Zinc recovery from sulphate electrolytes, containing copper and ferrous ions

G. Hodjaoglu, I. Ivanov*

Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad.G.Bonchev St., Building11, 1113 Sofia, Bulgaria

The influence of copper and ferrous ions on zinc recovery from sulphate electrolytes is investigated. It is found, using cyclic voltammetry that simultaneous deposition of Zn and Cu begins at a potential (*vs.* SSE) of -1.450 V. Simultaneous deposition of Zn, Fe, and Cu begins at a potential of -1.500 V. Deposition of Cu solely, takes place at more positive potentials. The presence of Cu^{2+} and Fe^{2+} ions results in Zn redissolution, decreasing the current efficiency of Zn electroextraction. Zn deposit, which contains 2.4 wt.% Cu and 0.25 wt.% Fe, is obtained upon 60 min deposition at -1.600 V in an electrolyte containing $Zn^{2+} - 50$ g/L, $H_2SO_4 - 130$g/L, $Cu^{2+} - 200$ mg/L, and $Fe^{2+} - 200$ mg/L .

Keywords: copper; deposition; iron; potentiodynamic scan; zinc electrowinning; zinc recovery.

1. INTRODUCTION

A major problem during the Zn electrowinning from waste streams is the harmful effect exerted by metallic impurities such as Ni, Co, Fe, Cu, Cd, Sb, Ge, Bi, etc. By advanced purification of the electrolyte, the concentration of metallic ions is decreased below limit, where their harmful effects are no longer present. Another possibility is the addition of various organic and inorganic substances to the electrolyte in order to improve the deposit structure and to inhibit the discharge of H^+ or the Zn redissolution process, and thus to increase the current efficiency.

Stender et al. [1–2] established that the Cu^{2+} (100 mg/L) decrease the potential of the Zn cathode with 50 mV (at 5 A/dm²) and the current efficiency of hydrogen evolution increases with the increase in the Cu^{2+} concentration. Because of the small overvoltage of Cu deposition on Zn, the Cu deposits on the cathode, forming numerous galvanic micropairs of intermetallic Zn–Cu compounds and the Zn cathode dissolves as a result of their action. According to Turomshina and Stender [3, 4], Cu and Fe, codeposited with Zn, act as microanodes or microcathodes in the galvanic micropairs, depending on the geometric configuration of the deposit. Thus, a small amount of Fe is able to intensify the harmful action of the noble Cu. The experiments show that such effect is observed only at increased temperatures because at a lower temperature, Fe is in passive state and acts

as a microcathode in the galvanic micropairs. As a result, the total effect of Cu and Fe on the Zn electroextraction is a sum of their partial effects. Maja et al. [5, 6] found that in the presence of 100 mg/L Cu^{2+} the current efficiency of Zn decreases from 90% to 0% after 4 h electroextraction at 60 mA/cm² and 40°C. According to Ault and Frazer [7] 5 mg/L Cu^{2+} decrease the current efficiency from 97.5 to 96.7 %. MacKinnon [8] and MacKinnon et al. [9] established that a significant difference between the cyclic voltammograms for the addition-free and Cu^{2+}-containing (1 and 5 mg/L) electrolytes is the potential at which the descending branch crosses the zero-current axis (crossover potential). The crossover potential occurs at or near the reversible potential of the system so that any departure is generally caused by impurity currents, side reactions such as H_2 evolution or perhaps the dissolution of a Zn-Cu alloy phase. Analysis of the coatings confirms that Cu co-deposits with Zn. At the higher (5 mg/L) Cu^{2+} concentration the voltammogram is characterized by higher current in the potential region prior to Zn deposition. At this concentration, Cu strongly depolarizes the Zn deposition reaction because the decomposition potential for Zn occurs at a less negative cathode potential compared to the Cu^{2+}-free electrolyte. The reverse scan is characterized by an increasing cathodic current that occurs after the anodic peak for Zn dissolution. Muresan et al. studied the influence of metallic impurities and the effect of additives on Zn electrowinning from sulphate electrolytes and from industrial waste product, known as the 'blue-powder', containing: Zn (25–45%), Pb (20–25%),

