A KINETIC MODEL FOR THE REDUCTION OF ZINC OXIDE BY IRON

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ABSTRACT

Dusts produced in electric arc furnaces (EAF) are hazardous residues containing significant amounts of zinc, mostly in the form of zinc oxide. A process to recover zinc from EAF dusts involves the reduction of zinc oxide with the metallic iron produced by the pre-reduction of iron oxide contained in the dusts. When iron is used as a reducing agent, the gas volume generated in the reactor is smaller and, since CO and CO_2 are not present, the condensation of zinc may be enhanced. In addition, the oxidized iron can be recovered by recycling the residue in the plant. In this work, the reduction of zinc oxide by iron was studied using a thermogravimetric technique. Briquettes of zinc oxide and iron powders were reacted in the temperature range of 900-1050 °C under a nitrogen atmosphere. The effect of temperature on the reaction rate was determined. The experimental findings were analyzed with the aid of a simple kinetic model that provided an adequate fit for the data.

INTRODUCTION

In the electrical steelmaking plants, electric arc furnace (EAF) dusts are produced containing significant amounts of zinc, mainly in the form of oxide and ferrite. The chemical composition of this material varies considerably among different plants and depends on the type and quality of the scrap used, and on the type of steel produced. The amount of EAF dust generated is typically about 1 to 2 % of the initial load. EAF dust is classified as a hazardous waste particularly due to the presence of Pb, Cd and hexavalent Cr.

Several pyro and hydrometallurgical processes for treating EAF dusts, aiming at removing and recovering valuable metals, have been recently developed. Among the pyrometallurgical processes, the ones that recover the metals by selective volatilization (Waels furnace, plasma furnace ZIA process) have greater relevance (Cowx et al., 1990; Eacott et al., 1984; Donald and Pickles, 1996; Tsuneyama et al., 1990). In these processes, the ZnO is reduced either by C or by CO (Tsuneyama et al., 1990). Nevertheless, these processes may present a drawback caused by the unacceptably high impurities (as S and Cu) content of the metallic iron produced, which render it inadequate to be recycled again in the EAF.

An alternative process involves the metallothermic reduction of the ZnO contained in the EAF dust by the iron produced during the pre-reduction of the FeO present in these fines (Queiroz, 2000). When the metallic iron is used as the reductant, the gas volume generated inside the reactor is lower and, since CO and CO_2 are not present, the condensation of Zn may be enhanced. Thus, the purity of the ZnO obtained is expected to be higher than in the carbothermic reduction processes. In addition, the oxidized iron may be recovered by recycling the residue.

The amounts generated and the concentration of Zn in the EAF dusts, between 17 and 23%, are relatively large. In addition, there are insufficient mineral reserves to furnish zinc for the producing industries in Brazil, making it most of the times necessary to import zinc ores.

Therefore, the recycling of EAF dusts and the recovery of Zn become attractive as a secondary production source of the metal.

There is a paucity of fundamental information available in the literature regarding the kinetics parameters and the mechanisms of the reduction of ZnO by metallic iron. The reduction kinetics of pure ZnO by pure solid iron in an inert atmosphere employing a thermogravimetric technique is studied in this work. The experimental system consisted of a thermogravimetric balance that continuously measured the weight loss of the briquettes during the reaction. A scheme and description of this equipment is given elsewhere (Queiroz, 2000).

A kinetic model for the reaction was developed and applied to some experimental data with the objective of establishing the mechanisms involved and determining the rate controlling steps of the reaction.

KINETIC MODEL

The reduction of ZnO by Fe is represented by the following reaction:

ZnO + Fe = Zn(g) + FeO, $\Delta H = 197.45$ kJ/mol - 1150°C   (1) Since reaction (1) is strongly endothermic, the equilibrium constant and, hence, the Zn partial pressure, increase significantly with augmenting the temperature.

The rate of the reaction between the particles of ZnO and Fe comprising the briquettes depend upon several factors. Major considerations to be made concern the rate of chemical reaction and the rate of transport of Zn vapor from the interior of the solid through the product layer. Consideration must also be made on the rate of heat transfer from the briquette surface to its interior where the endothermic reaction occurs. These phenomena, depending on their order of magnitude, imply that the rate-controlling step may be chemical, diffusive, thermal or mixed. However, a strict heat transfer control hardly took place in the experimental conditions employed in this work, since it required extremely low temperatures at the reaction interface. Therefore, the sequential steps of the reduction of ZnO by Fe inside the briquettes involve chemical reaction and diffusion of the Zn vapor inside the briquette. At this point, it is assumed an ideal topochemical kinetic model (Doraiswamy and Sharma, 1984; Fogler, 1992; Levenspiel, 1972; Smith, 1981; Sohn and Wadsworth, 1979; Szekely et al., 1976). If the briquette is very porous, the reaction may take place at any point in its interior. Additional complications are the occurrence of cracks and sintering in the briquette. Thus, for the sake of simplicity in developing the kinetic model to describe the rate of reaction (1), the following assumptions were made:

