Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). Part II: Downstream processing and zinc recovery by electrowinning

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A B S T R A C T

The characterization and the agitation leaching of electric arc furnace dust (EAFD) by diluted sulphuric acid have been studied in Part I, as a separate article. The aim of the present research work (Part II) is the development of a purification process of the leach liquor for the recovery of high-purity zinc by electrowinning. The proposed hydrometallurgical process consists of the following four (4) unit operations: (1) Removal of iron as easily filterable crystalline basic sulphate salt of the jarosite type, at atmospheric pressure, by chemical precipitation at pH: 3.5 and 95 °C. (2) Zinc solvent extraction by Cyanex 272 at pH: 3.5, T: 40 °C, with 25% extractant concentration. (3) Stripping of the loaded organic phase by zinc spent electrolyte (62.5 g/L Zn^{2+}) at T: 40 °C with diluted H_2SO_4 (3 mol/L). (4) Zinc electrowinning from sulphate solutions (at 38 °C) using Al as cathode and Pb as anode. The acidity of the electrolyte was fixed at 180 g/L H_2SO_4, while the current density was kept constant at 500 A/m².

1. Introduction

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 that restricts dumping of these hazardous materials has increased interest in their recycling [1]. The disposal and utilization of EAFD are problems for all steel industries in the world. Steel production in electric arc furnaces generates a considerable amount of flue dust, about 15–20 kg per ton of steel [2]. In this second article (Part II), the development of a hydrometallurgical process for the purification of the EAFD leach liquor and the recovery of zinc by electrowinning is described. The first stage of the proposed method (Part I) is agitation leaching with diluted sulphuric acid [3]. Zinc recoveries of up to 80% can be obtained in less than 1.5 h with less than 45% of the iron dissolved.

The hydrometallurgical processing of wastes is gaining importance in the metallurgical industries for the recovery of metallic values. During hydrometallurgical treatment, undesired species are also dissolved along with the metal of interest in the solution. These impurities can be removed by selective precipitation, cementation, solvent extraction, ion exchange or electrolysis methods. The modified zincex process [4] is a hydrometallurgical process that takes advantage of the zincex process long ago used in two industrial plants. The modified zincex process is used to obtain high quality zinc slabs from secondary raw materials. Atmospheric leaching, purification of the leached liquor (principally iron and aluminium by precipitation), solvent extraction and conventional electrowinning, are used in order to resolve impurity difficulties and recover zinc ingots. In Anglo-American's Skorpion Zinc refinery, after leaching with sulphuric acid, impurities such as iron, aluminium, and silica are removed from the solution by precipitation. Zinc is then selectively extracted by di(2-ethylhexyl)phosphoric acid (D2EHPA), enabling the electrowinning of zinc [5].

1.1. Iron removal by chemical precipitation

After EAFD leaching [3], iron is present as an undesirable constituent in zinc leach liquor and constitutes a severe impurity, which must be removed before electrolysis. It should be noticed that an iron level of less than 10 ppm in sulphate electrolyte is known to significantly reduce zinc current efficiency. The solvent extraction and recovery of zinc by electrowinning firstly requires the iron removal from the sulphate EAFD leach liquor. According to Cole and Sole [1] a comparison of the pH-dependence for the extraction of zinc showed that the extractants D2EHPA, Ionquest 801, Cyanex 272 and Cyanex 301 are not selective for Zn over Fe(III), because iron (III) is quantitatively extracted by organophosphorus extractants and forms more stable complexes than those of zinc.

The Laboratory of Metallurgy of the National University of Athens has developed and patented a process for the removal of iron, aluminium and chromium from nickel sulphate
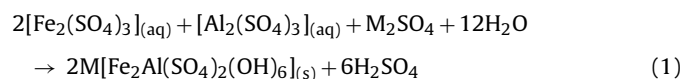
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leach liquors. The process relates to the precipitation of the above metal ions as crystalline, easily filterable chemical precipitates of the jarosite type, at atmospheric pressure without alkali addition [6].