*To whom all correspondence should be sent:
E-mail: isivanov@ipc.bas.bg

Fe (3–5%), Cu (0.5–1%), Cd (0.5–1%), Sb (0.05–0.1%), and Bi (0.03%). They found that $Al_2(SO_4)_3$, animal glue or horse-chestnut extract (HCE) added in the electrolyte increase the cathodic polarisation and promote levelling. HCE has a beneficial influence on the deposit quality, being a good levelling agent. Aluminium sulphate influences the reduction of Zn^{2+}, increasing the nucleation overpotential and the deposition rate of Zn on the cathode. The conjoint use of the studied additives results in more uniform, slightly bright deposits [10]. They established also that the presence of Cu^{2+} leads to an acceleration of the cathodic process. Copper is deposited before Zn, as indicated by the appearance of a cathodic peak at about –0.4 V vs. SCE. The height of the peak increases with Cu^{2+} concentration in the electrolyte. The corrosion potential of Zn in a Cu-containing electrolyte is more positive than in an electrolyte without the impurity and a second anodic peak, corresponding to Cu dissolution can be observed in the positive potential region during the reverse scan. The cathodic deposit, obtained in the presence of Cu^{2+} ions, is non-adherent with the substrate, and consists of porous microspheres [11].

There are numerous papers concerning the influence of the Cu^{2+} and Fe^{2+} ions on the process of Zn electroextraction such as Znamenskiy, Kardashevskiy and Stender [12]; Kiryakov [13]; Kiryakov and Baynietova [14]; Sheka and Karlisheva [15]; Jurin and Pyunnenen [16]; Pahomova [17]; Jurin and Hafsi Azdin [18]; Pomosov, Krimakova and Levin [19]; Wever [20]; Akiyama, Fukushima and Higashi [21]; Ohyama and Morioka [22]. However, the simultaneous action of Cu^{2+} and Fe^{2+} ions is not well studied.

The aim of this study is to establish the influence of Cu^{2+} ions and the common action of the Cu^{2+} and Fe^{2+} ions on the Zn electroextraction, as well as the possibility of separate deposition of Zn, Cu or Fe.

2. EXPERIMENTAL

The experiments were carried out in a thermostated (37 ± 1ºC), three-electrode glass cell without stirring of the electrolyte. The cathode was of Al, containing 0.2% Fe, manufactured by the Riedel de Haen (RdH-Al) with an effective area of 1.0 cm². It was placed vertical and parallel to the symmetry axis of the cell. Both counter anodes were Pt plates of 8.0 cm² total area. The reference electrode (SSE) consisted of a mercury/mercurous sulphate electrode in 0.5 M H_2SO_4 (SSE), its potential being +0.655 V (NHE).

The studies were carried out using a cyclic potentiodynamic technique. Potential scanning at a rate of 10 mV/s was performed with an EP 20A Elpan potentiostat (equipped with an IR compensator) and an EG 20 Elpan scanner. The cyclic voltammograms (CVAGs), were carried out in the range of 0.000 V to –1.650 V, and were recorded by Endim 622.01 X–Y chart recorder.

The composition of the base electrolyte (BE) was: 130 g/L H_2SO_4, and 220 g/L $ZnSO_4.7H_2O$ (50 g/L Zn^{2+}). Cu^{2+} ions were added in the form of $CuSO_4.5H_2O$ to the base electrolyte in concentrations of 50, 100, and 200 mg/L . Fe^{2+} ions were added as $FeSO_4.5H_2O$ to the electrolyte in concentrations of 50, 100, and 200 mg/L.

The quantity of electricity (q – in Coulombs), required for the dissolution of Zn or Cu, deposited during the cathodic process, was determinated by graphical integration of the respective anodic peak on the CVAG. The deposition of Zn was carried out at a potential of -1.600 V vs. SSE, and of Cu at potentials between –1.010 V and –1.470 V vs. SSE.

