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Extractive Separation of Zinc from Oxidic Solid Bulk Feed

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ABSTRACT

Dust from steel processing is a heterogeneous, multicomponent mixture of metal oxides of zinc, lead, and iron, and several trace elements such as cadmium, nickel, cobalt, and copper. The hydrometallurgical separation and downstream processing of nonferrous metals from dust of electric arc furnaces (EAF) was investigated. Solid–liquid extraction was carried out with aqueous acetic acid. In a next step, isolation of metals from the solvent phase and solvent recovery was tested. Besides isolation of intermediates, the electrochemical deposition of the metallic substances was investigated. Electrochemical deposition of zinc from aqueous feed needs high-grade purity of the feed electrolyte due to sensitivity of the hydrogen overvoltage. The effect of nickel on the break down of the hydrogen overvoltage is a major concern in electrochemical deposition of zinc from sulfate-based feed.

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Nickel contamination has to be kept at minimum concentration level. In contrast to sulfate-based electrolytes, the hydrogen overvoltage in acetic acid can be kept high, even when electrolyzing the extract phase without pretreatment of the extract phase.

Key Words: Zinc; EAF-dust; Electrolysis; Recycling.

INTRODUCTION

Several zinc-containing dusts are generated during operation of iron and steel mills or during recycling of scrap material. Because of their heavy metal content, these dusts create environmental problems.

Approximately 900,000 tons/year of electric arc furnace dust (EAF dust) are generated in the EC, while in the United States, up to 700,000 tons/year occur. In Europe, less than 50% of these dusts are processed, mainly by pyrometallurgical methods, while a large amount is still dumped because of limited recycling capacities. EAF dusts contain 20 to 35 wt% each of zinc and iron, up to 7 wt% of lead, and trace amounts of several heavy metals like cadmium, chromium, and nickel.[1–3]

EAF dust treatment creates important opportunities. (1) A hazardous waste can be rendered innocuous, and its products safely re-enter the environmental circle. (2) Significant and valuable quantities of already mined and concentrated zinc and other metals can be recovered and returned to economic recycle. Currently in Europe, only 12% of the annually produced zinc is recycled. If there were more efficient recycling paths available, natural resources could be preserved.[2]

At present, dust 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.[1,2]

In addition to the pyrometallurgical route, a new approach of hydrometallurgical separation, the extractive separation of zinc and lead from dust of electric arc furnaces, was investigated. Extractive separation (leaching) was carried out with aqueous acetic acid at different operating conditions.[3,4]

It was shown that extraction yields in high-separation efficiency for several metal oxides in oxidation state (II), while separation of metal oxides in oxidation state (III) is poor. Extraction of zinc oxide decreases with increasing amount of carboxylic acid in the aqueous solvent. The yield passes a maximum at the stoichiometric ratio of zinc and acetic acid. Extraction of lead oxide does not show this dependency. Solubility of both metal oxides is temperature dependent.[4]

In a next step, isolation of metals from the extract phase and solvent recovery were investigated. Based on the different solubilities of metal acetates in acetic acid,[5] precipitation of zinc acetate from the laden leach liquor by increasing the concentration of acetic acid was carried out. Solvent recovery can be carried out either by thermal decomposition or by solvent transfer.[6]

Besides isolation of intermediates, the electrochemical deposition of the metallic substances was investigated. Electrochemical deposition of zinc from aqueous feed needs high-grade purity of the feed electrolyte due to sensitivity of the hydrogen overvoltage.[6–8] Electrowinning of zinc from sulfate-based electrolytes is well investigated. The results of zinc deposition from acetate-based electrolyte are, therefore, compared with state-of-the-art electrowinning from sulfate-based electrolyte.