The jarosite/alunite group of isostructural minerals is described by the general formula $M(Fe_xAl_yCr_z)(SO_4)_2(OH)_6$, in which "M" may be Na^+, K^+, NH_4^+ or H_3O^+ and $x+y+z=3$. The precipitation occurs according to the following hydrolysis reaction [7]:

$$2[Fe_2(SO_4)_3]_{(aq)} + [Al_2(SO_4)_3]_{(aq)} + M_2SO_4 + 12H_2O$$
$$\rightarrow 2M[Fe_2Al(SO_4)_2(OH)_6]_{(s)} + 6H_2SO_4 \qquad (1)$$

1.2. Zinc recovery by solvent extraction

In an electrolytic zinc refinery process, the zinc sulphate solution is subjected to a series of purification steps to remove unwanted species such as iron, calcium, lead, manganese, magnesium and copper. The solvent extraction technique is one of the most versatile methods used for the removal, separation and concentration of metallic species from aqueous media and has been widely used in the extraction of zinc, from sulphate solutions.

Di(2-ethylhexyl) phosphoric acid (D2EHPA) has been extensively studied for extraction and separation of transition metals. The extraction takes place as cationic liquid ion exchange mechanism. The oxygen atom of the phosphoryl group ensures coordination with the ions extracted by forming chelating products. Pereira et al. [8] have examined the extraction of zinc using D2EHPA in order to recover zinc from an industrial effluent which contains several metallic species such as cadmium, cobalt, iron, lead, calcium, magnesium, manganese and nickel. The continuous mixer-settler tests showed that zinc could be selectively and quantitatively removed from the effluent (around 98%) using three extraction stages at pH = 2.5, extractant concentration = 20% and A/O = 1. Banza et al. [9] have proposed the extraction of cobalt and zinc with D2EHPA, followed by selective stripping with sulphuric acid solutions of different dilutions, from copper smelter slag leach liquor. Vahidi et al. [10] described a hydrometallurgical treatment involving solvent extraction of zinc using di-2-ethylhexyl phosphoric acid (D2EHPA) from an industrial leach residue. Zinc was extracted from the aqueous solution at pH 2.5 with 20% (w/w) D2EHPA in kerosene. Ritcey and Lucas [11] have used 0.5 mol/dm^3 Kelex 100 with 10% isodecanol in Solvesso 150 to determine the preferential extraction of Cu, Fe(III), Ni, Zn, Co, Fe(II), Mn, Ca and Mg from acidic solution, in the pH range 0.5–6.0. Sole and Hiskey [12] have also reported a comparison of the solvent extraction behaviour of the first row transition elements from acid sulphate solutions, with distribution coefficients shifting to lower pH with increasing sulphur substitution and decreasing pK_α values of the extractant.

The starting point for the CYANEX range of extractants is phosphine, PH_3. The best known of all Cytec CYANEX range of reagents is CYANEX 272 [13,14]. The selectivity series using Cyanex 272 is: Fe^{3+} > Zn > Cu > Co > Mg > Ca > Ni.

1.3. Zinc electrowinning

Electrolytic recovery of zinc is one of the oldest industrial processes, whose importance lies in the great worldwide demand for this metal that currently reaches an overall production of 9 million tonnes per year [15]. It is the main process step of hydro-electrometallurgical route for both from primary and secondary sources, while about 80% of the world zinc production is carried out by this technique [16]. The process is made possible by the high overpotential of hydrogen formation on the layer of zinc covering the aluminium cathode. To achieve this overpotential condition the temperature of the electrolyte should not be high, and the elec-

trolyte must be quasi pure [17]. It requires an electrolyte with a composition of 50–90 g/L Zn^{2+} and 120–200 g/L H_2SO_4, while it is usually carried out at high current densities in the range 400–700 A/m^2 [18]. Aluminium is used as the cathode because it forms no alloys with zinc. A major problem during the electrowinning of zinc, which becomes more critical when the raw material is a waste product, is the harmful effect exerted by metallic impurities since they decrease the current efficiency and diminish the purity of the zinc deposit [19].

