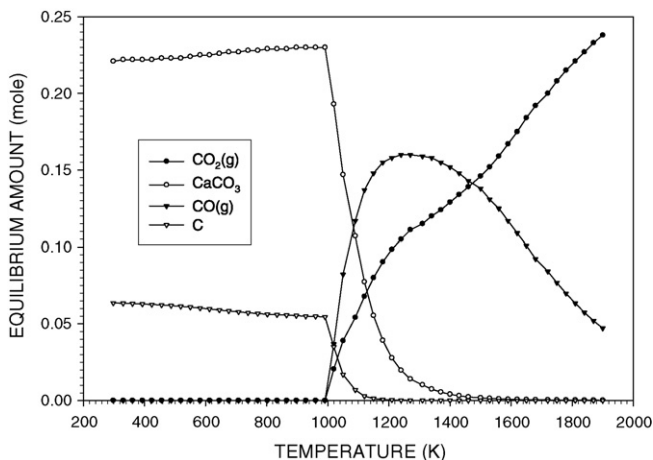

Fig. 6. Equilibrium amounts of the carbon-containing species as a function of temperature in the presence of 0.173 mol of carbon as a reducing agent.
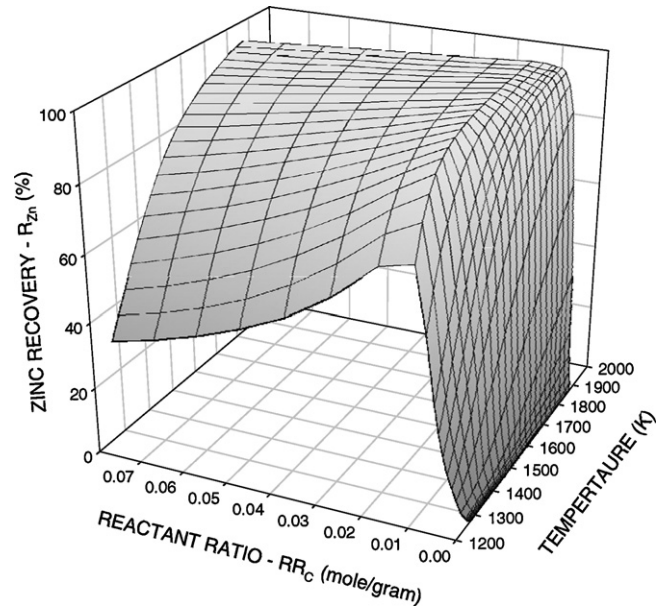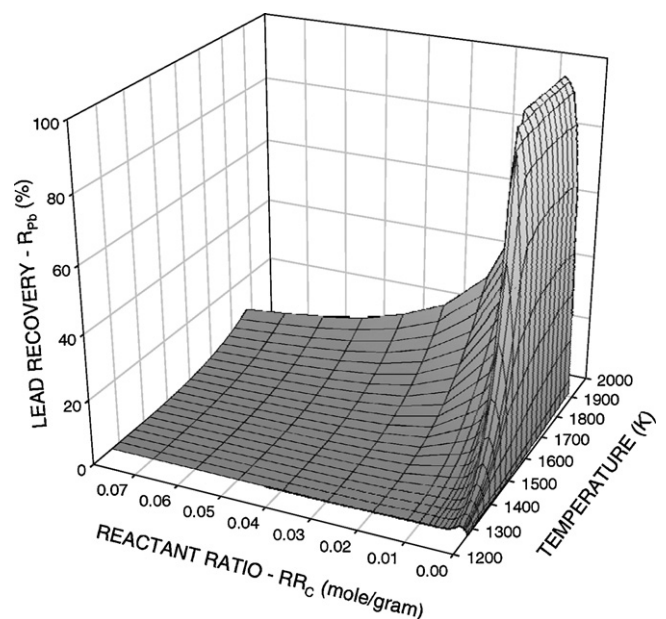

Fig. 8. Lead recovery (R_{Pb}) as a function of the reactant ratio (RR_C) and temperature.

Fig. 9. Iron recovery (R_{Fe}) as a function of the reactant ratio (RR_C) and temperature.

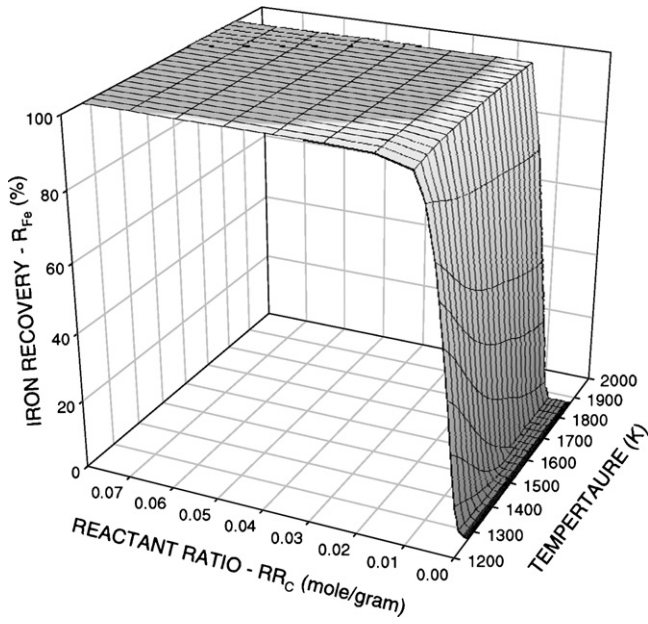Fig. 11. Selectivity factor for lead ($\log \beta_{Pb/Fe}$) as a function of the reactant ratio (RR_C) and temperature.

carbon dioxide in the gas phase. Therefore, the vapour pressure of zinc at equilibrium in the reduction process becomes lower than the corresponding value for pure liquid zinc at the same temperature and some of the zinc is produced in liquid form. This reduces the amount of gaseous zinc and therefore the zinc recovery decreases, particularly at low temperatures and high reactant ratios. The maximum zinc recovery of ninety nine-and-a-half percent was achieved at 1873 K and a reactant ratio of 0.008 mol/g.