The effect of nickel on the breakdown of the hydrogen overvoltage is a major concern in electrochemical deposition of zinc from sulfate-based feed. Nickel contamination therefore has to be kept at a minimum concentration level.[6,9]

EXPERIMENTAL PROCEDURE

All experimental work was performed in laboratory scale. The electrolyte solution had to be prepared by leaching samples of EAF dust in a glass beaker. The extraction experiments were carried out by suspending dust samples in aqueous acetic acid using the following operating conditions[4]:

- Temperature of extraction 20°C
- Time of extraction 30 minutes
- Concentration of acetic acid 20 wt%
- Liquid to solid (L/S) ratio by weight 10

Electrolysis was carried out in a batch electrolysis cell with electrolyte circulation. The electrolyte volume of about 350 mL in total was circulated by an adjustable peristaltic pump. For temperature control, the electrolyte passed a heat exchanger. The anodes were made of graphite; the dimension of the anode was $68 \times 105 \times 20$ mm. The cathode was made of aluminum; the dimension of the cathode was $68 \times 105 \times 2$ mm. The distance between electrodes could be varied between 20 and 50 mm; the active cathode area was 7800 mm^2. The electrolysis cell was made of polyethylene, and the connecting tubes were made of acid-proof neoprene.

The DC-power supply, with a maximum voltage source of 30 V and a maximum current source of 10 A, can either be operated at constant current or constant voltage.

Temperature and pH-value of the electrolyte solution, as well as current and voltage, were recorded automatically with a FLUKE Hydra Data-Logger.

Electrolysis experiments were carried out under the following operating conditions:

- Temperature of electrolysis between 20 and 45°C
- Time of batch electrolysis between 60 and 720 minutes
- Current between 1 and 5 A (current density between 125 and 625 A/m^2)
- Electrode distance 20 mm; for the determination of the decomposition voltage and current/voltage dependence an electrode distance of 50 mm was chosen

The composition of the electrolyte solution was also varied. In a first series of experiments, electrodeposition of zinc from synthetic solution of zinc acetate was carried out. In a second step, multicomponent-extract phase of EAF dust was electrolyzed.

The electrolyte concentration of several elements was measured by inductively coupled plasma (ICP) analysis. The same procedure was carried out with the cathodic deposit after dissolving in HNO_3. The yield of deposition and the current efficiency were derived from electrolyte-based mass balance and from analysis of the deposit.

RESULTS AND DISCUSSION

Determination of Electrochemical Properties for Zinc Deposition from Acetate Solution

Prior to investigation of zinc electrowinning from extract liquor, the electrochemical properties of zinc deposition from acetate-based electrolyte were determined. The target of this investigation was the determination of decomposition voltage, the specific electrical resistance, the optimum current density, and the optimum temperature of operation. Further, the effect of selected trace elements on zinc electrowinning was analyzed. Finally, the deposition of zinc from multicomponent-extract phase was investigated. Data analysis was based on electrochemical basics, briefly summarized in the following section.

The cathode reaction of zinc deposition is shown in eq. (1)

$$Zn^{2+} + 2e^- \rightarrow Zn\downarrow \tag{1}$$

and eq. (2) summarizes the corresponding anode reaction:

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O \tag{2}$$

The equilibrium potential of the overall process ΔE is derived from the electrode potentials of the respective half reactions according to eq. (3):

$$|\Delta E| = |E_{Cathode} - E_{Anode}| = |E_C - E_A| \tag{3}$$

The potential E of the cathodic and anodic half reactions at equilibrium is related to the standard electrode potential E^θ according to eqs. (4) and (5):

$$E_C = E^\theta + \frac{RT}{zF}\cdot \ln[Zn^{2+}] \tag{4}$$

$$E_A = E^\theta + \frac{RT}{zF}\cdot \ln[H^+] \tag{5}$$

For a significant rise of the current, the potential difference between the electrodes must exceed the decomposition-potential difference, E_D, shown in eq. (6):

$$E_D = |\Delta E| + |\Delta\eta| \tag{6}$$

According to eq. (6), the overvoltage, $\Delta\eta$, due to charge transfer, reaction, and diffusion, includes both the cathode reaction and the anode reaction, as summarized in eq. (7):