The present research work proposes a process for zinc recovery, by electrowinning, from sulphate leach liquors. More specifically, iron can be rejected from the solution, as easily filterable crystalline basic sulphate salt of the jarosite type, at atmospheric pressure, by chemical precipitation at 95 °C. Zinc is then extracted by Cyanex 272, leaving the other metals in solution. The loaded Cyanex 272 organic phase is then stripped by zinc spent electrolyte in order to produce a solution suitable for zinc electrowinning.

The resulting magnesium and manganese in the solution can be removed by hydrolytic precipitation, as easily filterable crystalline precipitate, at ambient temperature, using calcium hydroxide as a neutralizing agent [20,21].

2. Experimental

The leach liquor, which was used during experimentation, had been produced by EAFD agitation leaching with dilute sulphuric acid (1.5 mol/l). The average composition of the pregnant solution produced from EAFD agitation leaching with sulphuric acid is as the following [3]: Zn^{2+} = 14.0 g/L, Fe^{3+} = 13.0 g/L, Al^{3+} = 0.5 g/L, Cu^{2+} = 0.3, Mn^{2+} = 1.9 g/L and Mg^{2+} = 2.3 g/L. Elements concentration was determined by atomic absorption spectrophotometer (Perkin Elmer 4100) and inductively coupled plasma mass spectrometry (ICP-MS, X Series II, Thermo Scientific). The analysis of Fe (Fe^{2+} and Fe^{3+}) was performed with back-titration using potassium dichromate ($K_2Cr_2O_7$).

The produced precipitates as well as the zinc cathodes were mineralogically analyzed by X-ray diffraction (XRD), using a Bruker D8-Focus diffractometer with nickel-filtered Cu Kα1 radiation (=1.5405 Å), 40 kV and 40 mA. Their morphology was also examined by scanning electron microscopy (SEM) using a Jeol 6380LV scanning electron microscope. Experimental conditions involved 15 and 20 kV accelerating voltage. Chemical composition of the samples was carried out by an Oxford INCA energy dispersive spectrometer (EDS) connected to the SEM.

2.1. Removal of iron by chemical precipitation

In the first stage, iron was removed as jarosite by chemical precipitation [6]. The runs were conducted in a 5 L, five-necked, round bottomed split reactor, that was fitted with a glass stirrer, vapour condenser, thermometer and a pH electrode. The solution was placed in the flask and heated to 95 ± 0.5 °C by electrical mantle. The temperature of the liquid was controlled by a Pt-100 digital controller and the pH was measured using a Hamilton Chemotrode Bridge 200 combined pH electrode, specially designed for semi-solid and boiling water solutions. The pH of the solution was slowly raised to a pre-determined equilibrium value (pH 3.5), by adding CaO pulp (20%). It should be emphasized that, during the precipitation process, the pH increase rate was kept low in order to control supersaturation of iron and avoid the production of an amorphous precipitate.

2.2. Solvent extraction—stripping processes

All batch experiments were conducted in a 500-mL five-necked, round bottomed split reactor, which was fitted with a glass stirrer,

a vapour condenser, a thermometer and a pH electrode. The two phases (organic and aqueous) were contacted for 20 min by rapid stirring and the pH was controlled by small additions of 5 mol/L NaOH, using an automatic titration device. Heating was provided by an electrical mantle and the temperature of the liquid was controlled by a Pt-100 digital controller.

For the stripping test, the loaded organic was contacted with a synthetic zinc spent electrolyte (62.5 g/L Zn^{2+}). The stripping was undertaken for 30 min and the procedure was designed to raise the zinc level of the electrolyte to approximately 80 g/L Zn for subsequent electrowinning tests.

2.3. Zinc electrowinning

The electrolytic cell was a 1000 mL double walled pyrex cylinder, which was connected with a thermostat circulator using H_2O as heat exchange fluid. The temperature inside the cell was kept constant at 38 °C. Cathode was made from aluminium sheet 8 cm height by 10 cm wide and 1 mm thick. The anode was a Pb plate of the same dimension, placed at a constant distance of 25 mm from the cathode. The cathodes were polished with 600 grit silicon carbide paper, rinsed with deionized water and dried with hot air. The deposition tests were made for 4 h (at 500 A/m²) without agitation. DC power was supplied by a laboratory AFX 530 5A programmable power supply. The final electrolyte composition was fixed at 80.37 g/L Zn^{2+} and 180 g/L H_2SO_4. The mass of zinc produced was determined by the mass difference of the cathode before and after the electrowinning tests. The current efficiency was then determined by dividing the theoretical current to produce the deposit by the real supplied one. Zn deposits were examined by X-ray diffraction (XRD) to determine preferred orientation and by scanning electron microscopy (SEM) to determine the surface morphology and microstructure.