2. RESULTS AND DISCUSSION

### 2.1. Separate deposition of zinc and copper
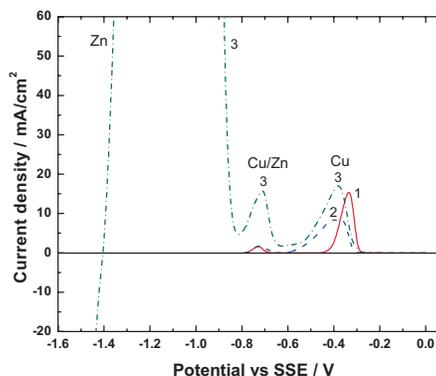
Figure 1. Anodic peaks of dissolution of Cu layers, deposited in an electrolyte, containing Zn^{2+} - 50 g/L, H_2SO_4-130 g/L and Cu^{2+} - 50 mg/L on an Al cathode at potentials (vs. SSE): 1) -1.330 V, 2) -1.430 V, 3) -1.470 V. Time of deposition - 15 min. Scan rate - 10 mV/s.

Figure 1 shows the anodic peaks of dissolution of Cu layers, deposited for 15 min in the base electrolyte, containing 50 mg/L Cu^{2+} at potentials of –1.330 V (curve 1), –1.430 V (curve 2), and –1.470 V (curve 3). A little peak at –0.725 V and large peaks at potentials (vs. SSE) between -0.300 and -0.400 V are observed on the curves 1 and 2. The more negative peak (2–7 mA) is, perhaps, a peak of dissolution of an alloy Zn-Cu phase. The more

positive peaks at potentials (*vs.* NHE) between +0.255 V and +0.355 V are close to the reversible potential of oxidation of Cu to Cu^{2+} (+0.337 V *vs.* NHE). In all cases the cathodic Cu deposits are non-adherent with the substrate, and are easily wiped and rinsed with water. The simultaneous deposition of Zn and Cu begins at a potential of -1.450 V (*vs.* SSE). Zn dissolution peak appears after deposition at more negative (-1.470 V) potential, and is much larger than the peaks of Cu dissolution (curve 3). The peak of Zn-Cu alloy dissolution is much higher (20 mA) than the peaks, obtained at the lower cathodic potentials because of the larger alloy amount.
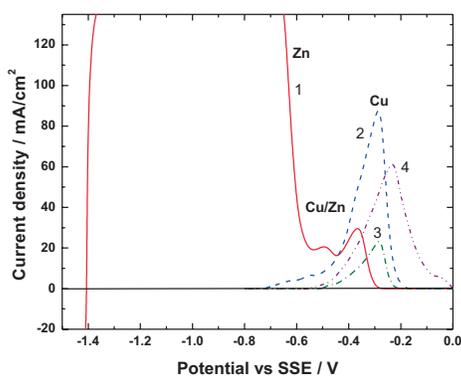

Figure 2. Anodic peaks of dissolution of Cu and Zn deposits. Scan rate - 10 mV/s. Deposition potential (*vs.* SSE): -1.470 V. Time of deposition - 30 min. 1) Zn^{2+} - 50 g/L, H_2SO_4-130 g/L and Cu^{2+}-100 mg/L, 2) Zn^{2+}-50 g/L, H_2SO_4-130 g/L, Cu^{2+}-100 mg/L and Fe^{2+}-50 mg/L, 3) Zn^{2+}-50 g/L, H_2SO_4-130 g/L, Cu^{2+}-100 mg/L and Fe^{2+}-100 mg/L, 4) Zn^{2+}-50 g/L, H_2SO_4-130 g/L, Cu^{2+}-200 mg/L and Fe^{2+}-200 mg/L.

