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Electrowinning of zinc from ammoniacal leach solutions obtained from carbonate-containing smithsonite ore

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Abstract: Zinc electrowinning from ammoniacal pregnant leach solution obtained by selective alkaline leaching of carbonate-containing smithsonite ore from Yahyalı, Kayseri, Türkiye, was investigated under additive-free conditions and in the presence of polyethylene glycol 2000 (PEG 2000), thiourea, and their combined addition. Under additive-free conditions, current efficiency reached a maximum of 86.4% at 400 A/m^2, then decreased at higher current densities due to dendritic growth at cathode edges and increased hydrogen evolution. Individual additions of 1 g/dm^3 PEG 2000 and 100 mg/dm^3 thiourea as organic additives improved deposit morphology and current efficiency but were insufficient to suppress dendritic growth at elevated current densities. The combined addition of 1 g/dm^3 PEG 2000 and 100 mg/dm^3 thiourea at 100 A/m^2 for 2 hours effectively suppressed dendritic growth and produced compact, uniform zinc deposits with a fine nodular structure, yielding a maximum current efficiency of ~95% and the lowest specific energy consumption of ~5.0 kWh/kg among the additive-containing conditions investigated. EDS analysis showed a zinc content of 91.11 wt% in the combined additive system, the highest among the conditions investigated, while XRD analysis showed reduced secondary phase intensities compared with additive-free and single-additive conditions. PLS composition was estimated from an XRF-derived mass balance rather than directly measured; the reported current efficiencies are apparent gravimetric values; and a complete Zn mass balance for the electrowinning stage was not established. These results demonstrate the potential of the combined PEG 2000 and thiourea additive system for zinc electrowinning from ammoniacal leach solutions derived from smithsonite ores.

Keywords: zinc electrowinning, smithsonite, ammoniacal leaching, organic additives, combined additive effect, current efficiency

1. Introduction

Zinc is the fourth-most-important non-ferrous metal in terms of global usage, after aluminum and copper, and more than 13 million tonnes of refined zinc are produced annually from ores, concentrates, and recycled materials (ILZSG, 2024). The primary application of zinc is galvanizing, which protects steel by enhancing the durability and service life of construction, transportation, and consumer products. Zinc is also widely used in copper alloying to produce brass, in aluminum-zinc die-casting alloys, in the production of rolled zinc sheets, and as a chemical component in rubber, fertilizers, and personal care products (Van Genderen et al., 2016).

The industry relies on two main zinc resources: zinc sulfide ores, which are easily separated from gangue minerals by flotation but are becoming increasingly depleted, and low-grade, non-sulfide zinc oxide ores. Non-sulfide zinc ores are primarily composed of economically significant minerals, including smithsonite, hemimorphite, hydrozincite, willemite, and sauconite. However, the generally low grades and complex mineralogical structures of these ores hinder efficient utilization, and leaching

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has therefore been adopted as a practical method for zinc extraction (Ehsani et al., 2021). While sulfuric acid leaching can extract zinc from oxide ores, it requires high acid consumption and complex purification steps. More recently, alkaline leaching systems using sodium hydroxide and ammonia solutions have proven efficient and selective for leaching zinc from oxide ores, including smithsonite, demonstrating greater selectivity than acidic alternatives (Frenay, 1985; Zhang et al., 2014; Ehsani et al., 2019; Ehsani et al., 2021). Additionally, energy consumption during electrowinning from alkaline solutions is reported to be lower than in conventional acidic systems (Ehsani et al., 2019).

Electrowinning is a major method for zinc production, accounting for about 80% of global zinc output. Most industrial operations use the acidic sulfate process, which has been extensively studied. However, the zinc industry continues to investigate alternative technologies to reduce capital investment and improve energy efficiency. Among these, electrowinning of metallic zinc from alkaline and ammoniacal solutions has attracted significant research attention (St-Pierre and Piron, 1986; St-Pierre and Piron, 1990). The effects of different parameters, including solution concentration, current density, temperature, cathode material, and impurities, on current efficiency and cell voltage have been investigated to minimize energy consumption in alkaline zinc electrowinning systems (St-Pierre and Piron, 1990; Afifi et al., 1991; Saba and Elsherief, 2000; Viswanath and George, 2011; Jiang et al., 2022).

Organic additives in zinc electrowinning, including quaternary ammonium salts, polymers, and surfactants, act as hydrogen evolution inhibitors and crystal growth modifiers, improving deposit smoothness, compactness, and current efficiency while mitigating the adverse effects of impurities (Sorour et al., 2017). In ammoniacal zinc electrowinning systems specifically, combinations of gelatin with polyoxyethylene ether or PEG-based additives have been shown to suppress dendritic growth, refine grain structure, and maintain high current efficiencies of approximately 95–99%, enabling smooth and compact deposits at low specific energy consumption (Gu et al., 2018; Zhao et al., 2021; Duan et al., 2023). Ammoniacal systems are particularly promising for processing low-grade oxide ores and ores with basic gangue minerals, as they avoid the high acid consumption and costly purification steps associated with conventional acidic electrowinning, and allow direct coupling of leaching with electrowinning of zinc from ammonia leachates (Gürmen and Emre, 2003; Duan et al., 2023). Researchers have also investigated alternative non-aqueous electrolyte systems, such as deep eutectic solvents based on urea/choline chloride ionic liquids, for zinc electrodeposition from zinc oxide, confirming Zn-rich deposit formation via instantaneous nucleation and diffusion-controlled growth mechanisms (Yang and Reddy, 2014; Yang and Reddy, 2015). Despite these advances, the combined effects of polyethylene glycol (PEG 2000) and thiourea on zinc electrowinning from ammoniacal leach solutions derived from smithsonite ore have not been systematically investigated.