3. Results and discussions

3.1. Removal of iron by chemical precipitation

The optimum pH value was determined at which maximum iron precipitation occurred with minimum zinc losses. All precipitates settled down quickly and were easily filtered. As it shown in Fig. 1, at pH 3.5, 99.9% of iron was precipitated with only 5.0% zinc losses.

The X-ray diffraction data of the above precipitate, after drying at 110 °C is shown in Fig. 2. The main mineralogical phases were jarosite {(K,H₃O)Fe₃(SO₄)₂(OH)₆}, anhydrite $CaSO_4$ and bas-
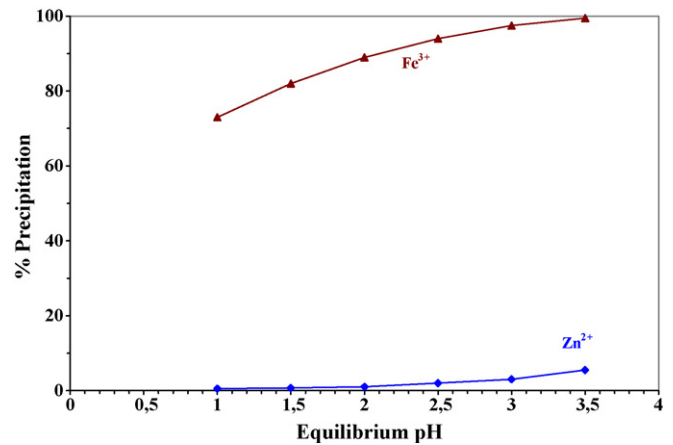

Fig. 1. Zinc losses in the precipitate during iron precipitation from leach liquor as jarosite.

sanite ($CaSO_4 \cdot 0.5H_2O$). All peaks were sharp and with high intensity a fact that was attributed to the high degree of the precipitate's crystallinity.

Scanning electron microscopy with X-ray energy dispersive analysis (EDS) was performed to gain further knowledge of the mineralogical species contained in the mixed precipitate and their morphology. The evaluation was carried out by secondary and backscattered electrons (BSE) mode. The jarosite particles appeared as spherical fine-grained particles, dispersed among crystals of $CaSO_4$. As shown in Fig. 3a, jarosite precipitate was in the form of aggregates of fine crystallites. The aggregates had an irregular shape and size of about 10–20 μm. On the other hand, $CaSO_4$ consisted of prismatic crystals of 10–30 μm in length and 5–10 μm in diameter (Fig. 3b).

The above mixed precipitate is now regarded either as a potentially useful material for replacing the gypsum in cement production [22], or as a raw material (as a source of iron) for Portland cement clinker production [23].