$$|\Delta\eta| = |\Delta\eta_C| + |\Delta\eta_A| \tag{7}$$

The cell voltage, E_{CELL}, which is necessary to operate the electrolysis process, has to overcome the decomposition voltage and the potential drop, IR_{CELL}. Equation (8) summarizes all contributions to the overall cell voltage, E_{CELL}:

$$E_{CELL} = |E_C - E_A| + |\Delta\eta_C| + |\Delta\eta_A| + iR_{CELL} = E_D + IR_{CELL} \tag{8}$$

wherein the voltage drop due to the electrical resistance, R, of the electrolyte is

$$IR_{CELL} = R\cdot I = \rho\cdot l\cdot \frac{I}{A} = \rho\cdot l\cdot i \tag{9}$$

In eq. (9), the resistance, R, is derived from the specific electrical resistance, ρ, the distance, *l*, between the electrodes and the electrode area, A, with the current density, I, derived from the ratio of the cell current, I, and electrode area, A. Experimentally, the specific electrical resistance was derived from determination of the cell voltage for varying electrode distance and constant current density, shown in Fig. 1.

For specified electrolyte composition ($c_{Zn} = 100\,g/L$, $T = 20°C$), the specific electrical resistance, $\rho = 0.635\,\Omega m$, can be derived from the slope of the graph from Fig. 1.

Figure 2 shows the comparison between the current/voltage curves of sulfate-based and acetate-based electrolytes for equivalent concentration of zinc of $c_{Zn} = 100\,g/L\ Zn^{2+}$. The electrode distance was kept constant at 50 mm and temperature was kept constant at $T = 20°C$. As represented by the different slope of the current/voltage curves, the specific electrical resistance of acetate-based electrolytes is about three times higher than the specific electrical resistance of sulfate-based electrolytes with comparable zinc content.

From Fig. 2, the decomposition voltage, E_D, of the acetate-based electrolyte was determined to be $E_D = 2.6\,V$, which is comparable for both electrolytes. Overvoltage due to charge transfer, diffusion, and reaction, according to eq. (6) is $\Delta\eta = 0.95\,V$, based on comparable equilibrium voltage of $\Delta E = 1.7\,V$.

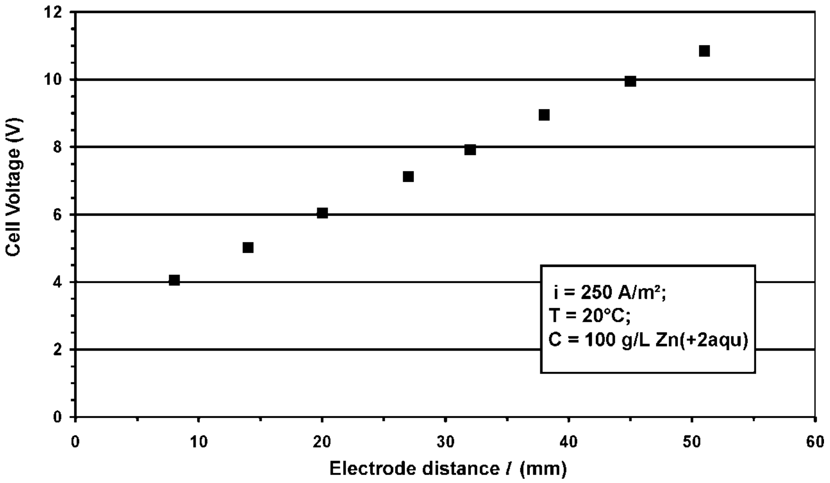

Figure 1. Voltage drop, IR_{CELL}, for $i = 250\,A/m^2$ const., $T = 20°C$, and $c_{Zn} = 100\,g/L\ Zn^{2+}$; experimental data.