Figure 2 shows the anodic peaks of dissolution of coatings, deposited for 30 minutes at a potential of –1.470 V. Only one peak at potentials between -0.200 and -0.400 V *vs.* SSE (+0.455 and +0.255 V *vs.* NHE) is observed on the curves, obtained in the presence of both, Cu^{2+} and Fe^{2+} ions in the base electrolyte (curves 2, 3 and 4) which is close to the reversible potential of the oxidation of Cu to Cu^{2+} (+0.337 V *vs.* NHE). In all cases this peak is higher and appears at more positive potentials than the peak obtained in the presence of only Cu^{2+} ions in the base electrolyte (curve 1). The more negative peak at -0.500 (curve 1) observed in the presence of Cu^{2+} only (and due to the dissolution of Zn–Cu phase) is absent in the presence of both, the Cu^{2+} and Fe^{2+} ions (curves 2, 3 and 4). Peaks of Fe dissolution are not observed in all cases. Obviously, the potential of Fe dissolution is very close to the

potential of Zn dissolution. Because the reversible potential of Fe dissolution to Fe^{2+} is –1.100 V *vs.* SSE (- 0.440 V *vs.* NHE), it can be supposed that at this potential the H_2 evolution takes place. Zn dissolution is taking place at this potential, too (Figure 1). Thus, the anodic peak of the Fe dissolution is masked by the cathodic peak of the H_2 evolution or by the anodic peak of Zn dissolution. The deposition of Zn in the presence solely of Cu^{2+} begins at a potential of –1.450 V, and in the presence of both, Cu^{2+} and Fe^{2+}, at –1.500 V. For this reason, the peak of Zn dissolution appears only on the curve, obtained at –1.470 V in the presence solely of Cu^{2+} (curve 1).

2.2. Influence of Cu^{2+} and Fe^{2+} ions on zinc deposition

Figure 3 shows the current efficiency of Zn (CEZn) deposition in the presence of Cu^{2+} and Fe^{2+} as a function of time. The current efficiency is 2% smaller (in the presence of 50 mg/L Cu^{2+}), and about 20% smaller (in the presence of 100 mg/L
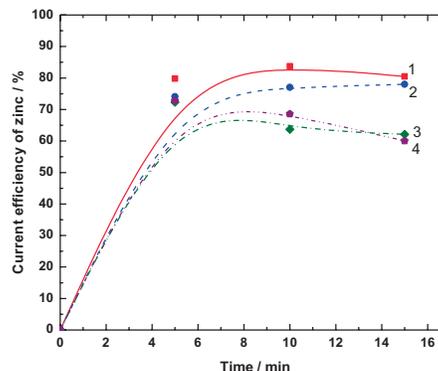

Figure 3. Current efficiency of Zn deposition at potential (*vs.* SSE): -1.600 V as a function of time: 1) Zn^{2+}-50 g/L and H_2SO_4-130 g/L, 2) Zn^{2+}-50 g/L, H_2SO_4- 130 g/L and Cu^{2+}-50 mg/L, 3) Zn^{2+}-50 g/L, H_2SO_4-130 g/L and Cu^{2+}-100 mg/L, 4) Zn^{2+}-50 g/L, H_2SO_4-130 g/L, Cu^{2+}-100 mg/L and Fe^{2+}-100 mg/L.

Cu^{2+}, and 100 mg/L Cu^{2+} and 100 mg/L Fe^{2+} simultaneously) than the CEZn obtained during deposition in the base electrolyte.

Copper content in the Zn coatings, obtained after one hour deposition at –1.600 V, is 1.75 wt.% (in the presence of 50 mg/L Cu^{2+}) and 2.70 wt.% (in the presence of 100 mg/L Cu^{2+}). The impurity content in the coatings, obtained from the electrolyte containing 100 mg/L Cu^{2+} and 100 mg/L Fe^{2+}, is 2.5 wt.% Cu and 0.1 wt.% Fe. The impurity content from electrolyte, containing 200 mg/L Cu^{2+} and 200 mg/L Fe^{2+}, is 2.4 wt.% Cu and 0.25 wt.%

