# Zinc recovery from blast furnace flue dust

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## Abstract

Blast furnace flue dusts are a mixture of oxides expelled from the top of the blast furnace, whose major components are iron oxides. They also contain zinc, silicon, magnesium and other minor element oxides in lesser amounts. The direct recycling of flue dust is not usually possible since it contains some undesirable elements (zinc and alkaline metals) that can cause operational difficulties in the blast furnace. Furthermore, in some cases the dust contains toxic elements (zinc, cadmium, chromium and arsenic) that make it hazardous and unacceptable for landfill. The fact that it is not possible to recycle this dust directly or to reject it as landfill, makes it necessary to consider the recovery of the valuable elements contained in it and to obtain a non-hazardous residue that can be stored without problem or can be used in agglomeration units in iron-making industries. To reach this objective a sequence of unit operations which consists of leaching, filtration, purification, extraction, stripping and electrolysis processes is required. In this research a blast furnace flue dust which principally consists of iron, with some zinc and other elements oxides has been examined. The preliminary results show that it is possible to leach selectively the valuable elements of the dust by sulphuric acid at low acid concentration and room temperature, giving high recovery using zinc (about 80%). The pregnant solution obtained is subjected to purification and extraction for eliminating its contaminants, and increasing its zinc concentration before electrowinning the zinc. © 1997 Elsevier Science B.V.

## 1. Introduction

Many metallurgical processes produce waste materials that until recently have been uneconomical and/or legally unnecessary to be treated. In the case of iron-making industry, there is a production of waste flue dust from blast furnaces, which in Iran could be as high as 42,000 ton/year. These materials are considered as hazardous, from

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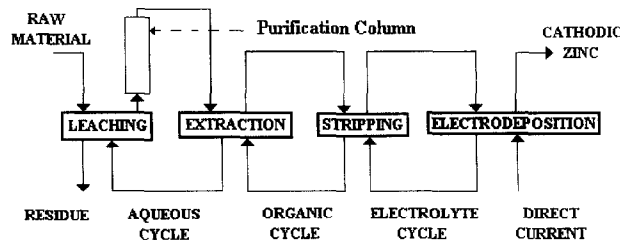* Corresponding author. Fax: +98-71-52725; E-mail: dmowla@succ.shirazu.ac.ir.

Fig. 1. Simplified diagram of sequential hydrometallurgical processes used in this research work.

the environmental point of view, but also due to the content of valuable metals, principally zinc. They could be considered as a source for recovery of valuable metals thus reducing environmental impact and several irregularities usually produced in blast furnaces [1]. One of these problems is the formation of scaffolds in the blast furnace. Scaffolds are accretion of materials which build up on the furnace wall and project towards the furnace center. A wedging or bridging of the charge materials occurs across the horizontal cross section as well as vertically along a part of the lining which interrupts smooth descent of the stock [2]. The scaffold can be kept under control by controlling the composition of input materials that cause it or by facilitating their exit from the furnace and also by taking actions to minimize its formation and promote its removal, as early as possible, when formed.

In this work, the main aim is concentrated on the first method. By separation of zinc and alkali metals from blast furnace flue dust, zinc as a valuable metal is produced and secondly, scaffolds and the other similar irregularities in the blast furnaces are controlled. For this purpose a hydrometallurgical process is used with the following conceptual steps [3,4] (see Fig. 1):

• Direct atmospheric leaching.
• Removal of some impurities of the leached liquor.
• Selective zinc extraction from the pregnant liquor.
• Zinc stripping from the organic extractant.
• Electro-deposition of zinc metal.

## 2. Experimental procedure

A sample of blast furnace flue dust 'A' from Isfahan Ironmaking Complex (IIC) furnaces in Iran was used in this investigation. This sample was magnetically concentrated with a permanent laboratory magnet of low intensity to obtain two different fractions: magnetic fraction 'AM' and non-magnetic fraction 'ANM'. According to the peaks detected and their intensities, the results of X-ray fluorescence were:

• majority elements: Si, Fe, C, Ca;
• minority, first order: Al, Mg, Zn;
• minority, second order: P, S, Mn, Ti, K, Na, Pb, Mo;
• trace: Cd, As, Sb, Co.

