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RESEARCHES ABOUT THE PROCESSES OF ZINC PRODUCTION FROM THE ELECTRIC ARC FURNACE DUST

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Abstract: The electric arc furnace dust, as a waste in steelmaking, may be collected and it can be used in the recovery process of heavy metals like zinc, even the percentages of these metals of commercial value are not economically feasible, (e.g. zinc with only 13% of mass). Thus, more studies are necessary aimed at making electric arc furnace dust, (EAFD), a sub product for civil construction. The paper presents some aspects in the investigation of kinetics of zinc leaching from electric arc furnace dust. It can observe that the more percent solid in the leaching solution increases, the more the rate of zinc leaching decreases. At high percent solid, the maximum zinc extraction which may be obtained depends on the zinc solubility in sodium hydroxide solution, which is lower concentration of sodium hydroxide. Also, the paper gives information about the hydrometallurgical process for the production of zinc powder from EAFD, in different mediums.

1. INTRODUCTION

The metal industry is one of the large size industries of world-wide, including iron and steel foundries and mills, as well as brass and bronze foundries. During the metal fusing process, the EAF can reach temperatures of 1600^0C, or even higher and many components of the charge, including iron, zinc, cadmium and lead are volatilised and entered the vapour phase. A large quantity of dust will be generated when the vapour is cooled and collected. Steel production is associated with a significant accumulation of wastes, as slag, sludge, flue dust and gasses. Some of these are recyclable, others are toxic, constituting hazardous wastes, which should be processed, in order to be reutilized or discarded properly in order to avoid environmental impact.

At present, one of the major concerns related to steel production in EAF is the generation of a considerable amount of flue dust, about 15-20 kg/ton of steel [4,5], in the steelmaking plant, 1-2% of dust being produced per ton of steel by EAF. This dust contains zinc about 15-25 wt. %, iron about 31-40 wt. % and the rest are cadmium, chromium, lead and nickel. Lead, cadmium and chromium are the most hazardous species in the dust, whereas zinc, due to the relatively large amount present, is the most valuable component. So, the fumes from a brass fusing furnace can have up to 65% or higher zinc. Zinc ferrite spinal accounts for 20-50% of zinc in the dust [8]. The four processes to dispose the dust are chemical stabilization, vitrification, pyrometallurgy and hydrometallurgy (or a hybridization of the last two). However, finding a cost-effective and environmental-friendly process remains the major challenge. The pyrometallurgical process, based on the Waelz kiln, is capable of processing the EAFD economically when the zinc content is higher than about 15-20%, [6]. Additionally, the plant must process at least 50.000 tons of feed per year. From the perspective of the simpler processes, which allow separation of zinc and iron, should prevail. The choice between pyrometallurgical or hydrometallurgical processing routes strongly depends on the dust characteristics, including particle size and the number of valuable elements and mineralogical phases, which in turn, may indicate the amount of leachable constituents.

Today, many of the commercially available processes for the treatment of EAFD are pyrometallurgical, such as rotary kilns, plasma and flame reactor processes. This enables the recovery of zinc bounded in a stable $ZnFeO_4$ structure and creates an iron oxide slag, which complies with environmental regulations. While pyrometallurgical processes face problems, such as high energy consumption and generation of worthless residues, hydrometallurgical processes are still only a promise for the future, despite the vast research done in this field. Still hydrometallurgical processes offer an interesting alternative for zinc recycling, if iron dissolution is controlled and the structure of zinc ferrites-which are normally difficult to leach-is broken, favouring a high recovery of zinc. So, zinc leaching from EAFD is a method of hydrometallurgy for zinc recovery and friendly environmental management. In the 1970 s, Amax Co. operated a pilot plant in New Jersey (USA), based on caustic leaching and purification of alkaline solutions by depletion of lead with zinc dust followed by electro-winning. This development was eventually abandoned due to a combination of technical and economic problems. A similar plant, based on direct caustic leaching was later built in France, but this also has been abandoned, [3]. In this paper, different techniques for zinc alkaline leaching from EAFD are investigated, aiming at the recovery of zinc. Sodium hydroxide was chosen as leaching agent as it is effective in the dissolution of zinc, without significant dissolution of iron, thus reducing the hazardous character of the solid residue. The objective of this study is to explore the technical and economic possibilities of increasing the leaching efficiencies of zinc from dusts in alkaline medium, by using a two stages process, fusing with caustic soda and then leaching. The experimental results on laboratory scale studies were reported in this paper.