As shown in Fig. 8, the behaviour of lead as a function of temperature and reactant ratio is similar to that observed for
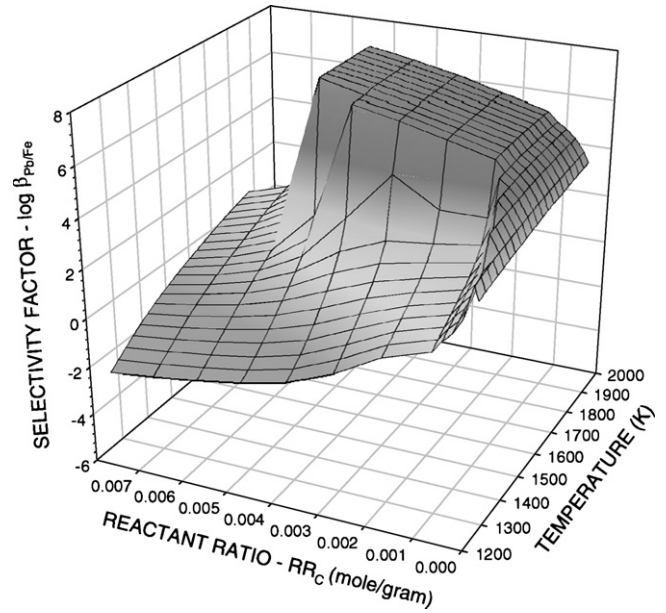
zinc. However, because of the lower thermodynamic stability of lead oxide in comparison to zinc oxide, high lead recoveries can be achieved at lower temperatures and reactant ratios. Lead recoveries of ninety percent could be attained at 1543 K for a reactant ratio of 0.003 mol/g and recoveries of ninety eight percent were achieved at 1663 K and a reactant ratio of 0.004 mol/g. The conditions over which lead recoveries in excess of ninety eight percent could be realized was limited to a narrow region at a reactant ratio of 0.005 mol/g and temperatures between 1633 and 1873 K, with the maximum lead recovery under these conditions being almost ninety nine percent. In a manner similar to
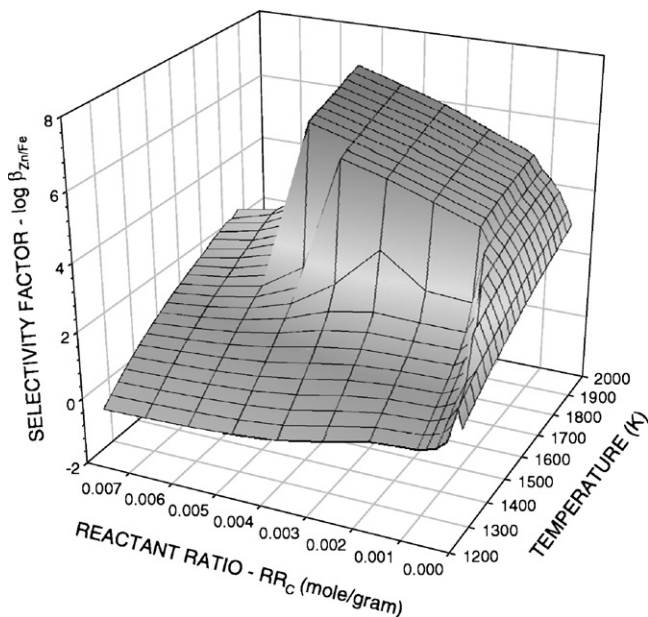

Fig. 10. Selectivity factor for zinc ($\log \beta_{Zn/Fe}$) as a function of the reactant ratio (RR_C) and temperature.
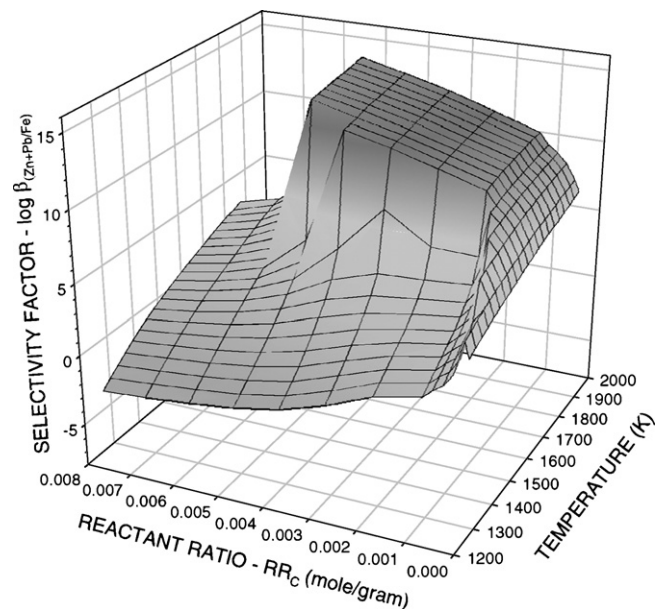

Fig. 12. Combined selectivity factor for zinc plus lead ($\log \beta_{(Zn+Pb/Fe)}$) as a function of the reactant ratio (RR_C) and temperature.
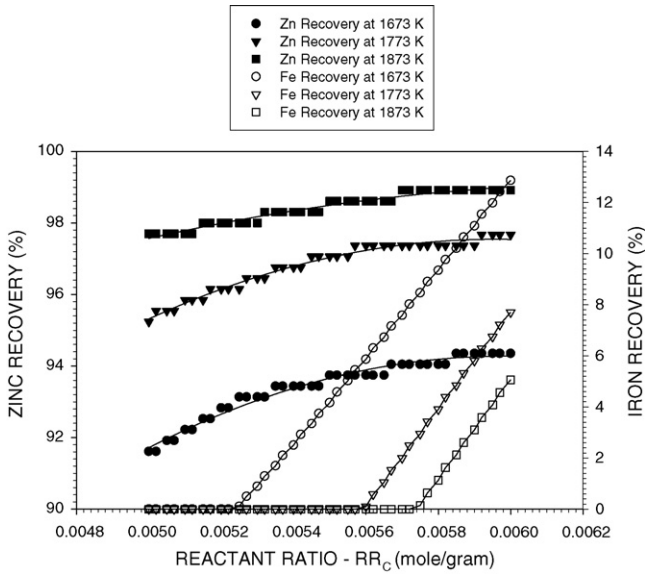
Fig. 13. Zinc and iron recoveries at 1673, 1773 and 1873 K for reactant ratios (RR_C) in the range of 0.005–0.006 mol/g.