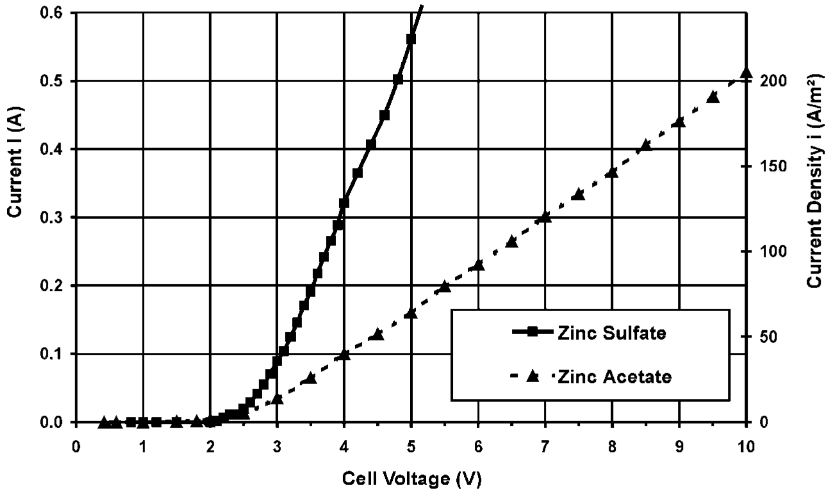

Figure 2. Comparison of zinc deposition from acetate- and sulfate-based electrolytes; electrolyte concentration: $c_{Zn} = 100\,g/L\ Zn^{2+}$, T = 20°C.

Figure 3 shows the dependency of the decomposition voltage, E_D, for varying electrolyte concentration. E_D decreases slightly with increasing zinc concentration. According to the conductivity properties of acetates, the specific electrical resistance, ρ, of aqueous zinc acetate passes a minimum at an electrolyte concentration of $c_{Zn} = 50\,g/L$. Therefore, in continuous mode of operation, the zinc concentration of the electrolyte is recommended to be adjusted to this concentration level, which is comparable with electrolyte concentration of zinc electrowinning from sulfate-based electrolyte.

Separation of Zinc from Acetate by Electrochemical Deposition

Prior to electrode position of zinc from the multicomponent-extract phase, the deposition of zinc from an analytical grade aqueous zinc acetate was investigated. The concentration of the electrolyte was kept constant at $c_{Zn} = 100\,g/L$. The electrode distance was 20 mm. From these experiments, the best operating conditions were found. The experiments showed that at T = 33°C and a current density between $i = 250$ and $i = 375\,A/m^2$, the current efficiency will pass a maximum. The results can be seen in Fig. 4.

In a next step, the influence of nickel on the current efficiency of the acetate-based electrolyte was investigated. In electrowinning of zinc from

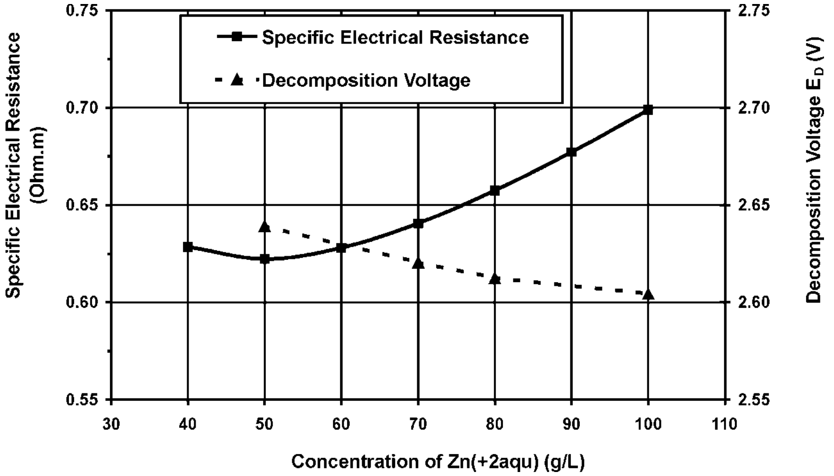

Figure 3. Decomposition voltage and specific electrical resistance of zinc acetate; electrode distance $l = 20$ mm, T = 20°C.