3.2. Zn solvent extraction by Cyanex 272

After the removal of iron as jarosite the composition of the leach liquor is the following: $Zn^{2+} = 9.04$ g/L, $Mn^{2+} = 1.55$ g/L, $Mg^{2+} = 1.92$ g/L and $Ca^{2+} = 0.49$ g/L. In order to determine the ability of Cyanex 272 to selectively extract zinc from the sulphate leach
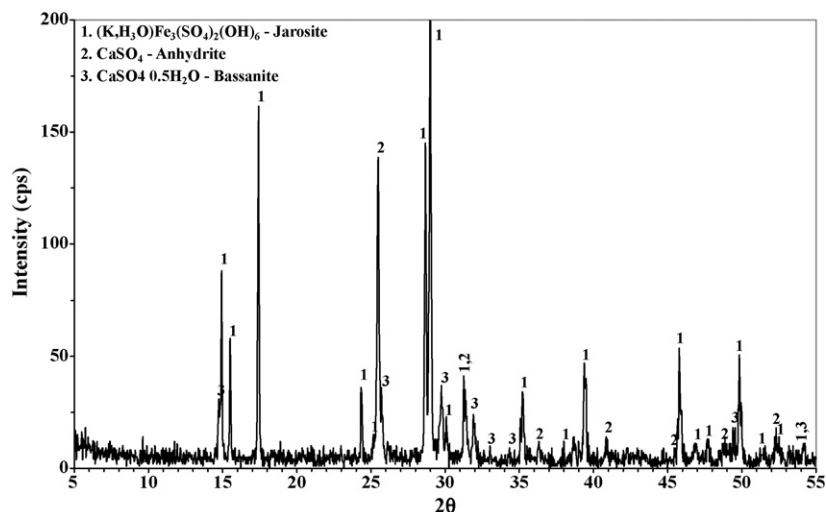

Fig. 2. Mineralogical phases of jarosite precipitate with CaO pulp.

(a) Jarosite agglomerates

(b) Prismatic crystals of CaSO$_4$
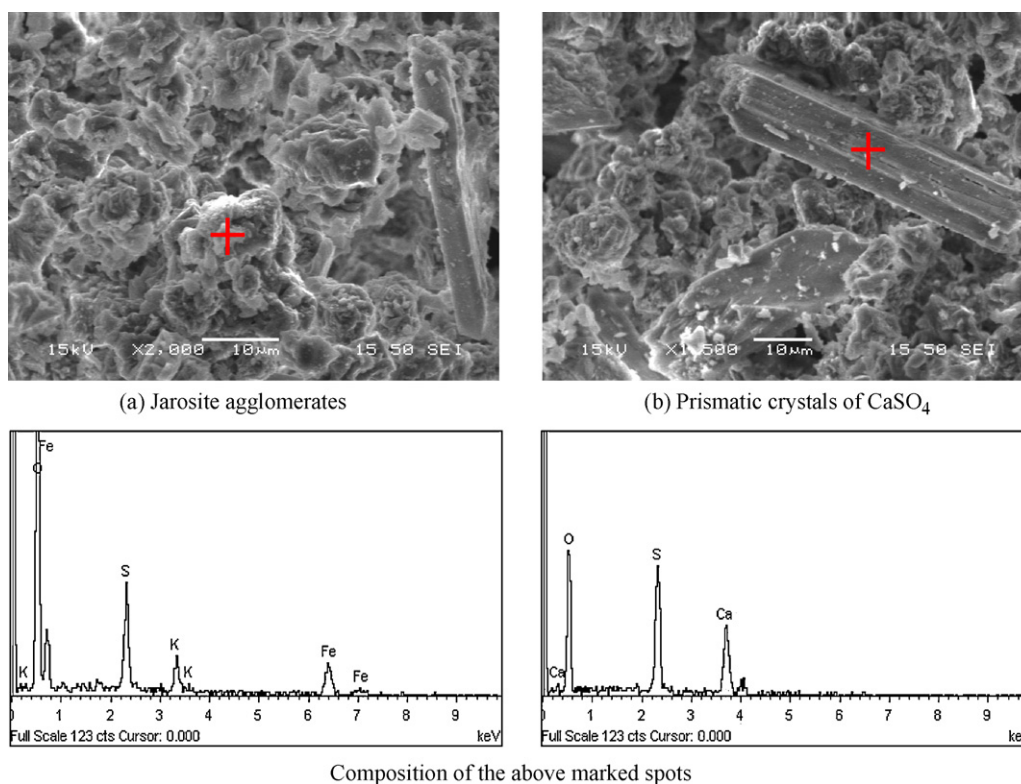
Composition of the above marked spots

Fig. 3. SEM micrographs and EDS analysis of the produced jarosite precipitate.

liquor, extraction tests were carried out at various equilibrium pH values, at certain other conditions. The results, presented in Fig. 4, show that Cyanex 272 can efficiently extract zinc in the pH range of 3.0–3.5, whereas cobalt, manganese and magnesium (calcium is rejected with the extractant Cyanex 272) are extracted at a pH above 3.5.

