ELEKTROLITIČKO IZDVAJANJE CINKA IZ PRAŠINE INDUSTRIJSKE ELEKTROLUČNE PEĆI

ZINC ELECTROWINNING FROM INDUSTRIAL ELECTRIC ARC FURNACE DUST

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Cilj ovog istraživanja je izdvajanje metalnog cinka iz prašine koja nastaje u industrijskoj elektrolučnoj peći (EAF prašina) postupkom elektrovininga. Ispitivanja su realizovana u laboratorijskim uslovima sa sumporno kiselim elektrolitima. Katodna gustina struje iznosila je 500 A/m^2. Temperatura elektrolita održavana je u opsegu 38±2 °C. Trajanje procesa je izračunato da bi se koncentracija Zn u elektrolitu smanjila za 30 g/l. Rezultati su pokazali iskorišćenje struje u opsegu od 50,4 % do 89,3 %, zavisno od sastava elektrolita i čistoće katodnih materijala. Rezultati ispitivanja potvrđuju da se EAF prašina može koristiti kao sirovina za elektrolitičko dobijanje cinka. Takođe, hemijska karakterizacija elektrolita na početku i na kraju svakog eksperimenta, kao i karakterizacija katodnih depozita dobijenih tokom procesa elektrovininga, skenirajuća elektronska mikroskopija sa energetski disperzivnom rendgenskom spektroskopijom (EDS), potvrdili su da nečistoće iz elektrolita imaju krucijalan uticaj na kvalitet depozita cinka.

***Ključne reči**: cink, elektrolučna peć, elektrovining, nečistoće, SEM EDS*

The aim of this study was a recovery of zinc metal from dust generated in the industrial electric arc furnace (EAF dust) by the electrowinning process. Investigations are realized in laboratory conditions with sulphury acid electrolytes. Cathode current density was 500 A/m^2. Electrolyte temperature was in the range of 38±2 °C. Process duration was calculated in order to reduce the Zn concentration in the electrolyte by 30 g/l. Results are shown that the current efficiency was in a range from 50.4 mass % to 89.3 mass % in accordance with the electrolyte composition and purity of the cathode materials. The results of the tests are confirmed that the EAF dust could be used as a raw material for electrolytic zinc recovery. Also, chemical characterization of the electrolyte at the start and at the end of each test, as so as the cathode deposits characterization, scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDS) of cathode deposits obtained during the electrowinning process, confirmed that the electrolyte impurities have the crucial influence on the quality of deposited zinc.

***Keywords**: zinc, electric arc furnace, electrowinning, impurities, SEM EDS*

1 Introduction

Zinc dust generated as waste material in industrial electric arc furnaces is used in order to obtain zinc oxide for the paint industry and zinc sulfate for the fertilizer industry. Electrolytic extraction of zinc metal from dust is a significant process for zinc extraction in countries such as India. The high chloride content in the ash limits the viability of the process due to severe corrosion on traditional lead anodes. Zinc dust generated as waste material in industrial electric arc furnaces is used to obtain zinc oxide for the paint industry and zinc sulfate for the fertilizer industry [1].

Today, approximately 30% of global zinc production arises from recycled zinc. The growing interest in secondary zinc materials, as a valuable resource, and stricter environmental legislation restricting the dumping of these hazardous materials has increased interest in their recycling [2]. The disposal and utilization of EAFD are problems for all steel industries worldwide. Steel production in electric arc furnaces generates a considerable amount of flue dust, about 15–20 kg per ton of steel [3-4]. In this article, the electrowinning process for obtaining zinc from the EAFD leaching solution is described.

In the first phase, the dust of the electric arc furnace is leached with water, then in the second stage with sulfuric acid, where the impurities dissolve together with zinc. Since the process of electrolytic production of zinc is extremely sensitive, especially to impurities that are more electropositive than zinc, impurities must be removed from the leaching solution by selective precipitation, cementation, solvent extraction, and ion exchange methods [5-7].

2 Experimental and discussion

All experiments were carried out in an electrochemical system shown in Figure 1, using different electrolytes obtained from dust generated in the industrial EAF. The electrolytes were obtained by multistage EAF dust leaching by sulfuric acid and purification of the leaching solution in order to remove harmful impurities. Duration of the electrowining process was calculated in order to reduce the concentration of Zn by 30 g/l.