Table 1
Chemical analysis of the blast furnace flue dust

| Compounds | Sample 'A' | Sample "AM" | Sample 'ANM' |
|---|---|---|---|
| $SiO_2$ | 9.42 | 9.30 | 9.62 |
| R.i.[a] | 27.3 | 25.6 | 29.3 |
| TFe | 24.0 | 25.5 | 21.3 |
| FeO | 4.03 | 4.30 | 3.33 |
| $Fe_2O_3$ | 30.0 | 31.6 | 26.7 |
| $Al_2O_3$ | 2.21 | 2.28 | 2.62 |
| CaO | 17.2 | 16.9 | 17.70 |
| MgO | 5.35 | 5.28 | 5.45 |
| P | 0.19 | 0.19 | 0.19 |
| S | 0.91 | 0.90 | 0.90 |
| MnO | 0.67 | 0.78 | 0.71 |
| ZnO | 2.52 | 2.48 | 2.47 |
| $TiO_2$ | 0.83 | 0.81 | 0.87 |
| $K_2O$ | 0.28 | 0.29 | 0.31 |
| $Na_2O$ | 0.12 | 0.13 | 0.13 |
| PbO | 0.04 | 0.03 | 0.03 |
| Mo | 0.02 | 0.10 | 1.01 |
| Cd [b] | 5.62 | 3.50 | 7.12 |
| As [b] | 4.51 | 3.62 | 8.20 |
| Sb [b] | 6.01 | 2.03 | 7.62 |
| Co [b] | 4.31 | 3.20 | 6.01 |

All values in percentages unless otherwise stated.
[a] Residual insoluable after leaching with aqua regia, including carbon.
[b] In g/t.

A quantitative chemical analysis of all the samples was carried out based on the results obtained by X-ray fluorescence examination. The samples were leached with aqua regia and the elements determined by atomic absorption spectrometry (AAS).
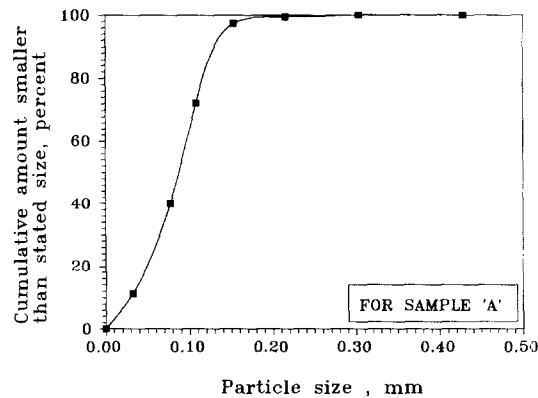


Fig. 2. Cumulative amount smaller than stated size of particles in the blast furnace flue dust as a function of particle size.

These analyses are shown in Table 1. By looking at the analysis, the need for magnetic separation was superfluous, and all the experiments were carried out on the original flue dust 'A'. Fig. 2 is a particle size analysis of sample 'A' obtained by dry sieving. In this figure, the weight percent accumulation data is plotted as a function of size of particles.

## 2.1. Leaching process

In the first step, leaching is used to transfer zinc to the solution phase. Selective solubility of zinc relative to iron compounds in this step is very critical. For this reason not every acid or base is suitable for leaching the blast furnace flue dust. Although hydrochloric acid, sulphuric acid, nitric acid and sodium hydroxide are employed for this purpose, sulphuric acid is chosen due to its high selectivity toward zinc extraction.
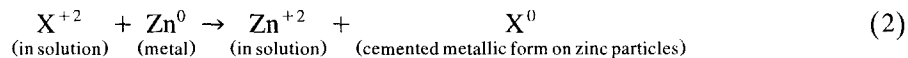
Leaching studies to determine optimum operational conditions, such as residence time, liquid-to-solid ratio, concentration of solution and temperature have been carried out in a magnetically stirred reactor. In these experiments, the reaction conditions were: stirred rate 800 $min^{-1}$, variable solid-to-liquid ratio, leaching reagent concentration varying between 0.125 and 1.0 M, maximum reaction time 1.0 h, and, temperature varying between 18 and 65°C in a reactor of 60 ml. In these experiments, the zinc and iron concentration and dissolution percent was determined by AAS. Minimum residence time was determined at different operating conditions. Then, considering this residence time, the effects of other parameters on zinc and iron dissolution were studied. Results of these experiments are described in the following sections.