Factorial design and analysis of experiments were used in order to determine the main effects and interactions of the solvent extraction factors. The factors studied and their levels are shown in Table 1. Parameters, which were kept constant during experimentation, were:

- stirring speed = 800 rpm;
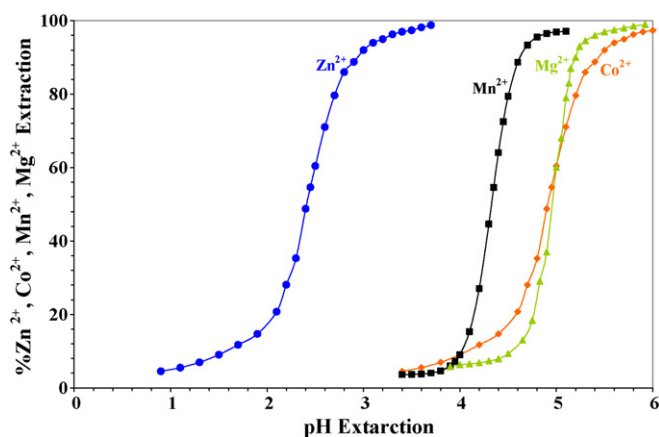- initial zinc concentration = 9.04 g/L.

The main response under investigation was the percentage of zinc extracted in the organic phase. The concentration of zinc after solvent extraction experiments and the percent extraction values are given in Table 2.

The data presented in Table 2 show that zinc could be efficiently extracted by Cyanex 272 in order to be concentrated for the electrowinning stage. To study the main effects and interactions of the factors on zinc extraction, a Yates's analysis and an analysis of variance were carried out on the percentages of Zn^{2+} extracted in the organic phase. The results are shown in Table 3. The main effects A (pH) and B (temperature) were found to be statistically significant at $\alpha = 0.01$ and positive. In the range of variables studied, the equilibrium pH (A) presented the largest effects. Based on the statistical analysis of the results, the optimum conditions determined for zinc solvent extraction by Cyanex 272, in one stage, were: pH 3.5, $T = 40\,^\circ C$ and Cyanex 272 = 25%.

3.3. Zn stripping by zinc spent electrolyte

Stripping of zinc from the loaded organic phases was conducted using zinc spent electrolyte. Its composition was selected on the basis of the industrial electrowinning applications. The industrial conditions for zinc electrowinning require an electrolyte composition of 50–90 g/L Zn^{2+} and 120–200 g/L H_2SO_4 [18]. On the basis of

Fig. 4. Zinc selectivity over cobalt, manganese and magnesium with Cyanex 272 at T: 40 °C. Organic phase: 25% Cyanex 272 in Exxsol D-80 with 5% TBP.

Table 1
Minimum and maximum levels of variables. Solvent extraction by Cyanex 272.

Factor	Variables	Zn^{2+} extraction by Cyanex 272		Units measured
		Low	High	
A	Extraction pH	3.0	3.5	pH units
B	Temperature	25	40	°C
C	Extractant concentration	25	30	% (v/v)

Table 2
Results of zinc solvent extraction by Cyanex 272.

Treatment code	Variables			Zinc concentration after extraction (ppm)	% Zn^{2+} extraction
	A (pH)	B (T)	C (c)		
(1)	−	−	−	203	97.74 ± 0.15
a	+	−	−	28	99.69 ± 0.15
b	−	+	−	64	99.29 ± 0.15
ab	+	+	−	15	99.83 ± 0.15
c	−	−	+	105	98.83 ± 0.15
ac	+	−	+	15	99.83 ± 0.15
bc	−	+	+	31	99.66 ± 0.15
abc	+	+	+	8	99.91 ± 0.15

Table 3
Yates' analysis and analysis of variance—response: % Zn solvent extraction by Cyanex 272.