Fe. In all cases the deposits of Zn are mat, grey in color, rough, and with dendrites on the edges.
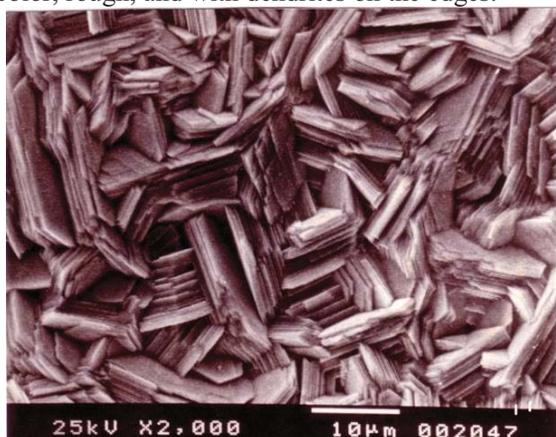
Figure 4. SEM micrograph of pure Zn. Deposition potential (*vs*. SSE): -1.600 V. Deposition time - 60 min.
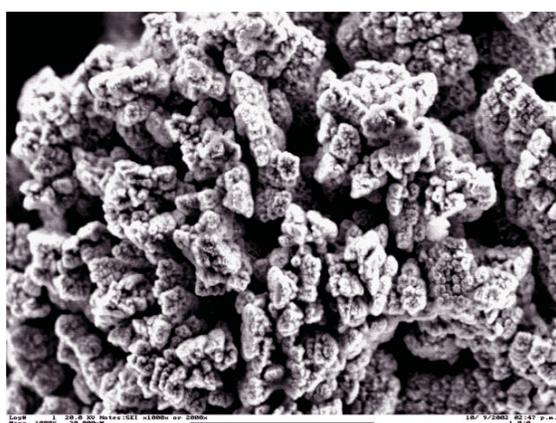
Figure 5. SEM micrograph of Zn, containing 2.4 wt.% Cu and 0.25 wt.% Fe. Electrolyte: Zn^{2+} - 50 g/L, H_2SO_4 – 130 g/L, Cu^{2+} - 200 mg/L and Fe^{2+} - 200 mg/L. Deposition potential (*vs*. SSE): -1.600 V. Deposition time - 60 min.

Figures 4 and 5 show SEM micrographs of Zn deposits, obtained in pure (base) electrolyte (Figure 4) and in an electrolyte, containing 200 mg/L Cu^{2+} and 200 mg/L Fe^{2+} (Figure 5). It can be seen that Cu (2.4 wt.%) and Fe (0.25 wt.%) change the Zn morphology and that dissolution takes place at the edges of the crystal grains.

CONCLUSIONS

1. Simultaneous deposition of Zn and Cu begins at a potential of -1.450 V (vs. SSE).

2. Simultaneous deposition of Zn, Fe, and Cu begins at a potential of -1.500 V *vs*. SSE. At potentials more positive than -1.500 V *vs*. SSE, deposition of Cu solely, takes place.

3. The current efficiency of Zn deposition decreases with the time due to the Zn redissolution which takes place in the presence of Cu^{2+} and Fe^{2+} ions. This process is a result of occurrence of Zn/Cu and Zn/Fe galvanic microelements, formed during simultaneous deposition of Zn, Cu, and Fe. Zn dissolves because it is more electronegative element than Cu and Fe.

4. Copper and iron, codeposited with zinc, change the deposit morphology and deteriorate the quality of the zinc produced.