The following methods have been used to characterize electrolytes and zinc deposits: Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Scanning electron microscope using energy dispersive X-ray spectroscopy (SEM-EDS).

In the first phase of the research, the influence of cathode type was investigated. Experiments 1 and 2 were performed using electrolytes of the same chemical composition (Ex-1 and Ex-2: Table 2). In the second phase, the influence of the electrolyte composition (the content of impurities) on the quality of the cathode deposits was investigated Ex-3 and Ex-4: Table 2). Table 1 shows the chemical composition of the cathodes, and Table 2 shows the composition of the electrolyte at the start and end of the process for all experiments. The technological parameters of the process are shown in Table 3.

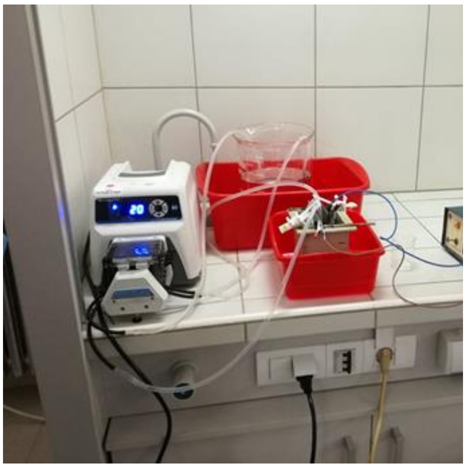


Figure 1. Electrochemical system for laboratory tests

Table 1. Chemical composition of the Al cathodes

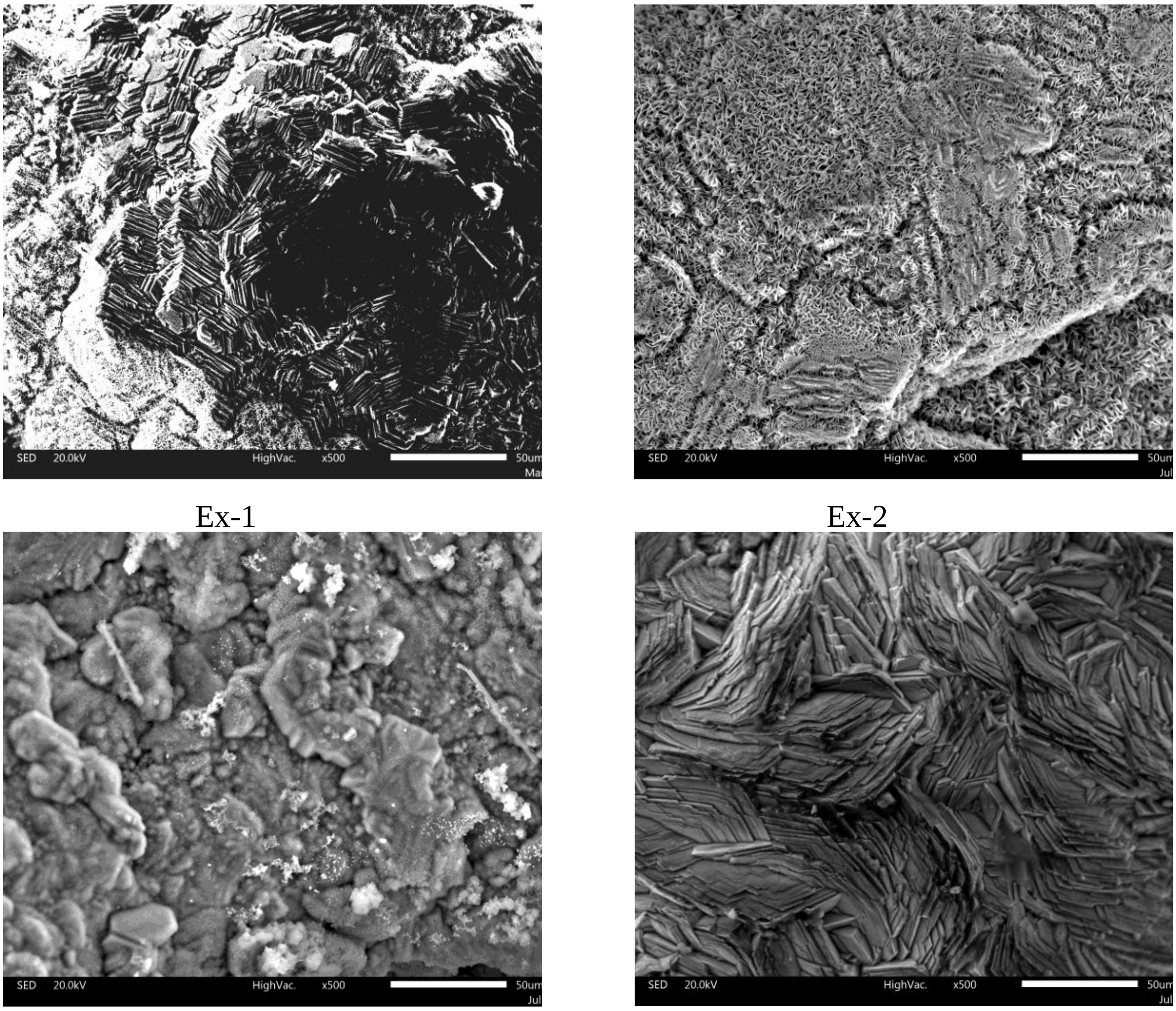
Element	Al (1 mm)	Al (5 mm)
	Content, ppm	
Ca	31.0	18.2
Co	1.6	0.98
Cr	7.8	7.0
Cu	22.5	65.8
Fe	2743.8	1999.4
Ga	88.9	87.7
Mg	<1	298.5
Mn	21.2	241.2
Ni	13.8	34.0
V	55.0	72.6
Zn	347.7	139.8

