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SOLID/LIQUID EXTRACTION OF ZINC FROM EAF-DUST

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ABSTRACT

The solid/liquid extraction of nonferrous heavy metals was investigated. This process may be of technical importance in the upgrading of dust from steel mills and from electrical arc furnaces (EAF-dust). Extraction was carried out with aqueous acetic acid. Objectives of the project were the evaluation of partition data and the investigation of extraction kinetics. The extraction efficiency of the substances in question is in general accordance with the high solubilities of acetates in water. Solubility is negatively affected by excess acetic acid. The dissolution rate of heavy metals of oxidation number (II) is high and can be modeled with a first-order rate law. The results show that acetic acid is an appropriate extractant for separating zinc and lead from oxidic solid feed material.

INTRODUCTION

Dust from electrical arc furnaces and steel mills is hazardous due to its high content of heavy metals. EAF-dust may have a zinc content up to 40 wt %, including different modifications such as ZnO, $ZnO \cdot Fe_2O_3$, etc. For environmental control, this dust has to be treated to detoxify it prior to disposal. Treatment should

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be done with clean, nonpolluting technologies that will result in environmentally friendly products and residues (1, 2).

The present capacity of recycling plants is limited, while the production of EAF-dust is still increasing. At present, treatment is done mainly by pyrometallurgical processes and new processes based on plasma technology. The Waelz process is state of the art in the pyrometallurgical separation of zinc from EAF-dust (3, 4).

Alternatively to the pyrometallurgical route, hydrometallurgical separation offers the advantage of low dust emission during processing. Consequently, hydrometallurgical processes, based on low cost, as well as flexible and clean operation, offer several advantages over pyrometallurgical upgrading (2, 5, 6).

The objective of this project was to examine the leaching properties of EAF-dust in aqueous acetic acid. Experiments were performed with different L/S ratios. The feed content of acetic acid and the temperature of operation were varied. The extraction efficiency of zinc from EAF-dust was compared with the solubility of pure zinc acetate in aqueous acetic acid of different concentrations. In addition, the rate of dissolution of zinc from EAF-dust was investigated.

EXPERIMENTAL PROCEDURE

The experiments were carried out by suspending dust samples in aqueous acetic acid according to the following operating conditions:

- temperature of extraction between 20 and 60°C;
- time of extraction between 30 and 90 min;

Table 1. Mean Composition of EAF-Dust in Comparison with the EAF-Dust Used in This Work

Major elements	Mean composition of EAF-dust (wt %)	Composition of EAF-dust used in this work (wt %)
Zn	18–45	42.5
Fe	15–30	13.7
Pb	2–7	5.8
Na	0.3–3	3.1
K	1–1.5	1.6
Ca	1–4.5	1.2
Mn	1–3	0.9
Mg	1.5–2	0.5
Al	0.3–1	0.5
Trace elements	(mg/kg)	(mg/kg)
Cu	3000–6000	5000
Cr	2000–6000	2000
Cd	300–2000	1000
Ni	200–300	200

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- concentration of acetic acid between 0 and 100 wt % and
- liquid to solid (L/S) ratio by weight between 10 and 2.5.

The solid/liquid equilibrium data were measured after a 24-h mixing period. The rate of extraction was investigated by taking samples of the extract phase with an analytical-grade filter and a glass syringe several times during extraction. The concentrations of several elements were then measured by ICP (inductively coupled plasma) analysis. The same procedure was carried out with the solid residue after it had been dissolved in aqua regia. The extraction yield was calculated from the ratio of the extract phase concentration to the total amount of the extract phase concentration and the residue phase concentration.

Table 1 shows the mean composition of EAF-dust (1, 4, 6) and the composition of EAF-dust used in the present project.

RESULTS AND DISCUSSION

Solubilities of Zinc Oxide in Aqueous Acetic Acid

Evaluation of the multicomponent solid/liquid equilibrium partition of zinc and lead, investigation of the temperature dependence of partition, and determination of extraction kinetics were objectives of this project.

The solid/liquid partition of analytical-grade zinc acetate and lead acetate in aqueous acetic acid was used as a means of comparison.

Figure 1 shows the solubility of analytical-grade zinc acetate and lead acetate in aqueous acetic acid. The solubility of zinc acetate decreases with increasing concentration of acetic acid, while the solubility of lead acetate shows an inverse trend.