Treatment code	Response Zn extraction (%)	Yates' analysis					Analysis of variance			
		1	2	3	Divisor	Effects	Indentification	$t = $eff/$S_e$	$t_{0.01} \Phi = 8$	Significance at $\alpha = 0.01$
(1)	97.74 ± 0.15	197.43	396.56	794.79	8	99.35 ± 0.094	Average			
a	99.69 ± 0.15	199.12	398.23	3.74	4	0.94 ± 0.19	A	5.00	3.36	S
b	99.29 ± 0.15	198.67	2.49	2.59	4	0.65 ± 0.19	B	3.46	3.36	S
ab	99.83 ± 0.15	199.57	1.26	−2.14	4	−0.54 ± 0.19	AB	−2.87	3.36	NS
c	98.83 ± 0.15	1.94	1.69	1.68	4	0.42 ± 0.19	C	2.24	3.36	NS
ac	99.83 ± 0.15	0.54	0.90	−1.23	4	−0.31 ± 0.19	AC	−1.65	3.36	NS
bc	99.66 ± 0.15	1.00	−1.40	−0.79	4	−0.20 ± 0.19	BC	−1.05	3.36	NS
abc	99.91 ± 0.15	0.26	−0.74	0.66	4	0.16 ± 0.19	ABC	0.88	3.36	NS

conclusions drawn from preliminary experiments, the conditions for the stripping of zinc from the loaded Cyanex 272 by zinc spent electrolyte were fixed at:

- H_2SO_4 concentration = 3 mol/L.
- Organic to aqueous ratio = 2/1.
- Temperature: 40 °C.
- Stirring speed: 800 rpm.
- Cyanex 272 organic phase: $[Zn^{2+}]_{org} = 8.98$ g/L.
- Synthetic zinc spent electrolyte: 62.5 g/L Zn.

At those conditions, zinc stripping by zinc spent electrolyte reached 99.5%.

3.4. Zinc electrowinning

After zinc solvent extraction by Cyanex 272 and its stripping by zinc spent electrolyte, the aqueous solution contained 80.37 g/L of Zn^{2+} (Zn spent electrolyte: 62.5 g/L and Zn for electrowinning: 17.87 g/L). The electrolyte acidity was fixed at 180 g/L H_2SO_4. The deposition tests were made for 4 h at 500 A/m², while the temperature was kept constant, at 38 °C. At those conditions, flat bright and smooth zinc deposits could be produced, while the current efficiency was satisfactory, reaching at 92%. The orientation of the zinc deposits was examined using XRD analysis and a typical pattern is given in Fig. 5. The XRD spectra showed that the preferred orientations of the grains are (0 0 2), (1 0 1) and (1 0 3). These types of orientations are commonly observed for industrially produced zinc deposits and have also been identified by other authors using similar conditions [24,25].

The surface morphology was examined by scanning electron microscopy. It consists of closely packed uniform nodules, comprised of sharply defined hexagonal zinc plate-like crystals, with no dissolution effects. At this point it should be noticed that the electrodeposited zinc, should not only have dendrites, to prevent dangerous short circuit phenomena, but it must have as little
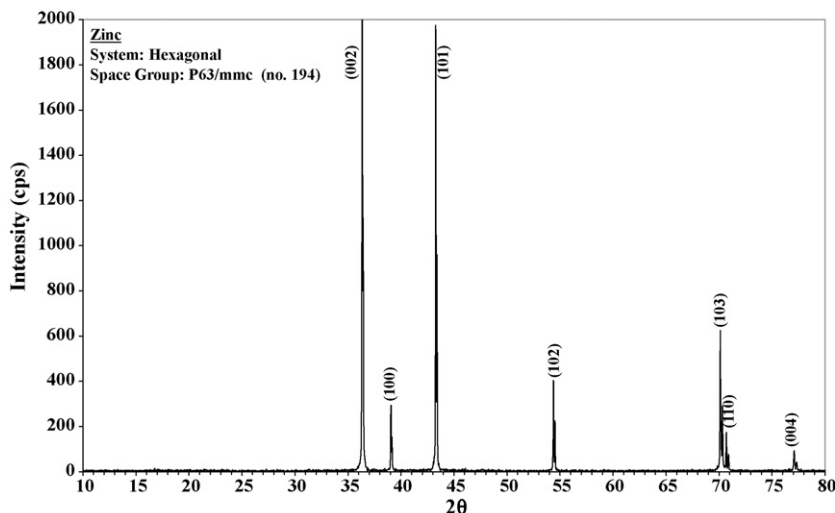