Fig. 15. Zinc recovery as a function of temperature and pressure for a reactant ratio (RR_C) of 0.003 mol/g.

zinc, but more pronounced because of the much higher boiling point of lead, the vapour pressure of lead under some reducing conditions can become lower than the equilibrium value with pure liquid lead at the same temperature. Thus the lead recovery decreases drastically at high temperatures and, in particular, low reactant ratios. These effects contribute to the formation of an extremely narrow region for high lead recoveries in the gas phase.

A three-dimensional mesh plot of the metallic iron recovery as a function of temperature and reactant ratio is shown in Fig. 9. From this figure it can be seen that significant iron production can only be avoided at low reactant ratios. In addition, at low
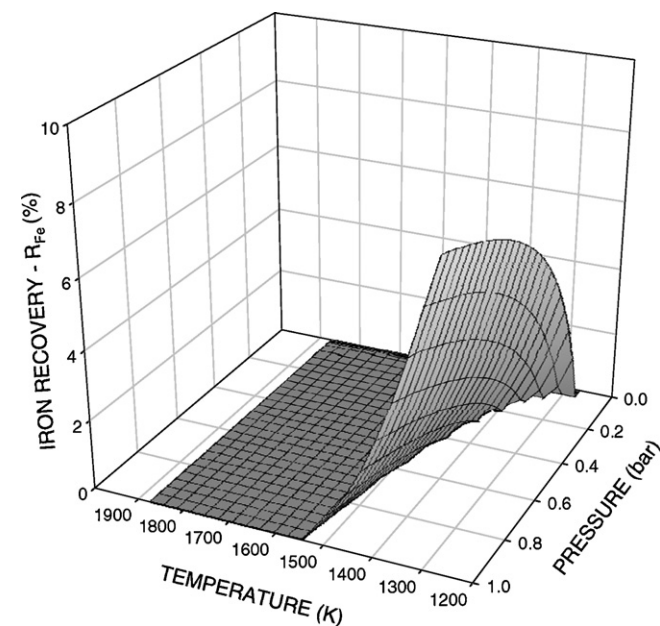
reactant ratios, the metallic iron recovery is lower at higher temperatures. At low reactant ratios, the amount of carbon is limited and the metallic iron produced by indirect reduction of FeO will be higher. Since carbon monoxide is more stable than carbon dioxide at higher temperatures, then the indirect reduction of FeO by carbon monoxide is more favourable at lower temperatures. Substantial iron production occurred above a reactant ratio of 0.01 mol/g and across the whole temperature range. For example, for a reactant ratio of 0.008 mol/g and a temperature of 1273 K, the metallic iron recovery was about seventy five percent. For reactant ratios, at and above 0.0125 mol/g and at all

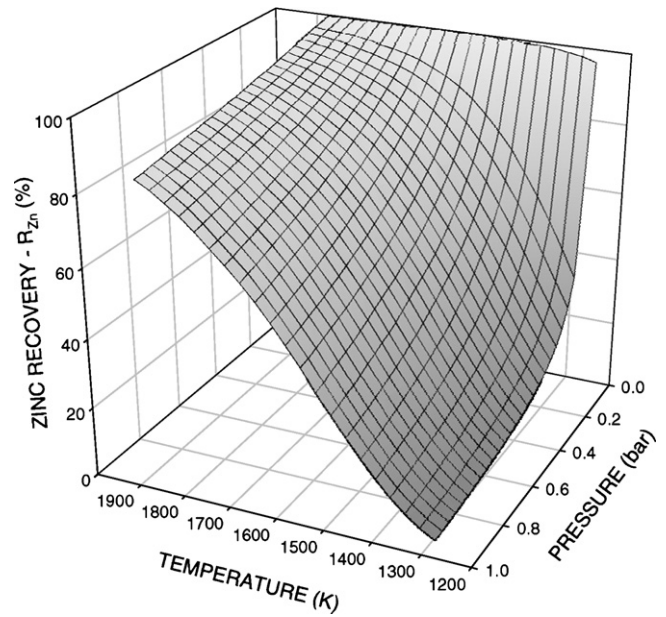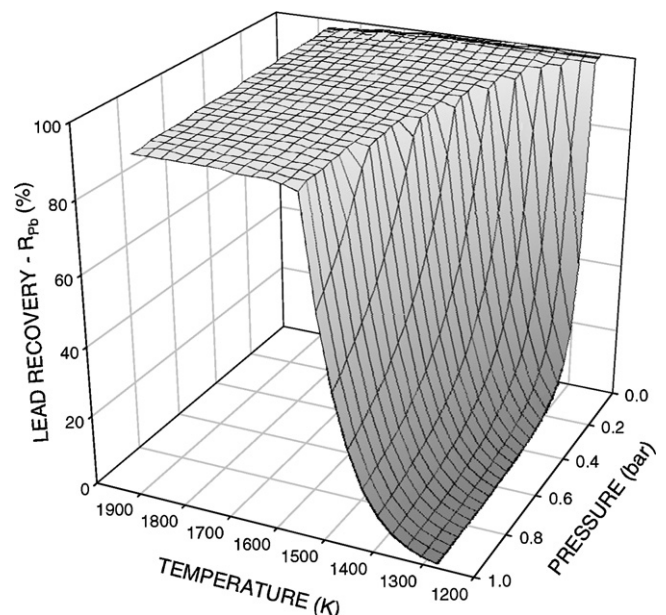Fig. 14. Iron recovery as a function of temperature and pressure for a reactant ratio (RR_C) of 0.003 mol/g.