Table 2. Chemical composition of the electrolyte at the start and end of the process

Element	Experiments							
	Ex-1		Ex-2		Ex-3		Ex-4	
	start	end	start	end	start	end	start	end
	Concentration, mg/l							
Al	126.3	98.6	126.3	173.3	35.4	42.8	32.4	45.9
Co	1.0	0.91	1.0	0.91	0.052	0.044	0.026	0.030
Cd	1.4	0.46	1.4	0.41	< 0.008	<0.008	<0.008	<0.008
Cu	0.055	0.34	0.055	0.012	0.020	0.025	0.035	0.035
Fe	11.4	10.3	11.4	10.4	0.38	0.28	0.35	0.36
Mn	2941.9	223.7	2941.9	343.2	1379.8	<0.007	1488.5	191.2
Ni	1.9	1.7	1.9	1.8	< 0.007	< 0.007	<0.007	<0.007
Sb	0.40	0.3	0.40	0.37	<0.011	<0.011	<0.011	<0.011
F^-	315.0	400.0	315.0	475.0	480.0	388.4	508.8	533.8
Cl^-	390.0	100.0	390.0	130.0	318.0	38.9	374.4	76.7
Element	Concentration, g/l							
Zn	122.0	97.9	122.0	105.92	120.6	93.65	90.64	63.9
H2SO4	109.45	111.8	109.45	110.5	125.0	148.5	135.0	147.5

Table 3. Technological parameters of the process

Technological parameters				
Experiment	Ex-1	Ex-2	Ex-3	Ex-4
Process parameters				
Anode	Pb+1% Ag			
Number of anodes, (pcs)	2			
Cathode	Al (5mm)	Al (1mm)	Al (1mm)	Al (1mm)
Number of cathodes, (pcs)	1			
Electrode arrangement in the system	A-K-A			
Cathodic current density, j (A/m2)	500			
Electrolyte volume, V (l)	5			
Electrolyte temperature, t (°C)	38±2			
Electrolyte circulation (number of cell volume changes/h)	2			
Process time for reduction of the concentration of Zn in the electrolyte by 30 g/l, (h)	25.6	30.76	25.11	25.11
The electrochemical equivalent for Zn, (g /Ah)	1.219			
Mass of the cathode deposit – theoretic, (g)	150			
Glue- start, mg/l	50			
Measurements during the process				
Glue, (mg /l 24 h)	50	50	50	50
Cell voltage, min-max, U (V)	3.4 – 3.6	3.3 – 3.7	3.4-3.6	3.2-3.35
Current, min-max, I (A)	4.75-4.85	3.9-4.2	4.9-4.95	4.85-4.99
Electrolyte temperature, t (°C)	38	37	38	36
Measurements after the end of the process				
Duration of the electrolysis process, (h)	25.6	30.76	25.11	25.11
Cathodic deposit mass (g)	75.6	115.5	133.95	131.6
Mass of anode sludge (g)	18.1	18.2	6.2	5.5
Current efficiency, η (%)	50.4	77.0	89.3	87.73