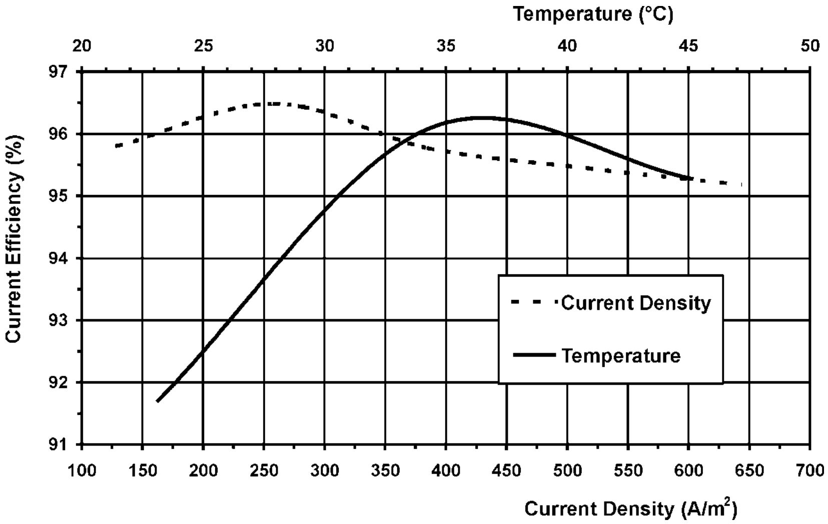

Figure 4. Influence of temperature and current density on current efficiency of zinc electrowinning from aqueous zinc acetate; electrolyte concentration $c_{Zn} = 100\,g/L$ Zn^{2+}, electrode distance $l = 20$ mm.

sulfate-based electrolytes, nickel causes severe problems even when only in traces.[6,9] When a critical concentration of Ni^{2+} is exceeded and several impurities are present simultaneously, zinc electrowinning will break down rapidly. The following guidelines for concentration limits of harmful impurities for sulfate-based electrolytes are reported[6]:

- As 0.01–1 mg/L
- Ni 0.05–3.0 mg/L
- Sb 0.05–0.1 mg/L
- Co 0.1–1.0 mg/L
- Fe 20–30 mg/L

However, in contrast to electrowinning of zinc from sulfate-based electrolyte, Fig. 5 shows, that even high concentrations of nickel (up to 50 mg/L) have little effect on the current efficiency of zinc deposition from acetate-based electrolyte.

Beside nickel, which was expected to affect hydrogen overvoltage negatively, the effect of lead, which is also leached from EAF dust in significant quantities, on the deposition of zinc was investigated. Figures 6 and 7 show electron-microscope images of zinc deposits with and without lead.

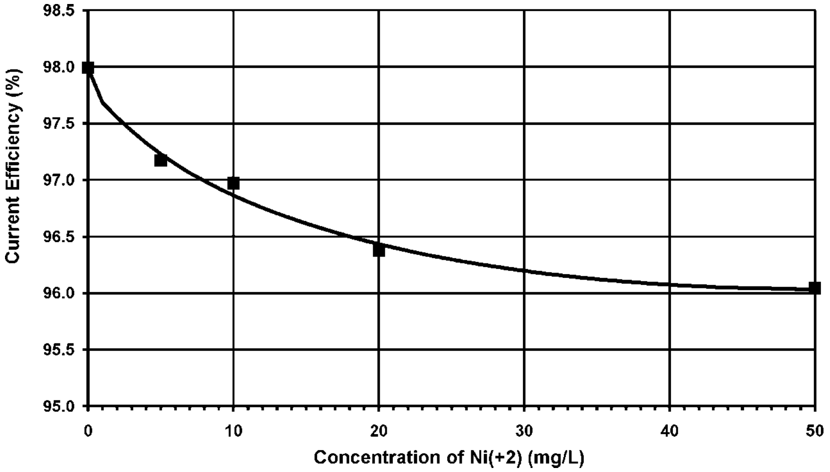

Figure 5. Effect of nickel contamination on current efficiency in zinc electrowinning from acetate-based electrolyte; $c_{Zn} = 100\,g/l\ Zn^{2+}$, $T = 33°C$, $i = 250\,A/m^2$, electrode distance $l = 20\,mm$.