Fig. 16. Lead recovery as a function of temperature and pressure for a reactant ratio (RR_C) of 0.003 mol/g.

temperatures in the range studied, the iron recovery was close to or equal to one hundred percent.

The selectivity factors for zinc, lead and zinc plus lead are shown in Figs. 10–12, respectively. In all cases, the reactant ratio range used in the calculations was 0 to 0.008 mol/g, as this region is of the most interest for selective reduction. For zinc, relatively high selectivity factors in the range of about 6–7 can be attained over a narrow range of reactant ratios and temperatures from 0.003 to 0.004 mol/g and from 1600 to 1873 K, respectively. For lead, the selectivity factors were higher than those for zinc, because of the lower stability of lead oxide and thus reduction occurs at lower reactant ratios. For example, lead selectivity

factors from 6 to 7.5 could be attained between reactant ratios of 0.001 to 0.005 mol/g and temperatures of 1573 to 1873 K. The zinc plus lead selectivity factors are shown in Fig. 16 and, as expected, the region over which selectivity factors in the range of 12 to 15 can be achieved is restricted to reactant ratios of 0.002 to 0.005 mol/g and temperatures of 1573 to 1873 K.

To better understand the conditions for maximum zinc recovery and minimum metallic iron production, both the zinc and the iron recoveries are plotted in Fig. 13 at 1673, 1773, and 1873 K for a narrow reactant ratio range of 0.005–0.006 mol/g. These selected conditions represent those over which zinc recoveries in the range of about 92–99% can be achieved and the iron recovery

Fig. 17. (a): Zinc selectivity factor ($\log \beta_{Zn/Fe}$) as a function of temperature and pressure for a reactant ratio (RR_C) of 0.001 mol/g. (b): Zinc selectivity factor ($\log \beta_{Zn/Fe}$) as a function 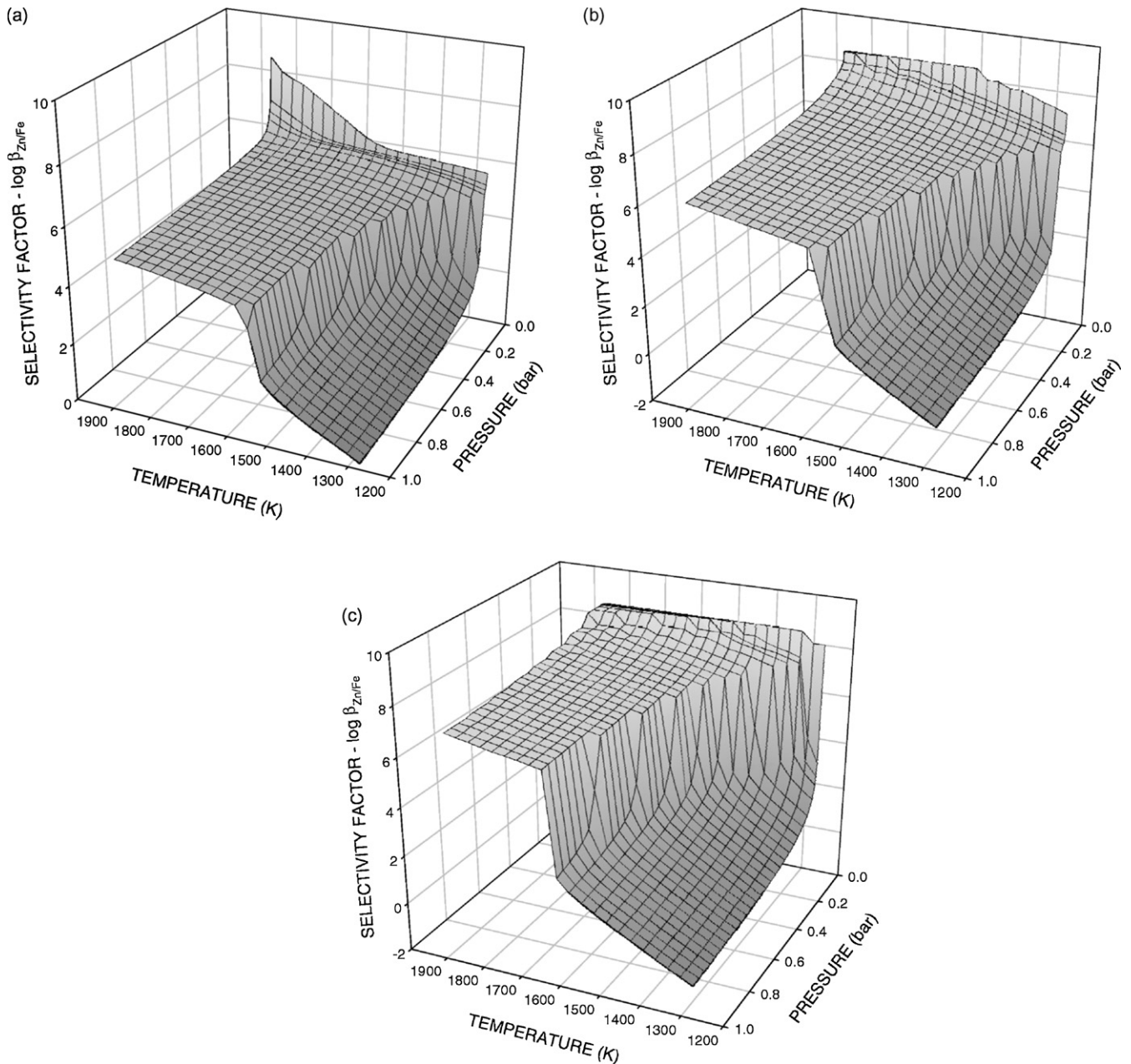of temperature and pressure for a reactant ratio (RR_C) of 0.003 mol/g. (c): Zinc selectivity factor ($\log \beta_{Zn/Fe}$) as a function of temperature and pressure for a reactant ratio (RR_C) of 0.005 mol/g.

is between zero and about twelve percent. It can be seen that the zinc recovery increases with both the reactant ratio and temperature. Similarly, the iron recovery increases with reactant ratio but on the other hand, decreases with increasing temperature. At any given temperature, the reactant ratio has to be increased in order to increase the zinc recovery, but the maximum zinc recovery cannot be attained without some metallic iron production. Thus, the optimum thermodynamic conditions for zinc recoveries approaching one hundred percent and no metallic iron production are limited by temperature but also more notably, by relatively small changes in the reactant ratio. In actual practice, this situation will be even more acute, as it is difficult to achieve not only isothermal conditions but also both the composition of

the dust and the carbonaceous reducing agent can vary and this will change the reactant ratio.