REFERENCES

1. A.G. Pecherskaya, V.V. Stender, *J. Appl. Chem.* (in Russian), **23**, 920 (1950).
2. V.V. Stender, A.G. Pecherskaya, *Non-Ferous metals* (in Russian), **4**, 45 (1950).
3. U.F. Turomshina, V.V. Stender, *J. Appl. Chem.* (in Russian), **28**, 372 (1955).
4. U.F. Turomshina, V.V. Stender, *J. Appl. Chem.* (in Russian), **28 (5)**, 467 (1955).
5. M. Maya, N. Penazzi, R. Fratesi, G. Roventi, *J. Electrochem. Soc.,* **129**, 2695 (1982).
6. M. Maya, N. Penazzi, R. Fratesi, G. Roventi, *Oberfläche-Surfaces,* **24**, 234 (1983).
7. A.R. Ault, E.J. Frazer, *J. Appl. Electrochem.,* **18**, 583 (1988).
8. D.J. MacKinnon, *J. Appl. Electrochem.,* **15**, 953 (1985).
9. D.J. MacKinnon, J.M. Brannen, P.L. Fenn, *J. Appl. Electrochem.*, **17**, 1129 (1987).
10. L. Muresan, G. Maurin, L. Oniciu, S. Avram, *Hydrometallurgy,* **40**, 335 (1996).
11. L. Muresan, G. Maurin, L. Oniciu, D. Gaga, *Hydrometallurgy*, **43**, 345 (1996).
12. G.N. Znamenskiy, V.V. Kardashevskiy, V.V. Stender, *J. Appl. Chem.*(in Russian), **34 (6)**, (1961).
13. G.Z. Kiryakov, *J. Phys. Chem.* (in Russian), **32 (11)**, 2561 (1958).
14. G.Z. Kiryakov, F.K. Baynietova, *Akad. Nauk. Kazah. SSR, Trudi Inst. Chim. Nauk* (in Russian), **3**, 64 (1958).
15. Z.A. Sheka, K.F. Karlisheva, *Dokladi Akad. Nauk SSSR*, **108 (1)**, 126 (1956).
16. A.I. Jurin, S.P. Pyunnenen, *Trudi Lenin-gradskogo Politehn. Inst.* (in Russian), **188**, 204 (1957).
17. G.N. Pahomova, *Non-Ferous metals* (in Russian), **9**, 33 (1965).
18. A.I. Jurin, H. Azdin, *J. Appl. Chem.* (in Russian), **52 (8)**, 1763 (1979).
19. A.V. Pomosov, E.E. Krimakova, A.I. Levin, *J. Appl. Chem.* (in Russian), **31 (5)**, 734 (1958).
20. G.T. Wever, *J. of Metals*, **11**, 130 (1959).
21. T. Akiyama, H. Fukushima, K. Higashi, Proc. Intern. Simp. on Extractive Metallurgy of Zinc, Tokyo, Japan, Chapter **9**, 141 (1985).
22. S. Ohyama, S. Morioka, 1985. Proc. Intern. Simp. on Extractive Metallurgy of Zinc, Tokyo, Japan, Chapter **14**, 219 (1985).

ИЗВЛИЧАНЕ НА ЦИНК ОТ СУЛФАТНИ ЕЛЕКТРОЛИТИ, СЪДЪРЖАЩИ МЕДНИ И ФЕРОЙОНИ

Г. Ходжаоглу, Ив. Иванов

Институт по физикохимия, Българска академия на науките,ул. „Акад. Г. Бончев", бл. 11, 1113 София, България

(Резюме)

Изследвано е влиянието на медните и феройоните върху извличането на цинк от сулфатни електролити. С използването на циклична волтамперометрия е установено, че едновременното отлагане на Zn и Cu започва при потенциал -1.450 V (спрямо SSE). Едновременното отлагане на Zn, Fe и Cu започва при потенциал -1.500 V. При по-положителни потенциали се отлага само Cu. В резултат на наличието на Cu^{2+} и Fe^{2+} йони протича процес на обратно разтваряне на отложения Zn, което понижава добива му по ток. Отлагането в продължение на 60 мин. при -1.600 V в електролит, съдържащ Zn^{2+} - 50 g/L, H_2SO_4 – 130 g/L, Cu^{2+} - 200 mg/L и Fe^{2+} - 200 mg/L води до получаването на Zn покритие, съдържащо 2.4 тегл.% Cu и 0.25 тегл.% Fe.