## 2.2. Purification process

Precipitation and cementation techniques are carried out for removal of the impurities from the leach liquor, principally iron, aluminum and manganese [5]. By controlling temperature and pH of solution, iron and aluminum ions existing in the pregnant solution were precipitated. In this step, the precipitation of ammonium jarosite ($NH_4Fe_3(SO_4)_2(OH)_6$) is applied in hydrometallurgical zinc refining to remove iron as a solid substance from acidic zinc leach solution [9,10]. Jarosite is also used as an outlet for impurities which would otherwise accumulate in the leaching circuit and which originate from the blast furnace flue dust. Examples of these are arsenic, aluminum and other minor and trace elements. The precipitation of jarosite is given by the following reaction:

$$NH_4^+ + 3Fe^{+3} + 2SO_4^{-2} + 6H_2O \rightarrow NH_4Fe_3(SO_4)_2(OH)_6 + 6H^+ \qquad (1)$$

For separation of ions such as cadmium and manganese, a fluidized bed column containing zinc powder or granules was used. In this reactor, cementation of cadmium and similar ions from solution occurs on zinc metal particles. The general reaction can be described as follows.

$$\underset{\text{(in solution)}}{X^{+2}} + \underset{\text{(metal)}}{Zn^0} \rightarrow \underset{\text{(in solution)}}{Zn^{+2}} + \underset{\text{(cemented metallic form on zinc particles)}}{X^0} \qquad (2)$$

The pregnant solution produced in the purification process contains the above impurities at concentrations near to allowable concentrations, given in Table 2.

Table 2
Allowable concentration of some elements in zinc electrowinning process [7]

| Element | Concentration (g/l) |
|---------|---------------------|
| Cadmium | 0.002–0.004 |
| Iron | 0.02–0.03 |
| Arsenic | 0.0001 |
| Antimuan | 0.0001 |
| Cobalt | 0.003–0.007 |

## 2.3. Extraction process

Selective zinc extraction from the pregnant liquor formed in the previous step, using liquid cationic exchangers such as LIX 622 and LIX 984, resulted in formation of an organic extract containing nearly all the leached zinc and an acid aqueous raffinate depleted of zinc. The general reaction for this step is as follows.

$$2RH_{org} + Zn_{aq}^{+2} = R_2Zn_{org} + 2H_{aq}^{+} \tag{3}$$

The equilibrium extraction isotherms for LIX 622 and 984 under low acid (pH = 1, 2, 3 and 4) conditions at 23 and 55°C are obtained experimentally and will be reported below.

## 2.4. Stripping process

The next step is the zinc stripping from the organic extract by means of a high acidity electrolyte.

$$R_2Zn_{org} + 2H_{aq}^{+} = 2RH_{org} + Zn_{aq}^{+2} \tag{4}$$

In this step, both loaded electrolyte of high purity, and organic phase are produced, the latter being recycled back to the previous extraction step. Similar to extraction process, the equilibrium stripping isotherms for LIX 622 and 984 under high acidity (200, 350, 450 and 500 g/l) conditions at 23 and 55°C were obtained experimentally and reported in the following sections.

## 2.5. Electrodeposition process

The last step of the process is the electrodeposition of zinc on aluminum cathodes from the loaded electrolyte according to Eq. (5). In this step, an acidic electrolyte which is stripped of zinc is produced and recycled back to the previous stripping step [7].

$$Zn_{aq}^{+2} + H_2O = Zn^0 + 2H_{aq}^{+} + \tfrac{1}{2}O_2 \tag{5}$$

Thus, a closed electrolyte circuit is established, fulfilling the following two tasks: (a) transferring the zinc from the organic extract to the electrowinning operation; and (b)

transferring the corresponding acidic solution generated by the electrolysis of zinc to the organic raffinate.

## 3. Results and discussion

In the leaching step, a comparison between different mineral acids and bases showed that sulphuric acid is an ideal leachant for separation of zinc and alkali metals from the blast furnace flue dust [8]. Selective leaching of zinc with respect to iron is the main characteristic of the sulphuric acid leaching process. Application of a fluidized bed reactor in the purification process is suitable for removal of some impurities from the pregnant solution produced by leaching. Because of low concentration of zinc ions in the pregnant solution produced from the leaching process, extraction and stripping steps are used to concentrate this solution. In these steps, employing two cationic exchangers such as LIX 622 and LIX 984 gives an electrolyte with at least 60 g of zinc ions per liter of solution. Use of standard conditions in the electrodeposition process can produce extra-pure zinc metal and a high acid solution which can be employed in the leaching step. Results of these sequential steps are given as follows.