- the reaction follows the unreacted core model (ideal topochemical model);

- there are no accumulation of heat and mass inside the briquette;

- there are no sintering in the briquette;

- there are no cracking of the briquette;

- the briquette volume remains constant during the reaction;

- the briquette is a perfect cylinder;

- the briquette is initially comprised of two finely divided and homogeneously mixed solids (ZnO and Fe);

- the reduction reaction is irreversible and first order;

- the Zn vapor has an ideal gas behavior.

According to the unreacted core model, the rate of Zn vapor generation from a cylindrical briquette, $\dot{N}_{Zn(g)}$, can be described by the expression (2):

$$\dot{N}_{Zn(g)} = 2 \cdot \pi \cdot r \cdot L \cdot \left(-\frac{dr}{dt}\right) \cdot \rho \qquad (2)$$

where: r is the radius of the reaction interface, L is the briquette length, T is the reaction time and ρ is the molar density of the unreacted briquette.

The fraction of zinc generated in the vapor phase (χ) is given by $\chi = 1 - \left(\frac{r}{R}\right)^2$ (3)

where: R is the radius of the briquette.

Assuming reaction (1) under chemical control, the rate of Zn vapor formation, $\dot{N}_{Zn(1)}$, may also be described by a first order kinetics law as:

$$\dot{N}_{Zn(1)} = 2 \cdot \pi \cdot k \cdot r \cdot L \cdot \left(C_{Zn}^* - C_{Zn}\right) \qquad (4)$$

where: k is the rate constant at the reaction temperature, $C_{Zn}^* = \dfrac{p_{Zn}^*}{R_g \cdot T} = \dfrac{K}{R_g \cdot T}$ is the equilibrium concentration of Zn(g), R_g is the gas constant, T is the absolute reaction temperature and C_{Zn} is the concentration of Zn(g) at the reaction interface.

When Zn(g) diffusion through the porous product layer controls the rate, the reaction rate is given by the diffusion rate of Zn(g) from the reaction interface to the briquette surface, $\dot{N}_{Zn(2)}$, as:

$$\dot{N}_{Zn(2)} = \frac{2 \cdot \pi \cdot L \cdot D_{ef} \cdot (C_{Zn} - C_{Zns})}{\ln(R/r)} \qquad (5)$$

where: D_{ef} is the effective diffusivity of Zn(g) in the porous product layer and C_{Zns} is the concentration of Zn(g) at the briquette surface.

Considering quasi steady state conditions:

$$\overset{\bullet}{N}_{Zn(g)} = \overset{\bullet}{N}_{Zn(l)} = \overset{\bullet}{N}_{Zn(2)} \qquad (6)$$

When chemical reaction controls the rate, the resistance offered by mass transfer is negligible, while for the case of control by mass transfer, the resistance offered by chemical reaction is negligible. The two rate controlling steps may occur simultaneously according to the following equation for the Zn(g) generation rate:

$$N_{Zn(g)} = \frac{Driving \cdot force}{R_r + R_d} \qquad (7)$$

where: R_r is the resistance offered by the chemical reaction process and R_d is the resistance offered by the mass transfer process.

When any of the resistances dominates, the reduction reaction presents a single control. However, frequently, more than one resistance dominates. In such case, the reaction presents a mixed control. It is usually very difficult that any one of the single rate-controlling steps may actually hold. For gas-solid reactions, the most common situation is the occurrence of an initial period during which the reaction approaches chemical control. The relative importance of the resistance offered by the chemical reaction diminishes while the relative importance of transport phenomena in the product layer increases with the reaction time. Notwithstanding, the reaction studied is solid-solid. For these reactions, solid-state diffusion through a dense product layer may become an important process being even the rate-controlling step.