The extraction of zinc acetate from EAF-dust was carried out in consideration of the acid content of the solvent phase, the temperature, and the total amount of solid feed. Table 2 shows representative results of the extraction experiments.

The results of multicomponent extraction from EAF-dust are shown in Fig. 2. Comparison of the solubilities of the pure substances with the results of EAF-dust extraction points out a decreasing extractability of lead with increasing acid concentration.

The yield of zinc extraction remains constant when the total amount of zinc in the solid feed is kept beyond the solubility limit of zinc acetate in aqueous acetic acid. The solubility of zinc from EAF-dust in aqueous acetic acid is nearly twice that for analytical-grade zinc acetate. The amount of zinc extracted will decrease after intersecting the actual solubility limit of the substance in aqueous acetic acid.

The solubility of iron passes through a maximum at an intermediate total concentration of acetic acid. As compared with the solubility of analytical-grade lead acetate, the multicomponent extraction from EAF-dust results in a decrease in the yield of lead extraction with increasing total acid concentration.

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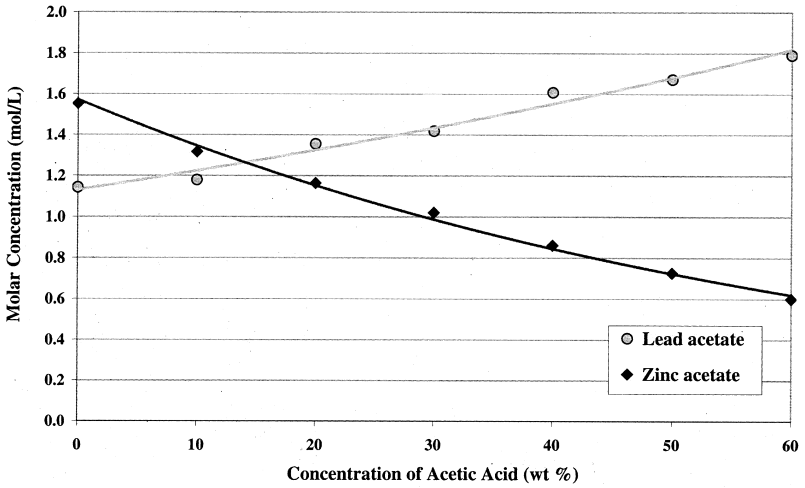

Figure 1. Solubility of analytical-grade zinc acetate and lead acetate in aqueous acetic acid. Temperature: 20°C.

Table 2. Representative Results of Zinc Extraction from EAF-Dust

Element	EAF-dust (wt %)	Solid residue (wt %)	Extraction yield (%)
Zn	42.54	17.96	82.1
Fe	13.69	31.13	6.4
Pb	5.83	5.15	55.1
Na	3.10	1.05	85.9
K	1.61	0.23	95.1
Ca	1.16	0.54	77.1
Mn	0.99	1.85	13.9
Mg	0.54	0.75	44.8
Al	0.50	0.79	29.9
Cu	0.45	0.47	51.5
Cr	0.19	0.37	22.2
Cd	0.06	0.01	88.6
Ni	0.02	0.05	8.2

Feed concentration of acetic acid: 20 wt %; temperature: 20°C; duration: 30 min; L/S ratio: 10.

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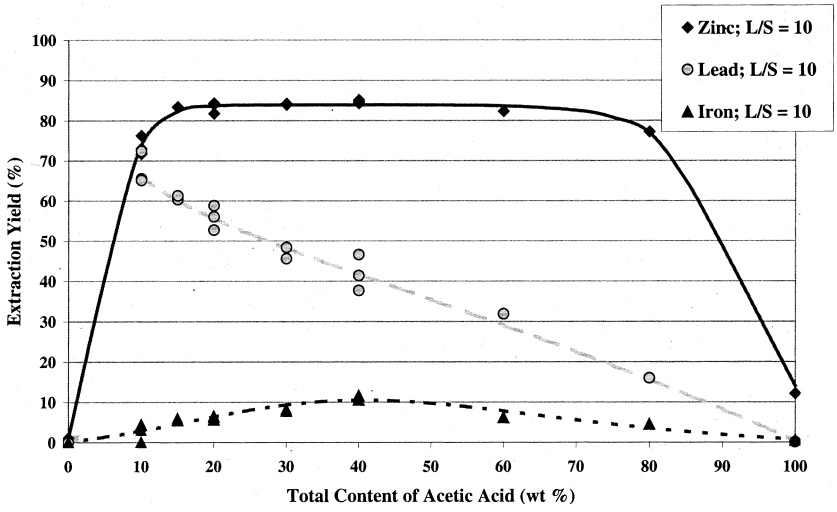