### 3.1. Leaching step

In this process various parameters which affect the rate of dissolution of zinc with respect to iron are investigated. Optimum values for these variables are determined experimentally and shown in the following subsections.

### 3.1.1. Effect of sulphuric acid concentration

The effect of sulphuric acid concentration is investigated in the concentration range of 0.125–1.0 M. The results obtained are shown in Figs. 3 and 4. From these tests it could be deduced that the rates of zinc and iron dissolution are functions of the acid
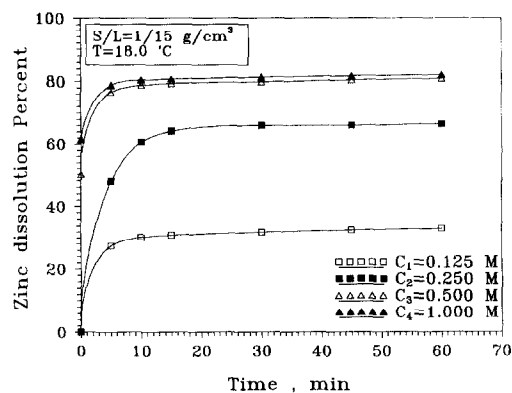
Fig. 3. Zinc dissolution percent as a function of time in $H_2SO_4$ leaching process for sample 'A'.
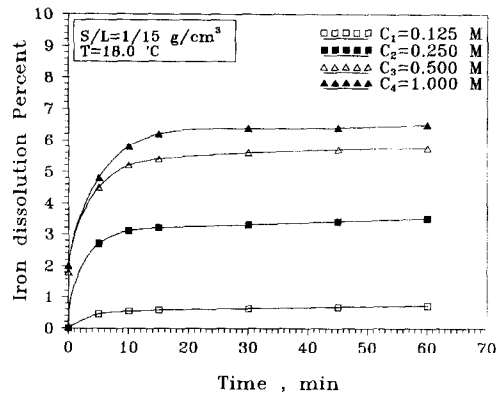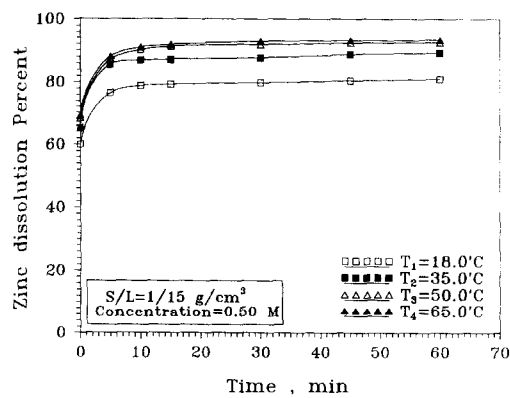
Fig. 4. Iron dissolution percent as a function of time in $H_2SO_4$ leaching process for sample 'A'.

concentration in the investigated range. Fig. 3 shows that the optimum value of acid concentration of about 1.0 M is suitable for the leaching process.

### 3.1.2. Effect of temperature

The effect of temperature on extent of dissolution was studied at 18, 35, 50 and 65°C. The results are given in Figs. 5 and 6. Although the rate of dissolution of the zinc is not strongly dependent on the temperature, the dissolution rate of the iron species is sensitive to the temperature, which means that it is necessary to work at room temperature to obtain simultaneously high extraction rate of zinc and low dissolution rate for iron.

### 3.1.3. Effect of solid-to-liquid ratio

According to the results obtained above, the best sulphuric acid concentration may be 1.0 M, when the usual solid-to-liquid ratio is selected. In this state, sulphuric acid concentrations less than 0.5 M are not sufficient to leach these species completely.