Re-writing the equations (4) and (5) in the form resistance multiplied by a flux equals the driving force:

$$\frac{1}{2 \cdot \pi \cdot k \cdot r \cdot L} \cdot \overset{\bullet}{N}_{Zn(g)} = C^*_{Zn} - C_{Zn} \qquad (8)$$

$$\frac{\ln(R/r)}{2 \cdot \pi \cdot L \cdot D_{ef}} \cdot \overset{\bullet}{N}_{Zn(g)} = C_{Zn} - C_{Zns} \qquad (9)$$

Adding equations (9) and (10) and rearranging:

$$\overset{\bullet}{N}_{Zn(g)} = \frac{C^*_{Zn} - C_{Zns}}{\dfrac{1}{2 \cdot \pi \cdot k \cdot r \cdot L} + \dfrac{\ln(R/r)}{2 \cdot \pi \cdot L \cdot D_{ef}}} \qquad (10)$$

Finally, assuming mixed control and the unreacted core model, the combination of equations (2) and (10) gives:

$$-\frac{dr}{dt} = \frac{C^*_{Zn} - C_{Zns}}{\dfrac{\rho}{k} + \dfrac{\rho \cdot r \cdot \ln(R/r)}{D_{ef}}} \qquad (11)$$

Solving equation (11) with the initial condition t = 0; r = R, using the definition of fraction of zinc generated in the vapor phase, given by (3) and rearranging:

$$R_r \cdot \left[1 - (1 - \chi)^{1/2} \right] + R_d \cdot \left[\chi + (1 - \chi) \cdot \ln(1 - \chi) \right] = t \qquad (12)$$

In this equation, $R_r = \dfrac{1}{k_r} = \dfrac{R \cdot \rho}{k \cdot \left(C^*_{Zn} - C_{Zns} \right)}$ is the chemical reaction resistance and $R_d = \dfrac{1}{k_d} = \dfrac{R^2 \cdot \rho}{4 \cdot D_{ef} \cdot \left(C^*_{Zn} - C_{Zns} \right)}$ is the mass transfer resistance.

The resistances R_r and R_d were calculated through a matrix algorithm.

RESULTS AND DISCUSSION

The kinetic model developed above was applied to cylindrical briquettes, 25.4 mm in diameter, of –200 mesh (Tyler) ZnO and electrolytic Fe powders reacted in the temperature range of 900-1050 °C under an argon atmosphere.

Initially, the experimental data for the four temperatures were fitted with the model for chemical control ($R_d \rightarrow 0$), or $1 - (1 - \chi)^{1/2} = \dfrac{t}{R_r}$. The results are presented in Figure 1 and exhibit a comparatively poor fit. When the data were fitted with the model for mass transfer control ($R_r \rightarrow 0$), or $\chi + (1 - \chi) \cdot \ln(1 - \chi) = \dfrac{t}{R_d}$, it becomes apparent the better fit at all temperatures, according to Figure2.

It should be noticed that R_r and R_d are given by the inverse of the slopes of the lines in Figures 1 and 2, which are equal to the respective constants, k_r and k_d. The values of k_r, k_d, R_r, R_d, $\%R_r = \dfrac{100 \cdot R_r}{R_r + R_d}$ and $\%R_d = \dfrac{100 \cdot R_d}{R_r + R_d}$ are presented in Table I.

Table I – Chemical reaction and mass transfer rate constants and resistances.

T (°C)	$k_r \times 10^3$ (min^{-1})	$k_d \times 10^4$ (min^{-1})	R_r (min)	R_d (min)	% R_r	% R_d
900	1.03	2.37	971	4219	19	81
950	2.03	5.30	493	1887	21	79
1000	3.75	16.00	267	625	30	70
1050	5.77	36.20	173	276	39	61

An exam of the values found for the two resistances indicate that the reduction reaction was probably under mixed control at all temperatures. This finding is supported by the very good fit for the data at all temperatures obtained using the model for mixed control, represented by equation (12), as shown in Figure 3. The adequacy of the mixed control model for the reaction, under the conditions investigated, is demonstrated since equation (12) has a slope equal to one and the actual slope determined from the data was 0,996.

It is also observed from Table I that the relative importance of chemical reaction increases while the relative importance of mass transfer decreases with augmenting temperature. This result and the high values of activation energies for the two phenomena involved, calculated from the Arrhenius plots presented in Figure 4, $Ea_r = 150$ kJ/mol and $Ea_d = 239$ kJ/mol, suggest that, for the solid-solid reaction studied, the mass transfer process is most likely the solid-state diffusion through the FeO layer formed. In this case, an additional equation describing such process must be added to the model.