Figure 2. Mutual effect of multicomponent extraction from EAF-dust on the solubilities of zinc and lead. Temperature: 20°C; L/S ratio: 10.

Figure 3 shows the extractability of zinc oxide from EAF-dust for different L/S ratios. The tests were carried out for varying total concentrations of acetic acid in the aqueous feed solution. The solubility of analytical-grade zinc acetate in aqueous acetic acid is considered as a comparative value.

The results confirm yield control by the stoichiometric ratio of acetic acid to zinc oxide. Beyond the limit of solubility, the concentration of zinc in the extract phase is in correspondence with the total amount of extractable zinc.

Besides temperature, the solubility of zinc depends on the nature and the reactivity of the substance in the solid feed phase. Several substances such as zinc oxide, calcium zincate, zincite, and zinc carbonate are very soluble in aqueous acetic acid. These substances are nonmagnetic.

Zinc ferrite and the spinel of zinc ferrite and magnetite, which are magnetic, have poor solubilities in aqueous acetic acid (1, 4, 6).

The solubilities of several metal acetates increase with increasing temperature. Table 3 summarizes representative data showing that the temperature dependence of solubility is significant (3, 7, 8). Both the yield of zinc extraction from EAF-dust and the rate of extraction are, therefore, temperature dependent.

Derived from experimentally observed solubility data, the yield of extraction can be based on the mass balance of Eqs. (1) and (2). Precise determination of multicomponent interaction, which affects the solubility of zinc acetate positively, will need further investigation (9). At present, the enhancement of the sol-

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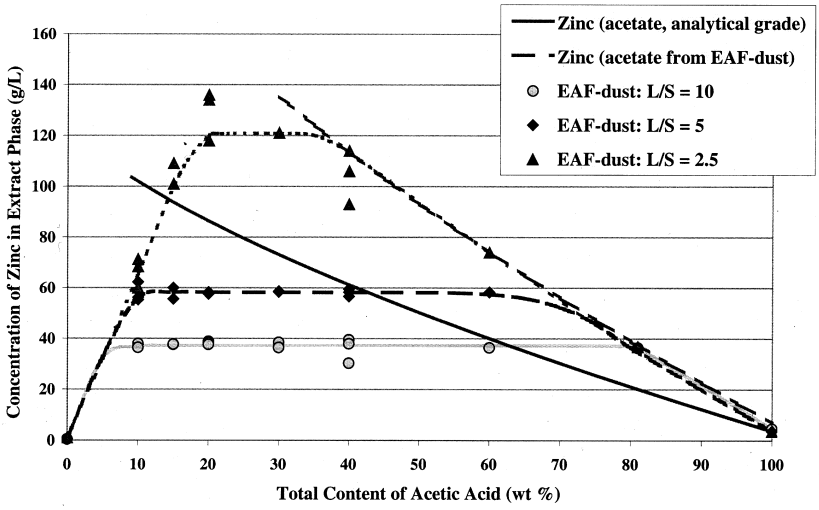

Figure 3. Total solubility of zinc acetate from EAF-dust in aqueous acetic acid. Temperature: 20°C; L/S ratio: 2.5, 5, 10.

Table 3. Solubilities of Several Metal Acetates in Water

Acetate	Temperature (°C)	Solubility (g/100 g solvent)	
Zinc acetate	20	29.5	(8)
	100	44.6	(7)
Zinc acetate dihydrate	20	31.1	(7)
	25	40	(3)
	100	66.6	(3,7)
Lead acetate	20	44.3	(7)
	50	221	(7)
Lead acetate trihydrate	15	45.6	(7)
	100	200	(7)
Iron(II) acetate	20	Very soluble	(7)
Iron(III) acetate	20	Insoluble	(7)
Copper(II) acetate	20	7.2	(7)
	100	20	(7)
Nickel acetate	20	Soluble	(7)

Values reported in the literature (3, 7, 8).