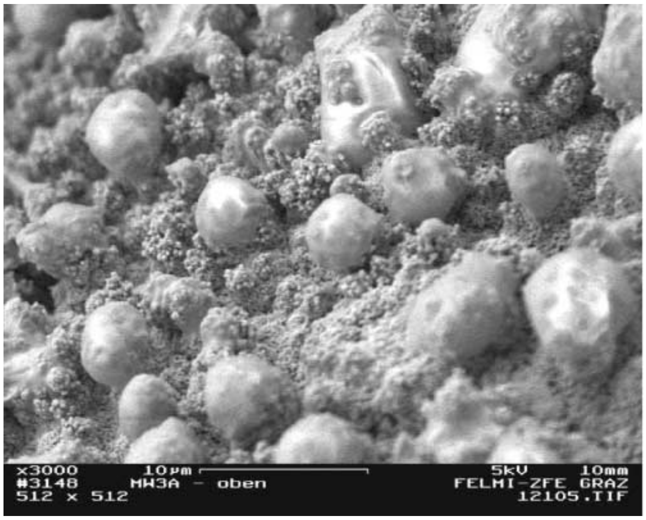

Figure 6. Cathode deposit of zinc, lead, and trace elements from acetate-based electrolyte; T = 33°, $c_{Zn} = 50\,g/L$, $c_{Pb} = 5\,g/L$, $i = 375\,A/m^2$, electrode distance $l = 20\,mm$.

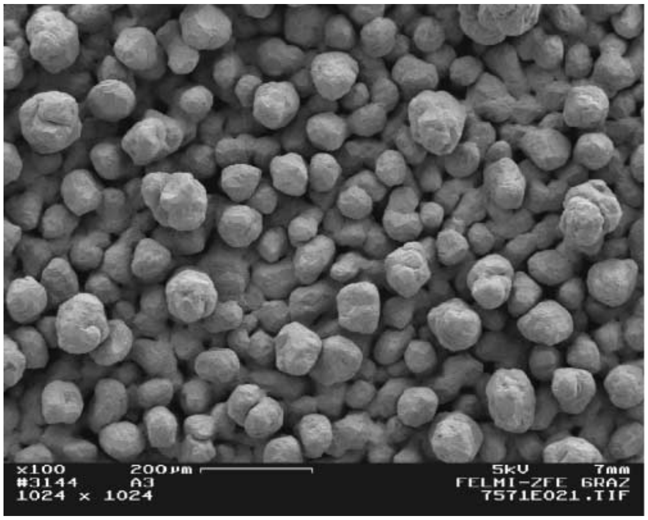

Figure 7. Cathode deposit of zinc from zinc acetate; T = 33°C, $c_{Zn} = 50\,g/L\ Zn^{2+}$, $i = 375\,A/m^2$, electrode distance $l = 20\,mm$.

The morphology of the deposit is different and depends on the presence of lead. When lead is added (about 5 g/L Pb^{2+}) to the electrolyte, the crystalline structure of the zinc deposit is of submicron scale. When pure zinc acetate is used, the cathode deposit is of bigger scale with an average particle diameter of 100 μm.

Electrochemical Deposition of Zinc from Multicomponent-Extract Phase

Finally, the multicomponent-extract solution obtained from EAF-dust leaching was electrolyzed without any further pretreatment other than solid removal. The target of these tests was the evaluation of the minimum technological demand in downstream processing of the extract phase prior to electrodeposition of zinc. The zinc content of the electrolyte, c_{Zn}, was about 40 g/L. The lead content was $c_{Pb} = 5\,g/L$. Further, the electrolyte was laden with several trace elements according to their solubility in aqueous acetic acid. Table 1 shows the mean composition of the extract phase.[4]

Figure 8 summarizes the results of several batch-electrolysis experiments, performed without pretreatment of the extract phase. In these series of experiments, the current density was varied between $i = 125$ and $i = 625\,A/m^2$. According to the different equilibrium voltage, deposition of lead is favored over zinc deposition at the beginning of the electrolysis process. Overall current