Fig. 5. Representative XRD spectra for electrodeposited zinc at the current density of 500 A/m².
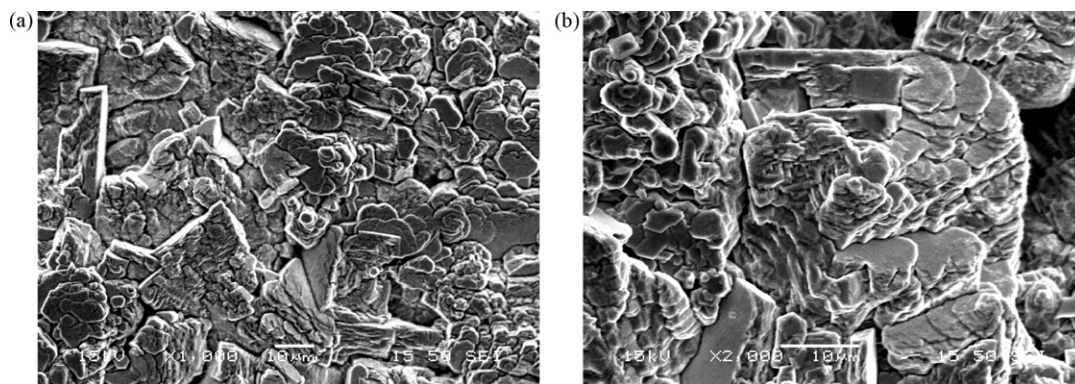
Fig. 6. SEM micrographs of zinc deposits from electrolyte containing 80.37 g/L of Zn^{2+} at 500 A/m^2 and 38 °C.

spongy structure as possible (Fig. 6), as well, because it must be melted. If the deposit was porous it would incorporate a considerable quantity of salts which, during melting, could promote foam formation. This foam could decrease the melting yield due to metal entrainment [26].

The crystal size ranged from a few micrometers to 50 μm. The formation of coarser platelets should be attributed to the absorption of the evolved hydrogen (due to the relatively high current density) on the active sites, preventing the formation of increased number of nucleation sites. This enables zinc to be deposited on lesser number of nuclei that cause the deposited crystals to grow [27]. The crystal facets appeared to be rough and textured. EDS spectra of all deposits displayed only the bands associated with Zn. This confirms the high purity of recovered Zn, free of heavy metals impurities, such as Pb which may result from anode corrosion, and without contamination of sulphur from the baths.

4. Conclusions

Based on the data presented in this paper, a hydrometallurgical process for zinc recovery, by electrowinning, from real sulphate leach liquors, is suggested. The process comprises of several stages. The conclusions from the testwork for each stage are the following:

(1) Iron was precipitated by 99.9% at 95 °C, as easily filterable crystalline basic sulphate salt of the jarosite type. Zinc losses in the precipitate reached 5%.
(2) Zinc was extracted by bis(2,4,4-trimethylpentyl) phosphinic acid. Cyanex 272, diluted in Kerosene with 5% TBP, could extract Zn, at pH 3.5, $T = 40$ °C and extractant concentration = 25%.
(3) The loaded with zinc Cyanex 272 was stripped with zinc spent electrolyte in order to produce a solution suitable for zinc electrowinning. Zinc spent electrolyte solution (3 mol/L H_2SO_4 and 62.5 g/L Zn^{2+}) could recover zinc at $T = 40$ °C and phase ratio O/A = 2.
(4) Zinc electrowinning was carried out at constant current density of 500 A/m^2, using aluminium as cathode and Pb as anode, while the electrolyte contained 80.37 g/L of Zn^{2+}. The preferred orientations of the produced zinc grains were (0 0 2), (1 0 1) and (1 0 3). Their surface morphology consisted of hexagonal zinc plate-like crystals, whose facets appeared to be rough and textured.

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