2.3. Effect of reduced pressure

The effects of reducing the total pressure from 1.00 to 0.001 bar, on the iron, zinc and lead recoveries for a reactant ratio of 0.003 mol/g are shown, in Figs. 14–16, respectively. At this low reactant ratio, the amount of metallic iron was relatively low under all conditions. Furthermore, not only relatively low temperatures but also high pressures favoured metallic iron production. In addition, relatively high temperatures and low pressures favoured high zinc and lead recoveries. For exam-

Fig. 18. (a): Lead selectivity factor (log $\beta_{Pb/Fe}$) as a function of temperature and pressure for a reactant ratio (RR$_C$) of 0.001 mol/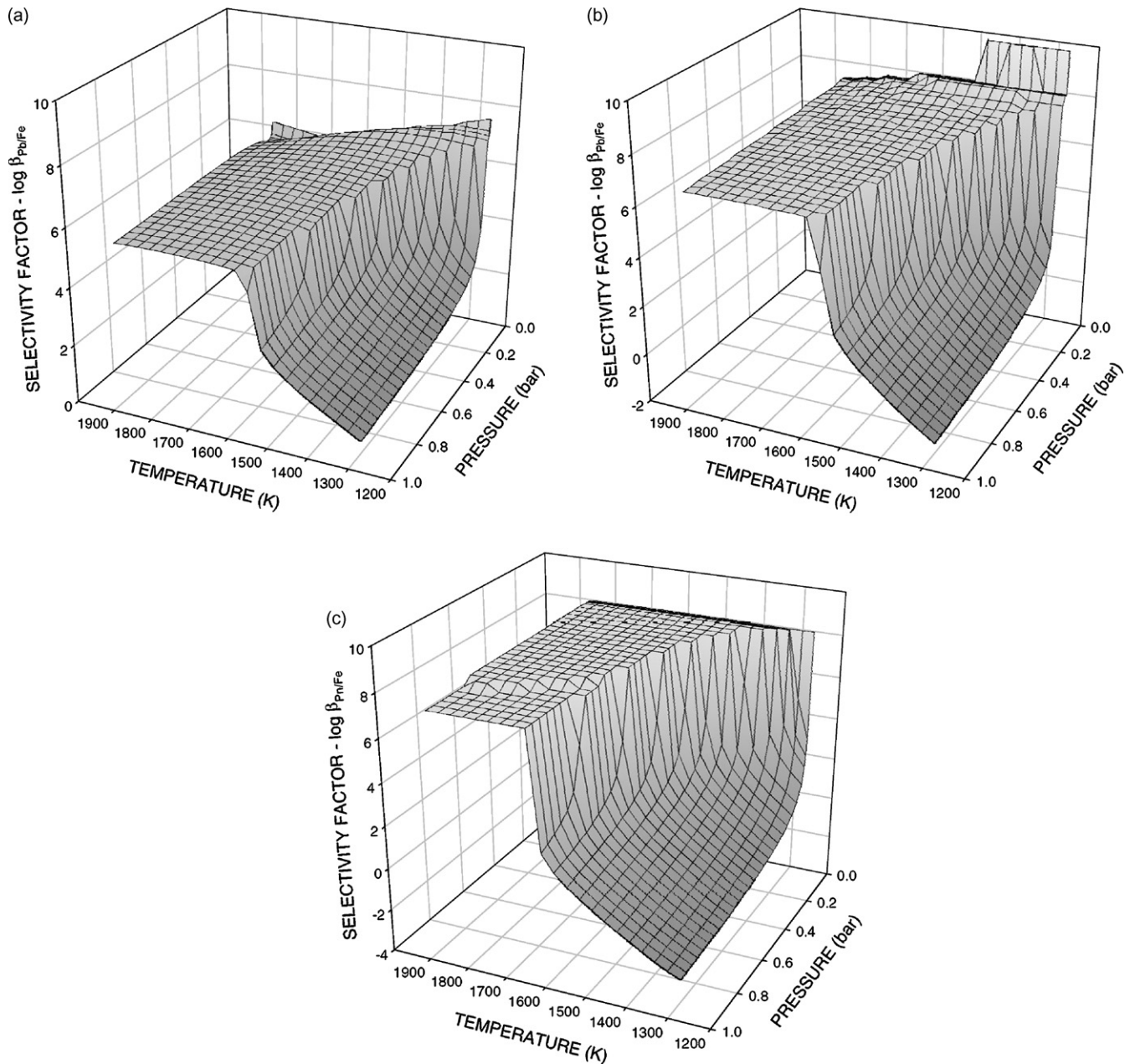g. (b): Lead selectivity factor (log $\beta_{Pb/Fe}$) as a function of temperature and pressure for a reactant ratio (RR$_C$) of 0.003 mol/g. (c): Lead selectivity factor (log $\beta_{Pb/Fe}$) as a function of temperature and pressure for a reactant ratio (RR$_C$) of 0.005 mol/g.

ple, in the case of lead it is possible to achieve essentially one hundred percent recovery at pressures below about 0.01 bar at 1273 K. This divergent behaviour of iron versus the non-ferrous metals indicates that it should be thermodynamically possible to even further facilitate the separation of zinc and lead from the iron by utilizing reduced pressures.