2. THEORETICAL CONSIDERATIONS

The solubility of zinc oxide in water at 25^{0}C can be described by the following reactions, [1,7]:

$$\begin{aligned} &ZnO + 2H^+ \leftrightarrow Zn^{2+} + H_2O \\ &K_{s1} = 1{,}58 \cdot 10^{11} \end{aligned} \tag{1}$$

$$\begin{aligned} &ZnO + H^+ \leftrightarrow ZnOH^+ \\ &K_{s2} = 1{,}58 \cdot 10^{2} \end{aligned} \tag{2}$$

$$\begin{aligned} &ZnO + 2H_2O \leftrightarrow Zn(OH)_3^- + H^+ \\ &K_{s3} = 1.26 \cdot 10^{-17} \end{aligned} \tag{3}$$

$$\begin{aligned} &ZnO + 3H_2O \leftrightarrow Zn(OH)_4^{2-} + 2H^+ \\ &K_{s4}\, 2{,}00 \cdot 10^{-30} \end{aligned} \tag{4}$$

where K_{si} are the constants for the solubility equilibria, i=1...4. Eqs. (1) – (4) allow the determining of the total concentration of zinc in an aqueous solution, as function of pH, according to Eq. (5):

$$[Zn_T] = K_{s1}[H^+]^2 + K_{s2}[H^+] + K_{s3}[H^+]^{-1} + K_{s4}[H^+]^{-2} \tag{5}$$

Eqs. (1) – (5) are used to calculate the equilibrium diagram of solid zinc oxide and the zinc ionic species, as it is shown in Fig. 1, [2]:

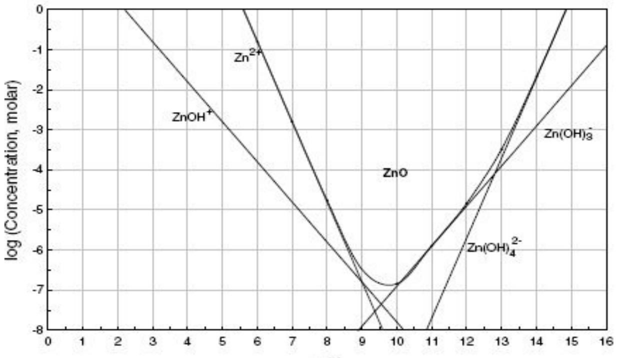
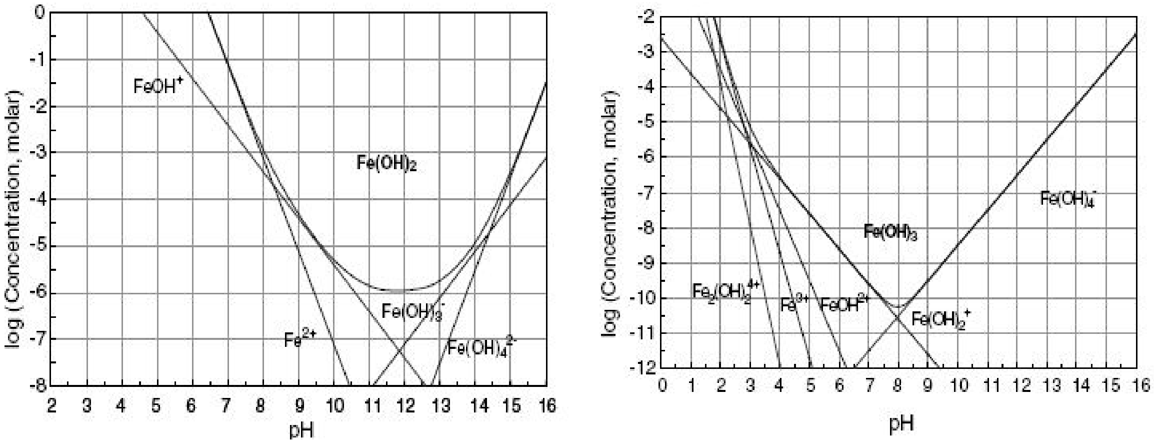


Figure 1. Solubility of ZnO depending on pH, at 25^0C

Similarly, the solubility of iron (a) and (b) in equilibrium, with their respective hydroxides are shown in Fig. 2, [2].



a. b.

Figure 2. Solubility of ferrous (a) and ferric (b) hydroxides as a function of pH, at 25^0C

Fig.1 and 2 present the equilibrium diagrams which indicate that zinc can be dissolved in either acidic or alkaline medium, whereas iron, the metal that predominates in the dust, is more readily soluble in acidic medium. Therefore, the alkaline leaching becomes a more attractive alternate
ve, as no additional purification step for iron removal is necessary.