Fig. 5. Zinc dissolution percent as a function of time in $H_2SO_4$ leaching process for sample 'A'.
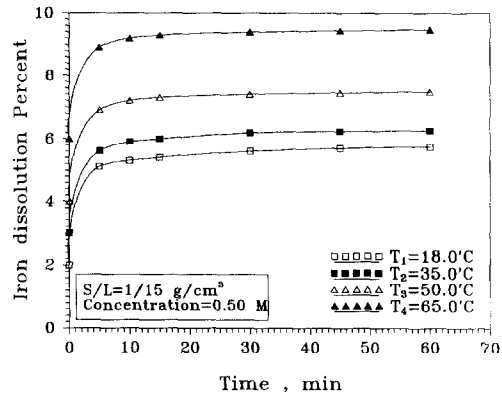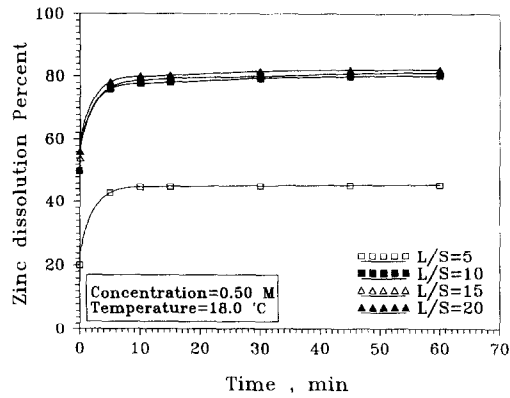
Fig. 6. Iron dissolution percent as a function of time in $H_2SO_4$ leaching process for sample 'A'.



Fig. 7. Zinc dissolution percent as a function of time in $H_2SO_4$ leaching process for sample 'A'.
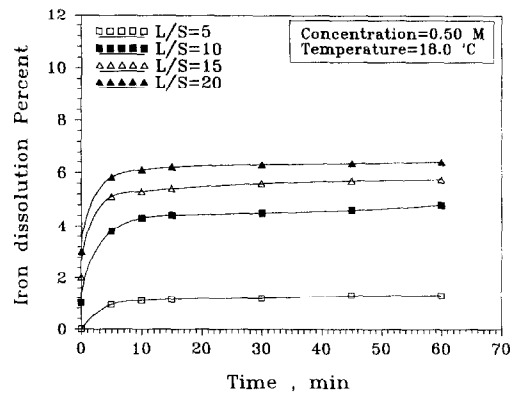


Fig. 8. Iron dissolution percent as a function of time in $H_2SO_4$ leaching process for sample 'A'.

Under these conditions and with a solid-to-liquid ratio of $1/10$, and a residence time of 1.0 h, 82% of Zn and 5% of Fe are leached. Figs. 7 and 8 show that although the extent dissolution of zinc is not affected by liquid-to-solid ratio, this is not the case for iron.

Therefore, it could be deduced that the optimum operational conditions for leaching is the use of a 1.0 M solution of sulphuric acid with a residence time of 10 min and a solid-to-liquid ratio of 1/10 at room temperature.

### 3.2. Extraction and stripping steps

In solvent extraction and stripping steps isotherms at 23°C for organic extractant, LIX 622 and 984 are obtained experimentally and are shown in Figs. 9–12. In these extraction experiments, the liquid phases were prepared as synthetic solutions containing similar amount of zinc ions which are obtained from the blast furnace flue dust leaching process. In Fig. 9a and b the extraction isotherms at 23°C for LIX 622 (15 vol% in Shell 140) at O/A ratio of 1/1 are shown, and the effect of aqueous solution pH on extraction isotherm is indicated in these figures. Fig. 10 shows stripping isotherms at various acid phase concentrations, with an O/A ratio of 5/1 and at room temperature. Fig. 11a and b and Fig. 12 are the same isotherm but for LIX 984 as the other organic
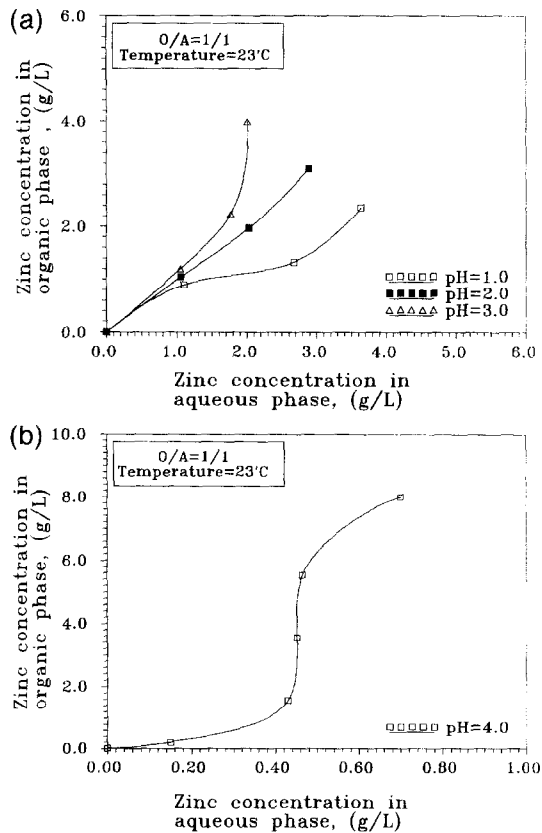