Figs. 17(a)–(c) and 18(a)–(c) show three-dimensional mesh plots of the effects of pressure and temperature on the selectivity factors for zinc and lead, respectively, at low, intermediate and high reactant ratios of 0.001, 0.003 and 0.005 mol/g. In general, the minimum temperature required for reasonably high selectivity factors (i.e. over six) decreases with decreasing pressure. At low reactant ratios there is insufficient reducing agent for complete reduction of the non-ferrous metal oxides. Furthermore, at the higher temperatures, more of the reducing agent is utilized for the reduction of the iron oxide to the sub-oxides and this reduces the amount of available reducing agent for the non-ferrous metal oxides and the selectivity factor decreases. On the other hand, at high reactant ratios, the formation of metallic iron is promoted, particularly at the lower temperatures. This decreases the selectivity factors at the lower temperatures and also results in an increase in the minimum temperature at which reasonable selectivity factors can be obtained. At extremely low pressures, there are significant increases in the selectivity factors

and this effect is even further enhanced at higher temperatures for zinc and at the lower temperatures for lead. At intermediate temperatures, for example at 1453 K, for a reactant ratio of 0.003 mol/g and a total pressure of 0.001 bar, zinc or lead selectivity factors in the range of 8–10 ten can be achieved. Therefore, the zinc plus lead selectivity factors would be in the range of 16–20. These values can be compared to the much lower individual values of about six to seven and to the combined zinc plus lead values of twelve to fifteen, which can be obtained at atmospheric pressure (i.e. 1 bar) under the optimum conditions.

2.4. Effect of dust and gas composition

The above calculations were performed for the standard dust composition but it would be expected that the composition of the dust would have an effect on the recovery and the separation of the zinc and the lead. There are three possible effects of the various dust components as follows:

(1) A change in the amount of a species, which calcines during the reduction process, for example, calcium carbonate ($CaCO_3$) or calcium hydroxide will affect the equilibrium gas composition.
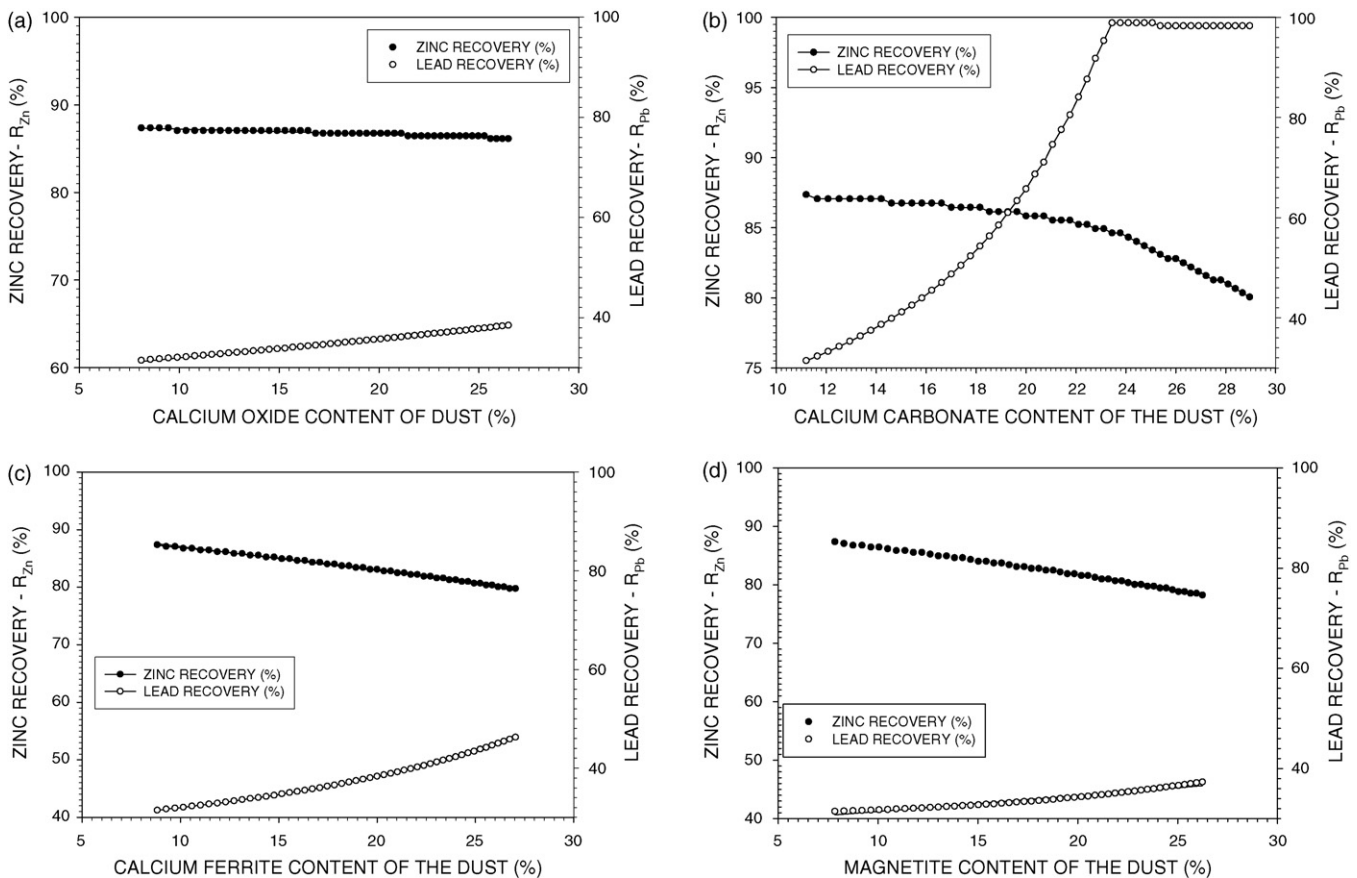

Fig. 19. (a): Zinc and lead recoveries as a function of the amount of calcium oxide in the dust at 1573 K and a reactant ratio (RR_C) of 0.006 mol/g. (b): Zinc and lead recoveries as a function of the amount of calcium carbonate in the dust at 1573 K and a reactant ratio (RR_C) of 0.006 mol/g. (c): Zinc and lead recoveries as a function of the amount of calcium ferrite in the dust at 1573 K and a reactant ratio (RR_C) of 0.006 mol/g. (d): Zinc and lead recoveries as a function of the amount of the magnetite in the dust at 1573 K and a reactant ratio (RR_C) of 0.006 mol/g.