3. EXPERIMENTAL RESEARCHES

The tests were made by using sodium hydroxide as a leaching agent, (solid/liquid ratio was 1:10) and considering the next four situations: *a*-conventional leaching in one litter closed flask, heated by a thermostatic mantle and provided with a mechanical stirrer and a water cooled condenser in order to avoid solution losses by evaporation. The concentration of sodium hydroxide was considered between 2 and 6M, the temperature was 25^0C and respectively 90^0C, the time was up to 240 minutes; *b*-pressure leaching in a 0,6 litter PARR autoclave, the concentration of sodium hydroxide was considered 6M, the temperature was between 120^0C and 200^0C, the time was 240 minutes; *c*-pre-treatment of the sample, (a 200 kg sample collected from the EAFD), in a microwave oven which has 1

KW and 2,45 GHz, during 2 minutes, followed the conventional leaching described at point *a*. The sodium hydroxide concentration was 6M, the temperature was 90^0C, the time was 240 minutes; *d*-leaching under ultrasonic agitation in a 0,5 litter beakers, considering that the concentration of sodium hydroxide was 6M, the temperature was 55^0C and the time was 60 minutes. Considering the situation *a*, the influence of sodium hydroxide concentration on zinc recovery from leaching the EAFD at 90^0C is presented in Fig.3.

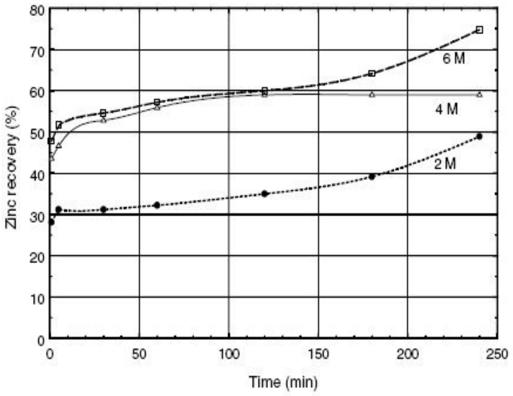


Figure 3. Influence of NaOH concentration on the dependence between the zinc recovery and time, with leaching at 90^0C

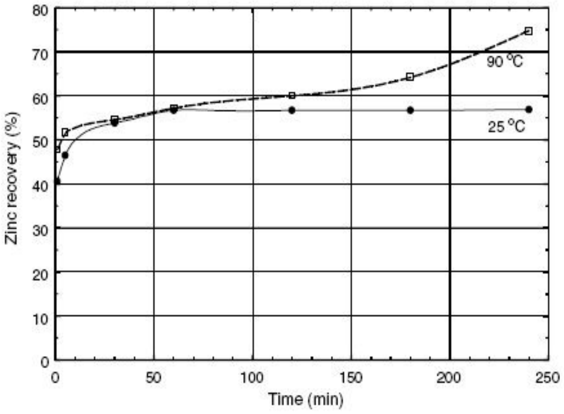


Figure 4. Influence of temperature on zinc recovery for a NaOH concentration of 6M

The picture shows that the NaOH concentration increases go to the increasing of zinc recovery. A maximum concentration of 6M was used, considering that the solution becomes very viscous and difficult manipulated above this concentration. During the initial instants of leaching, the dissolution of zinc is very fast, for all concentrations investigated, tending to a maximum value of zinc extraction, depending on the NaOH concentration at longer leaching times. It can observe that in about 10 minutes of leaching, more than 50% of the recovered zinc was already dissolved. The additional extraction obtained after 2 hours of leaching, achieved for 2 and 6M concentration of NaOH, may be associated to the dissolution of some entrapped zinc or, alternatively, to the destruction of zinc ferrites. In the same time, only 0,3% of the iron in the dust was dissolved, confirming the alkaline leaching selectivity. The influence of temperature at zinc recovery, for 6M NaOH concentration is presented in Fig.4. As it was expected, it can observe that the recovered zinc increases when the temperature increases, too. For longer leaching times, this increase is more significant due to the increase of the solubility of the metal that is associated with the higher temperature. Considering the situation *b,* we have presented, in Fig.5, the results of zinc recovery after 4 hours of leaching in a 6M NaOH solution and using an autoclave at 120, 150 and 200^0C (0.2; 0.59 and 1.6 MPa, respectively). It can be observed that the highest recovery of zinc takes place after 30 – 60 minutes and the temperature does not influence this phenomenon. About 10% of the recovered zinc can be observed at 120^0C at longer leaching times.