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ubility of zinc acetate by the overall composition of the extract phase by a factor of nearly 2 can be explained with decreasing activity. The formation of caustic acetates may be a further reason for enhancement. Nevertheless, for the experimentally determined solubility of zinc acetate, the optimum concentration of acetic acid in the aqueous feed can be calculated according to Eq. (1):

$$\frac{C_{Zn(Ac)_2,aq}\,(g/L)\cdot 2\cdot MM_{HAc}(g/mol)}{MM_{Zn(Ac)_2}(g/mol)} = C_{HAc}(g/L). \tag{1}$$

As a consequence, the ratio of the solvent phase to the solid feed phase can be determined for a specified weight fraction of soluble zinc, X_{Zn}, in the solid feed phase. The correlation is shown as follows:

$$\frac{\dot{L}}{\dot{S}} = \frac{\dot{V}m^3/s)}{\dot{m}(kg/s)} = \frac{MM_{HAc}\,(g/mol)\cdot 2\cdot X_{Zn}(-)}{C_{HAc}\,(g/l)\cdot MM_{Zn}\,(g/mol)}. \tag{2}$$

Kinetics of Zinc Oxide Extraction

Extraction of zinc with aqueous acetic acid from oxidic dust is a heterogeneous neutralization reaction, which can be assumed to be spontaneous. Rate control of the extraction process is, then, mass transfer controlled. Modeling can be based on Eq. (3):

$$\frac{dM}{dt} = \frac{D\cdot A\cdot(c_s - c)}{\delta}. \tag{3}$$

For constant volume ($dM = V\,dc$), the time, t, that it takes the concentration of the solution to rise from its initial value, c_0, to concentration, c, is found by integration according to Eq. (4) on the assumption that the liquid film thickness, δ, and the interfacial area, A, remain constant.

$$\int \frac{dc}{c_s - c} = \int \frac{D\cdot A}{V\cdot\delta}\,dt. \tag{4}$$

After rearranging, the correlation between the time of extraction, t, and the corresponding concentration in the solvent phase, c, shown in Eq. (5), can be evaluated:

$$\ln\frac{c_s - c_o}{c_s - c} = \frac{D\cdot A}{V\cdot\delta}\cdot t. \tag{5}$$

If pure solvent is used at the beginning, $c_0 = 0$, the concentration of zinc in the extract phase can be expressed by Eq. (6):

$$c = c_s\left(1 - e^{-\frac{D\cdot A}{V\cdot\delta}\cdot t}\right). \tag{6}$$

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Equation (6) shows that under the mentioned boundaries the solution approaches saturation exponentially (10).

With the specific mass transfer area a = A/V and the mass transfer coefficient k = D/δ, Eq. (4) can be rewritten according to Eq. (7):

$$c = c_s(1 - e^{-k \cdot a \cdot t}). \quad (7)$$

Modeling of the extraction process was based on the interpretation of rate data with Eq. (7). The rate of extraction was investigated between 20 and 60°C. The L/S ratio was kept constant at 10. The concentration of acetic acid was 20 wt % in each experiment. The results are shown in Fig. 4.

Due to the different leaching properties of the various oxidic species of zinc, modeling of the results indicates a mixed mechanism of extraction. Data interpretation was best performed with an extended version of Eq. (7), considering mass transfer control of the dust fraction 1 with high solubility and rate control of the dust fraction 2 with poor solubility properties. The integrated correlation of the rate law is shown in Eq. (8):

$$c = \{c_{s,1} \cdot (1 - e^{-k_1 \cdot t})\} + \{c_{s,2} \cdot (1 - e^{-k_2 \cdot t})\}. \quad (8)$$

The kinetic data of extraction were analyzed with Eq. (8) and are shown in Fig. 4. The k values and the saturation concentrations are listed in Table 4.