Table 1. 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

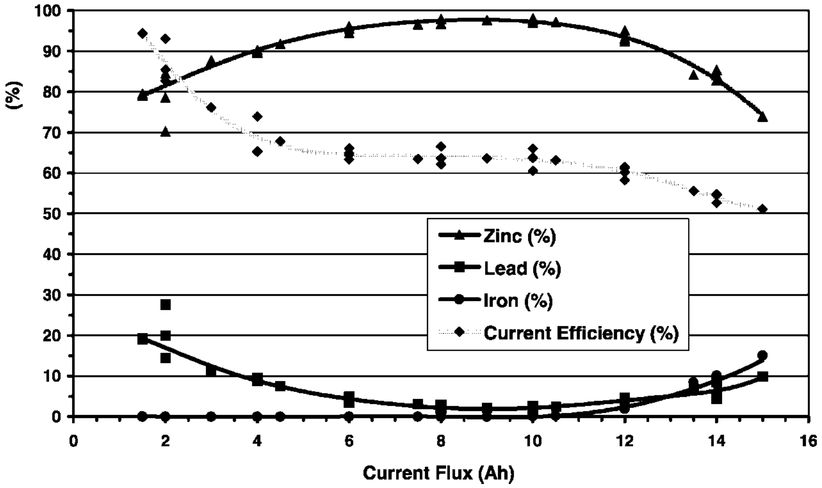

Figure 8. Results of several electrolysis experiments from multicomponent-extract phase performed at current densities between $i = 125 - 625\,A/m^2$; $T = 33°C$.

efficiency is above 90%. A second-phase deposition of zinc mainly determines the electrolysis process. Overall current efficiency drops to less than 70%. At constant current, the overall voltage of zinc deposition increases, because of the decreasing electrolyte concentration due to batch operation.

When lead is present, it is assumed that hydrogen overvoltage decreases due to the formation of submicron zinc deposit. Also, the negative effect of sodium and potassium on current efficiency has to be mentioned. Different current densities do not significantly affect the morphology of the deposit, the composition, and the current efficiency.

The zinc content of the deposit continuously increases throughout the second phase, although high-grade quality of 99.99% cannot be obtained due to coprecipitation of several trace elements and even iron.

CONCLUSION

Extraction, refining, and electrowinning of zinc from oxidic dust is an alternative route to pyrometallurgical processing. Extraction with aqueous acetic acid has proven applicable in extraction of zinc from multicomponent EAF dust. Extractability and the yield of extraction depend on the nature of the oxidic species.

After solid–liquid extraction, direct electrolysis of zinc from the multicomponent extract phase was investigated. It was shown that in contrast to sulfate-based electrolytes, zinc can be separated from acetate-based electrolytes by electrowinning even at high-level contamination of the electrolyte with nickel. The best operating conditions for the electrolysis of zinc from acetate solution were determined: the current density, I, should be kept between 200 and 500 A/m^2. Ideal temperature for the zinc electrolysis was found to be $T = 35°C$. Current efficiency during batch experiments was high at the beginning when the concentration of zinc was $c_{Zn} = 100\,g/L$. The lead concentration of the electrolyte has a significant influence on the morphology of zinc deposition.

With pretreatment of the extract phase by means of precipitation and cementation, it is possible to prepare the acetate-based electrolyte for high-grade deposition of zinc with a quality of 99.99%.

NOMENCLATURE

A	active area of the electrode (m^2)
c	concentration of electrolyte (g/L)
E	electrode potential (V)
E^θ	standard electrode potential (V)
E_{CELL}	cell potential; electromotive force (V)
E_D	decomposition voltage (V)
η	potential drop, overvoltage (V)
I	current (A)
i	current density (A/m^2); $i = I/A$
L/S	weight ratio of liquid feed extractant to solid dust (−)
l	distance between electrodes (mm)
κ	conductivity (S/m); $\kappa = 1/\rho$
R	resistance (Ω)
ρ	specific electrical resistance; resistivity (Ω·m)

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