Fig. 9. (a) Extraction isotherms for LIX 622, 15 vol% in kerosene (Shell 140) for sample 'A'. (b) Extraction isotherm for LIX 622, 15 vol% in kerosene (Shell 140) for sample 'A'.
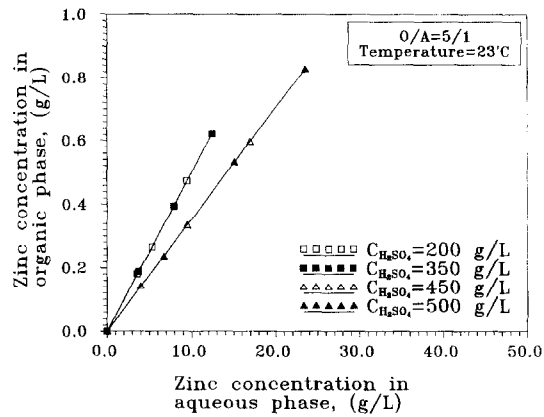
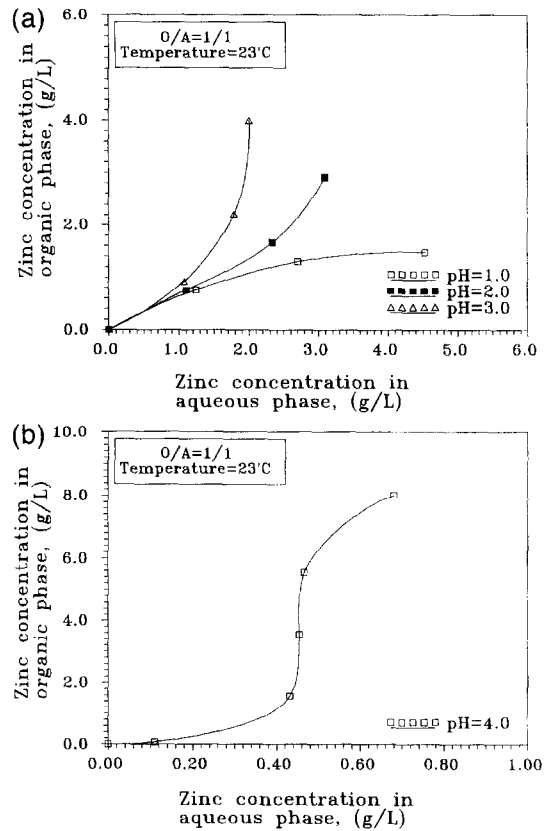Fig. 10. Stripping isotherms for LIX 622, 15 vol% in kerosene (Shell 140) for sample 'A'.



Fig. 11. (a) Extraction isotherms for LIX 984, 15 vol% in kerosene (Shell 140) for sample 'A'. (b) Extraction isotherm for LIX 984, 15 vol% in kerosene (Shell 140) for sample 'A'.
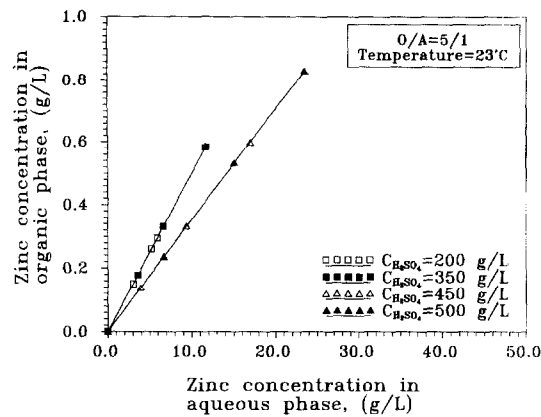
Fig. 12. Stripping isotherms for LIX 984, 15 vol% in kerosene (Shell 140) for sample 'A'.

extracting agent. A simple comparison between these isotherms and those obtained for LIX 622 show that the effects of pH on extraction and acid concentration on stripping process are the same for both extractants. For this reason, the McCabe Thiele plot used for these isotherms indicates that nearly equal number of stages can be predicted for a given input/output composition in organic and aqueous streams. Using these isotherms, extraction and stripping units can be designed and developed easily [6].