(2) A change in the amount of some of the components, such as lime (CaO), in the initial dust will affect the equilibrium composition after reduction.

(3) A change in the amount of a reducible oxide, such as iron oxide, will affect the consumption of the reducing agent.

These effects can act either independently or in combination. For example, an increase in the amount of calcium carbonate in the dust not only results in an increased amount of carbon dioxide in the gas phase, over the temperature range of reduction, but additional lime is present which affects the equilibrium composition of the reactant products. Fig. 19 (a), (b), (c) and (d) show the effects of independently increasing the amounts of calcium oxide, calcium carbonate, calcium ferrite (CaO·Fe$_2$O$_3$) and magnetite, respectively, on the zinc and lead recoveries. The reduction temperature was 1573 K and the reactant ratio was 0.006 mol/g. Increasing the amount of calcium oxide alters the equilibrium distribution, with more of the free iron oxide being converted into calcium ferrite and the metallic iron recovery decreases. Furthermore, the zinc recovery decreases, while more of the liquid lead is recovered in gaseous form. Calcium carbonate introduces both calcium oxide and carbon dioxide into the system. The additional carbon dioxide causes the atmosphere to become more oxidizing and also results in the dilution of the gas phase. These effects, in combination with the presence of the supplementary calcium oxide, results in even further liquid lead being converted to gaseous lead and there is a dramatic increase in the lead recovery, but again the zinc recovery decreases. Magnetite consumes additional reducing agent and again the zinc recovery decreases while the lead recovery increases. Calcium ferrite provides both lime and magnetite, which affects the final equilibrium composition and the consumption of the reducing agent and the zinc recovery decreases while more of the liquid lead is converted into gaseous lead.

The addition of an unreactive gas, such as nitrogen, should result in a reduction in the partial pressures of both zinc and lead and also carbon monoxide and carbon dioxide in the gas phase and this would be expected to improve the recoveries of the metals. The effects of the increasing amounts of nitrogen on the zinc and lead recoveries were calculated for a constant reactant ratio of 0.006 mol/g at 1273 K and at atmospheric pressure (1 bar). The results are shown in Fig. 20 (a) and (b) for zinc and lead, respectively, where the equilibrium amounts of the various species are plotted as a function of the carbon to nitrogen molar ratio. For zinc, increasing the amount of nitrogen increases the equilibrium amount of zinc in the gas phase, since the amount of zinc oxide that is reduced increases and also the amount of liquid zinc decreases. For lead, the amount of lead oxide is low and the major effect is the conversion of liquid lead to gaseous lead as the molar ratio decreases. These improvements in the zinc and lead recoveries become more significant as the carbon to nitrogen molar ratio decreases. Fig. 20(c) shows the behaviour of the major iron-containing species as a function of the carbon to nitrogen molar ratio. It can be seen that the equilibrium amounts of the iron oxide-containing species, in particular
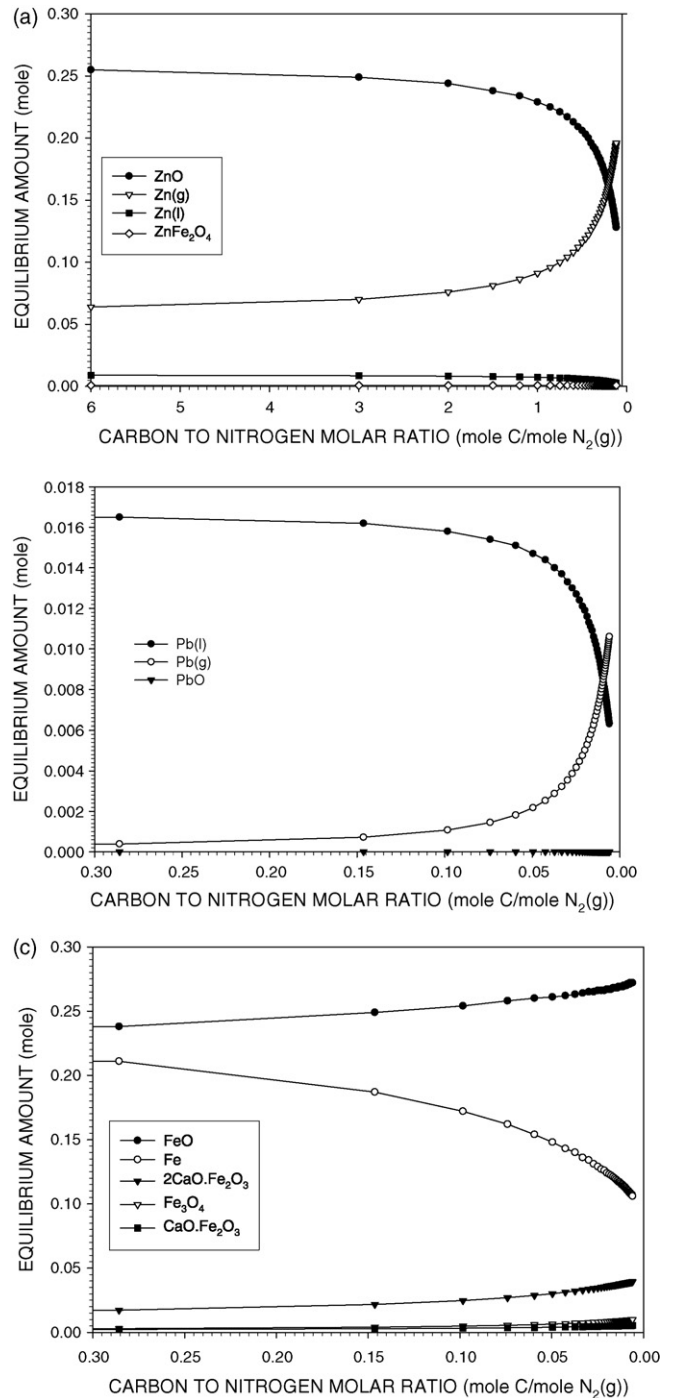