CONCLUSIONS

The following conclusions may be drawn from the work performed:

1. The chemical and mass transfer control models respectively provided a comparatively poor and better fit for the experimental data for the whole range of temperatures investigated;

2. The mixed control model adequately represented the reduction of –200 mesh (Tyler) ZnO powder by electrolytic Fe powder contained in briquettes 25.4 mm in diameter at all temperatures. Thus, the reaction was under mixed control for the conditions studied;

3. The relative importance of chemical reaction increased while the relative importance of mass

transfer decreased with augmenting temperature. This result and the high values of activation energies for the two phenomena involved, $Ea_r = 150$ kJ/mol and $Ea_d = 239$ kJ/mol, suggest that, for the solid-solid reaction studied, the mass transfer transfer process was most likely the solid-state diffusion through the FeO layer formed.
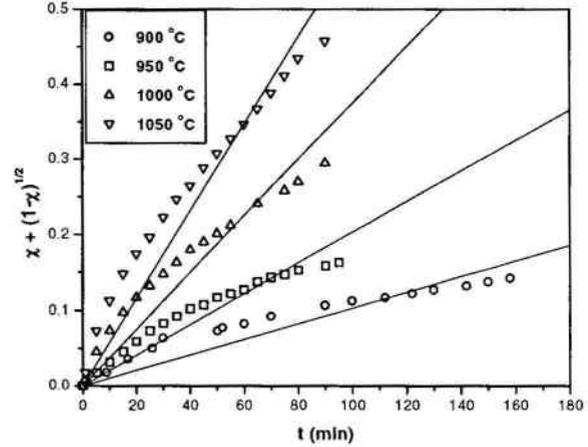

Figure 1 – Results of the chemical control model applied to the experimental data.
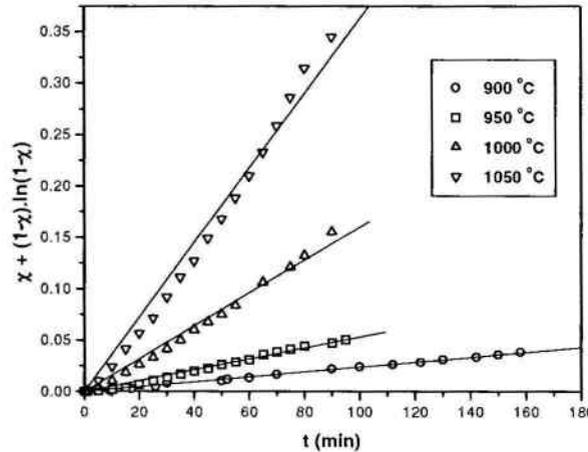

Figure 2 – Results of the mass transfer control model applied to the experimental data.
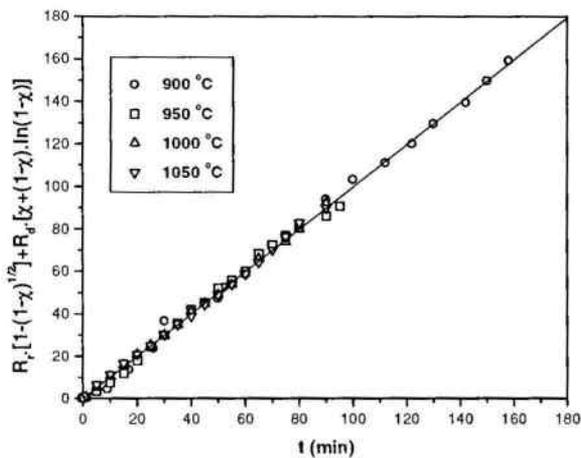
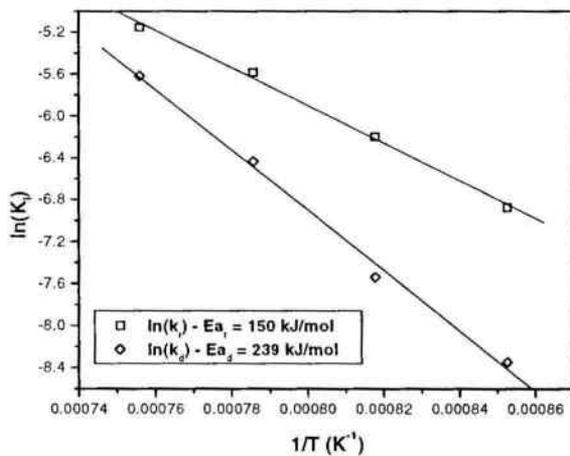Figure 3 – Results of the mixed control model applied to the experimental data.

Figure 4 – Arrhenius plots for chemical reaction and mass transfer rate constants.

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