A possible explanation of this behaviour is the precipitation of the dissolved zinc, as zinc ferrite.

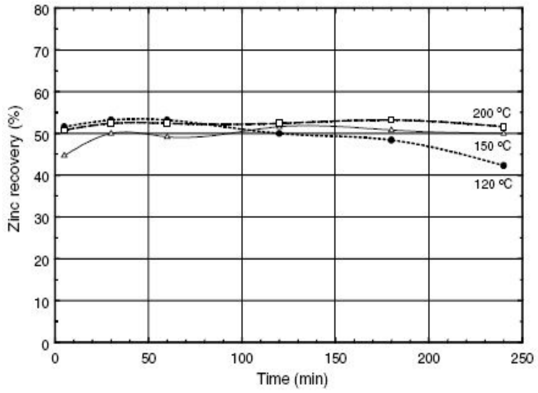


Figure 5. Influence of temperature of the dependence between the zinc recovery and time, in pressure leaching for a NaOH concentration of 6M

Ferrites and other metallic oxides are materials which have the property to absorb a significant quantity of radiation in microwave frequencies, situation *c*. As a consequence, they have a faster heating and, in the same time, another phenomenon takes place – the nucleation and propagation of cracks in the particles, making them more amenable to leaching. If it is used a microwave radiation to heat the pulp of EAFD and the solution of sodium hydroxide, in a Teflon reactor, it can observe a small increase in the recovery of zinc, but only in a short period of time. We have considered that this improvement of zinc recovery may be attributed to the partial dissolution of zinc ferrites. In this study, microwave radiation was used as a treatment stage prior to conventional caustic leaching. The EAFD sample, placed into a ceramic crucible, was heated using a microwave oven, about 2 minutes, till 600^0 – 700^0C, (it observed that longer heating times caused a sintering phenomenon, an undesirable effect). Immediately after the heating, the sample was transferred to the leaching reactor and it was mixed with a solution of NaOH with 6M concentration. Table 1 summarizes the results of this experiment. It also can be observed that the microwave treatment did not improve the recovery process of zinc. We have considered that this aspect has happened due to the heating time which has been long enough to cause an incipient sintering of the low melting point phases, but which was not sufficient to induce the formation of cracks in the particles. This is the reason because no further analyses were made with this technique.

Table 1. Zinc recovery from EAFD, situation c, leached in a NaOH solution with 6M concentration, at 60^0C

Time, [min]	Zinc recovery, [%]
5	49,7
30	53,7
60	55
120	56,3
180	60,4
240	60,4

Considering the tests made in situation *d,* it was observed that the ultrasound was beneficial in the selective chloride acid leaching of zinc from pellets produced by a double kiln treatment of EAFD. This effect was attributed to a combination of improved pore penetration capacity of the leaching boundary agent and product layer breakdown and localized temperature increases. In this case of investigation, we have expected that the ultrasonic situation would improve the dispersion of fine and agglomerated particles, in enhancing zinc recovery. So, a few preliminary tests were made at the environmental temperature. Table 2 presents the results, considering different values of time.

Table 2. Zinc recovery from EAFD leached in a NaOH solution with 6M concentration, at 55^{0}C, using ultrasonic agitation

Time, [min]	Zinc recovery, [%]
5	50,3
30	53,1
60	55,9

Comparing Table 2 with Fig.3 and 4, it can observe that no improvements in zinc recovery were achieved in situation *d*. The temperature of 55^{0}C during the leaching was a consequence of the energy dissipation due to the ultrasonic agitation, since no additional heating was used. Despite the different temperature from the tests of Fig.4, the results are comparable, since during the first hour of leaching, the effect of temperature was found to be very limited.

4. CONCLUSIONS

Considering all the experimental results anterior presented in this paper, it can observe that the most significant obtained result was a 74% zinc recovery after conventional leaching, (situation *a*), for 4 hours and using a solution of NaOH with 6M concentration. The alkaline leaching routes investigated present some distinct advantages over either the acid leaching route or the pyrometallurgical processes: the solid residues are considerably less toxic than the original EAFD, since most of the heavy metals (such as cadmium and lead) are leached and the solid phase is reached in iron oxides and quartz, presenting also some zinc ferrites which are very difficult to leach. Further, the low iron content in the solution makes the process attractive, so that the recovery of zinc as a metal in a downstream electrolysis after a simple purification process is a viable alternative.

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