Fig. 20. (a): Effect of the carbon to nitrogen molar ratio on the equilibrium amounts of the zinc-containing species at 1273 K and a reactant ratio (RR$_C$) of 0.006 mol/g. (b): Effect of the carbon to nitrogen molar ratio on the equilibrium amounts of the lead-containing species at 1273 K and a reactant ratio (RR$_C$) of 0.006 mol/g. (c): Effect of the carbon to nitrogen molar ratio on the equilibrium amounts of the iron-containing species at 1273 K and a reactant ratio (RR$_C$) of 0.006 mol/g.

wustite, increase with the carbon to nitrogen ratio. Thus, the corresponding amount of metallic iron decreases, which results in an increase in the zinc and lead selectivity factors in a manner similar to that described previously for the effect of reduced pressure.
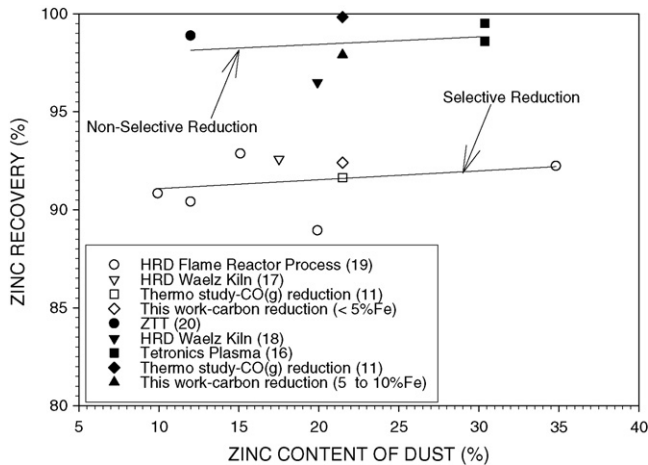
Fig. 21. Comparison of the zinc recoveries from the present thermodynamic calculations with the results obtained in previous work.

3. Comparison with previous results

As mentioned earlier, there are two major options with regards to the pyrometallurgical treatment of EAF dust; selective reduction and non-selective or total reduction. From Fig. 13, it can be seen that for reactant ratios at or below 0.005 mol/g, there is a range of temperatures over which there is no metallic iron recovery but the zinc recovery is relatively low. At a reactant ratio of 0.006 mol/g, some metallic iron is recovered under all conditions and the zinc recovery is correspondingly higher. Thus, as discussed previously, the thermodynamic range of operating conditions, in particular the reactant ratio, for truly selective reduction is extremely narrow. For the purposes of comparison, with regards to the present work, selective reduction is defined by the conditions of a reactant ratio of 0.005 mol/g and a metallic iron recovery of greater than 0.0002 percent (i.e. the default value) but less than five percent. On the other hand, non-selective reduction is defined by the conditions of a reactant ratio of 0.006 mol/g and a metallic iron recovery in the range of 5–10%. This approach, for these conditions, gives average zinc recovery values of 92.4 percent for selective reduction and 97.9 percent for non-selective reduction. A comparison of these results with those from a previous thermodynamic study on the reduction of EAF dust by carbon monoxide and also data from actual HTMR processes [16–20] are presented in Fig. 21. The results have been divided into two groups based on whether the reduction was selective or non-selective (i.e. involved the reduction of a significant amount of iron or total reduction) and are plotted against the zinc content of the dust. It can be seen that with selective reduction, zinc recoveries in the range of about 90–92% can be achieved, while much higher recoveries in the range of 97–99% are attained when there is significant recovery of metallic iron.

4. Conclusions

1. The equilibrium composition of a mixture of a control EAF dust with carbon, as a reducing agent, in the temperature range of 1273–1873 K was calculated using the SOLGAS-MIX solver of Outokumpu HSC Chemistry® 5.1. The results

showed that recoveries of over ninety eight percent could be attained for zinc or lead vapours under the optimum conditions. In contrast to the non-ferrous metals, the reduction of iron oxide to metallic iron was favoured by low temperatures and high reactant ratios.

2. Separation of the two non-ferrous metal vapours from the iron, in oxide form, was quantified as a function of temperature and the reactant ratio using the selectivity factor

$$(\beta): \beta_{A/B} = \frac{X_A}{X_B}\frac{Y_B}{Y_A}$$

where X and Y are the concentrations of the two metals, zinc or lead and iron, respectively, in the two different phases, that is, the gas phase (A) and the condensed phase (B). Values of $\log \beta_{Zn/Fe}$ or $\log \beta_{Pb/Fe}$ in the range of 6–7 were readily realized. Since the regions, over which these high selectivity factors for zinc and lead were achieved, overlap to a considerable degree, then zinc plus lead selectivity factors ($\log \beta_{Zn+Pb/Fe}$) in the range of 12–15 could be attained for reactant ratios from 0.002 to 0.005 mol/g and temperatures from 1573 to 1873 K. The optimum conditions for zinc recoveries approaching one hundred percent and metallic iron recoveries of zero are restricted not only by temperature but also more significantly by the narrow range of the reactant ratio under isothermal conditions.

3. High zinc and lead recoveries are favoured by high temperatures and low total pressures. On the other hand, high metallic iron recoveries are favoured by low temperatures and relatively high pressures. Therefore, reducing the total pressure enhances the separation of the non-ferrous metals, with maximum individual selectivity factors in the range of 8–10 and zinc plus lead selectivity factors in the range of 16–20 at low pressures.

4. Independently increasing the amounts of calcium carbonate, calcium oxide, calcium ferrite and magnetite, resulted in a decrease in the zinc recovery and an increase in the lead recovery. The addition of a non-reactive gas, such as nitrogen, to the system resulted in increases in the non-ferrous metal recoveries and a decrease in the metallic iron recovery and therefore the separation of the non-ferrous metals was improved, in a manner similar to the behaviour observed under reduced pressure.

5. The conditions in the present study, which resulted in zinc recoveries in the range of about 92–99% and negligible or low metallic iron recoveries, were categorized into either selective reduction or non-selective reduction, respectively. These results were compared with other thermodynamic calculations and industrial results, and there was reasonable agreement between the present results and those obtained in previous work.

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