Ex-1 Ex-2

Ex-3 Ex-4

Figure 2. SEM images of zinc deposit

Based on SEM EDS analysis of cathode deposits (Figure 2) obtained from the same starting electrolyte (Ex-1 and Ex-2), of which composition is shown in Table 2 using different electrode systems: (Ex-1: cathode Al (5 mm) and anode Pb + 1% Ag and Ex-2: cathode Al (1 mm) and anode Pb + 1% Ag) it can be concluded follows:

- In Ex-1, an inhomogeneous, porous deposit was obtained over the entire surface of the cathode (the deposit is transparent) containing lead, manganese, and cadmium, with low current efficiency of 50.4%.

- In Ex-2, a cathode deposit was obtained with less impurity and fewer holes, with a current efficiency of 77.0%.

- In both experiments, the concentration of Co, Cd, Mn, Cl, and Zn decreased during the process, while the concentration of Cu increased. The decrease in Cd content is almost identical in both experiments (Ex-1: 67.14% and Ex-2: 77%) and is a consequence of deposition on the cathode having in mind the position of Cd in the voltage series [5-6.]. The decrease in chlorine ion concentration occurs as a consequence of the separation of elemental chlorine and the formation of chlorine-based compounds [5]. The decrease in the concentration of Ni and Co is a consequence of the simultaneous deposition on the cathode due to the lower overvoltage in relation to the value for zinc [6-7]. The concentration of Mn decreases as a consequence of the formation of manganese dioxide at the anodes and its deposition in the form of anode sludge. Based on the study of the influence of the type of cathode on the quality of zinc deposits, it can be concluded that the use of aluminum cathode of 1 mm (chemical composition shown in Table 1.) obtained cathode zinc of commercial quality while the quality of zinc obtained using aluminum cathode of 5 mm Table 1.) far below commercial quality. It should also be noted that in the second experiment, less current efficiency was achieved.

In the third and fourth experiments, the influence of the very low content of impurities in the electrolyte on the current efficiency and the quality of deposits (Ni, Co, Cd, Cu) was investigated. The results showed an current efficiency of 89.3% (Ex-3) and 87.73% (Ex-4), respectively. The results confirm that zinc electrolysis is an extremely sensitive process, especially to impurities from electrolytes that are more electropositive than zinc, and that in order to obtain a quality deposit and achieve high current efficiency, the impurity content in the electrolyte must be very low [7].

The resulting anode sludge contains from 35.77% to 58.72% Mn (in the form of MnO_2), and it can be used in zinc production for oxidation processes after washing and drying.

3 Conclusion

The results of laboratory tests of obtaining electrolytic zinc from electrolyte obtained by leaching and purification of filter dust of electric arc furnaces confirmed that electrolysis of zinc is an extremely sensitive process, especially to impurities that are more electropositive than zinc. These metals precipitate together with zinc and form cathode surfaces with low overvoltage of hydrogen evolution. In order to obtain a quality cathode deposit of zinc, it is necessary that the process electrolyte is almost completely free of impurities. In all experiments, a decrease in the concentration of chlorine ions was observed, which can be explained by the reactions at the anode, which leads to the separation of elemental chlorine and the formation of chlorine-based compounds. Anode sludge, which is almost pure MnO_2 in composition, can be used in zinc production for oxidation processes or as a commercial product after washing and drying.

Acknowledgments

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4 References

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