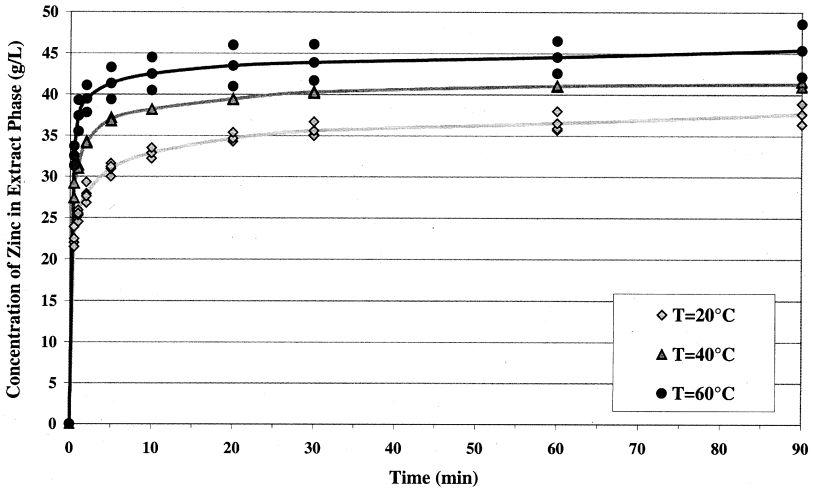

Figure 4. Rate of extraction of zinc from oxidic dust. Solvent: acetic acid 20 wt %; L/S ratio: 10.

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Table 4. Results of Rate Data Analysis with Eq. (8)

Temperature i(°C)	Value of the highly soluble fraction of zinc k_1 (min^{-1})	Value of the fraction with poor solubility k_2 (min^{-1})
20 - 60	3.1	0.1
	Value of the highly soluble) fraction of zinc $c_{S,1}$ (g/L	Value of the fraction with poor solubility $c_{S,2}$ (g/L)
20	26.3	10.5
40	33.9	6.8
60	39.1	5.2

Concentration of acetic acid: 20 wt %; temperature: 20, 40 and 60°C; L/S ratio: 10

The numeric value of k_1 indicates mass transfer control of the extraction process for the major portion of the oxidic zinc. However, extraction of a minor amount of the zinc is controlled by chemical reaction.

SUMMARY

Extraction of zinc from oxidic dust is an alternative route to pyrometallurgical processing. Extractability and the yield depend on the nature of the oxidic species. EAF-dust is specified by a high amount of zinc oxide, which has very good extraction properties. Extraction with aqueous acetic acid results in high solubility for the stoichiometric ratio of acetic acid in the solvent phase to the zinc content of the solid phase. Due to decreased chemical activity, the multicomponent interaction of several species of the feed dust results in an enhancement of the solubility of zinc acetate in aqueous acetic acid, as compared with the solubility of analytical-grade zinc acetate. Solubility is highly temperature dependent. The rate of extraction of zinc oxide from EAF-dust is primarily controlled by mass transfer. However, experimental results indicate that the extraction rate for a minor amount of the zinc is controlled by chemical reaction.

NOMENCLATURE

A	area of the solid-liquid interface (m^2)
a	specific mass transfer area (m^2/m^3); a = A/V
c	bulk concentration of solute at time t (kg/m^3)
c_0	bulk concentration of solute at time t = 0 (kg/m^3)
c_S	concentration of the saturated solution (kg/m^3)
$C_{Zn(Ac)_2,aq}$	solubility of zinc acetate in water (g/L)

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C_{HAc}	mass concentration of acetic acid (g/L)
D	diffusion coefficient (m^2/s)
δ	thickness of liquid film surrounding the particles (m)
k	overall mass transfer coefficient (m/s); $k = D/\delta$
L/S	weight ratio of liquid feed extractant to solid dust (-)
$\dot{m}$	flux of feed solid dust (kg/s)
MM_{HAc}	molecular mass of acetic acid (g/mol)
$MM_{Zn(Ac)_2}$	molecular mass of zinc acetate (g/mol)
MM_{Zn}	molecular mass of zinc (g/mol)
M	mass of solute transferred in time t (kg)
V	volume of solution (m^3)
$\dot{V}$	flux of the liquid feed (m^3/s)
X_{Zn}	weight fraction of soluble zinc in the dust phase (-)

Subscripts:

aq	aqueous
HAc	acetic acid
MeO	metal oxide
$Me(Ac)_2$	metal acetate
s	saturated
0	at time t = 0

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