### 3.3. Electrodeposition step

It is well-documented that zinc deposition in the electrowinning process is very sensitive to small quantities of certain impurities [7]. Previous studies have indicated that
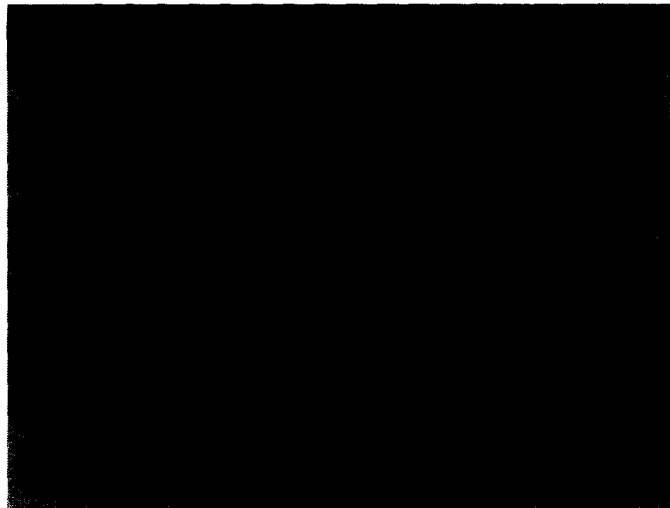


Fig. 13. SEM photomicrograph (×100) showing the zinc deposit morphology, under the following electrolysis conditions: 60 g/l $Zn^{2+}$, 250 g/l $H_2SO_4$, 35°C temperature, 3.0 h deposition time, 50 mA/cm$^2$ current density, animal glue-free electrolyte, commercial Al cathode and pure Pb anode.

Fig. 14. SEM photomicrograph (×500) showing the zinc deposit morphology, under the following electrolysis conditions: 60 g/l $Zn^{2+}$, 250 g/l $H_2SO_4$, 35°C temperature, 3.0 h deposition time, 50 mA/cm$^2$ current density, animal glue-free electrolyte, commercial Al cathode and pure Pb anode.

very small amounts of cadmium and arsenic in the ranges of parts per billion can greatly reduce the current efficiency [7]. In the purification process used in this work, we have tried to reach low levels in actual practice. Chemical analysis of the pregnant aqueous solution produced from the stripping cycle indicates that this is a suitable electrolyte for



Fig. 15. SEM photomicrograph (×1000) showing the zinc deposit morphology, under the following electrolysis conditions: 60 g/l $Zn^{2+}$, 250 g/l $H_2SO_4$, 35°C temperature, 3.0 h deposition time, 50 mA/cm$^2$ current density, animal glue-free electrolyte, commercial Al cathode and pure Pb anode.

zinc deposition on aluminum cathodes. By application of standard conditions used in zinc electrodeposition cells, extra-pure zinc metal is obtained.

The SEM photomicrograph in Figs. 13–15 show the morphology of zinc deposits obtained under experimental conditions described below each figure. As shown in these figures, because of high acidity of electrolyte and some additional impurities, hydrogen evolution takes place and therefore current efficiency greater than 75% is not obtained.

## 4. Conclusions

Recovery and separation of metals, especially zinc, from blast furnace flue dust is a practical idea in iron-making industries. The fact that it is not possible to recycle this dust directly or to reject it as landfill, makes it necessary to consider the proposed process used in this work, to obtain a non-hazardous residue that can be stored without problem or can be used in agglomeration units. By application of sequential hydrometallurgical processes as described, high purity zinc is produced while at the same time, by avoiding the possibility of production of scaffolds in blast furnaces, the smooth operation of blast furnaces will increase productivity and reduce the cost of pig iron.

## Acknowledgements

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