In this study, zinc was leached from smithsonite ore from Yahyalı, Kayseri, Türkiye, using ammoniacal leaching, and metallic zinc was recovered from the resulting pregnant leach solution by electrowinning. The study systematically investigated the effects of PEG 2000 concentration, thiourea addition, and their combined addition on deposit phase composition, surface morphology, elemental content, current efficiency, and specific energy consumption. The study aimed to determine optimum conditions, including additive type, concentration, and current density, to maximize current efficiency and minimize energy consumption. The combination of ammonia-based leaching and organic additive-assisted electrowinning provides an effective, energy-efficient route to recover zinc as Zn-rich deposits from local smithsonite ores, contributing to the broader development of alternative hydrometallurgical processes for non-sulfide zinc resources.

2. Materials and methods

2.1. Materials

In this study, zinc-containing carbonate (i.e., smithsonite) ore from Yahyalı, Kayseri, Türkiye, was used. The ore was crushed to -3.36 mm using a jaw crusher, ground in a ball mill, and sieved to obtain particles smaller than 355 μm. A representative sample was then selected from the prepared material for further analysis. Table 1 presents the chemical composition of the ore sample determined by XRF. Besides zinc, the ore contains notable amounts of iron and silica as major constituents, along with minor concentrations of lead and cadmium, which may influence the leaching selectivity and electrowinning

performance. The moisture content and loss on ignition (LOI) of the ore sample were 1.1% and 28.5%, respectively, determined at 105 °C for 2 hours and 1000 °C for 20 min. The high LOI value agrees with the carbonate nature of smithsonite, reflecting significant CO_2 release upon thermal decomposition. The mineralogical composition of the ore was characterized by X-ray diffraction (XRD) and reported in detail elsewhere (Ehsani et al., in press).

Table 1. Chemical composition of the smithsonite ore sample determined by XRF

Compound	ZnO	Fe_2O_3	SiO_2	Al_2O_3	PbO	Cd	C	S
%	21.2	11.7	18.2	9.87	0.51	0.07	5	0.04

Ammonium hydroxide solution (25% NH_4OH, TEKKİM) and deionized water were used as leaching reagents. Polyethylene glycol 2000 (PEG 2000, Merck), polyethylene glycol 400 (PEG 400, ZAG), and thiourea (ZAG) were used as organic additives in the electrowinning experiments. All leaching and electrowinning experiments were conducted in borosilicate glass beakers with magnetic stirring.

2.2. Methods

2.2.1. Leaching experiments

A preliminary ammoniacal leaching step was performed to produce the pregnant leach solution (PLS) used for zinc electrowinning. Leaching was carried out in a borosilicate glass beaker using a magnetic stirrer at 600 rpm, maintained at ambient temperature (approximately 25 °C). Based on the findings reported by Ehsani et al. (2021) and Ehsani et al. (in press), the ammonia concentration and solid-to-liquid ratio were fixed at 6 mol/dm^3 NH_3 and 0.15 g/cm^3, respectively.

For each test, 60 g of the ore sample was added to 400 cm^3 of ammoniacal solution and leached for 120 min under continuous agitation. After leaching, the slurry was separated by gravity filtration using qualitative filter paper, and the resulting PLS was collected for use as the electrolyte in the electrowinning studies.

The dissolution of smithsonite in aqueous ammonia solution proceeds through the selective complexation of zinc with ammonia molecules, forming soluble tetrammine zinc complex ions according to Eq. (1) (Ehsani et al., 2021):

$$ZnCO_3 + 4NH_3 \leftrightarrow Zn(NH_3)_4^{2+} + CO_3^{2-} \quad (1)$$

The selectivity of ammonia leaching for zinc over the dominant gangue minerals, goethite and calcite, in the smithsonite ore is attributed to ammonia's strong complexation with zinc ions, which stabilizes dissolved zinc as the tetrammine complex in alkaline solution. The cadmium present in the ore also dissolves under these conditions due to the similar chemical behavior of cadmium and zinc in ammoniacal solutions (Ehsani et al., 2021), resulting in a pregnant leach solution containing both $Zn(NH_3)_4^{2+}$ and $Cd(NH_3)_4^{2+}$ complex ions, which subsequently co-deposit during electrowinning.

The Zn and Cd contents of the initial ore and the corresponding leaching residue were determined by XRF, and the dissolution efficiencies were calculated from the difference between the initial and residual Zn and Cd contents. Zn and Cd dissolution efficiencies of 56.3% and 50.6%, respectively, were obtained under these conditions. Based on this XRF-derived mass balance, the PLS contained approximately 14.4 g/dm^3 Zn and 53 mg/dm^3 Cd. The PLS obtained under these conditions was directly used as the electrolyte in the subsequent electrowinning experiments. The relatively high Zn/Cd concentration ratio in the PLS indicates that zinc was the dominant electroactive species during electrowinning. In contrast, cadmium was present as a minor impurity capable of partial co-deposition under cathodic polarization conditions.

2.2.2. Electrowinning experiments

Zinc electrowinning experiments were carried out using an adjustable DC power supply (UNI-T UTP3315TFL-II, 30 V, 5 A). All experiments were performed in a borosilicate glass beaker containing 200 cm^3 of PLS as the electrolyte, maintained at ambient temperature (approximately 25 °C). The electrolyte pH was measured using pH test strips immediately before (pH 12) and after each

electrowinning experiment (pH 11–12) to monitor pH changes during electrolysis. This relatively limited change can be attributed to the buffering behavior of the NH_3/NH_4^+ system, which maintains the alkaline conditions through the equilibrium between ammonia and ammonium ions. In particular, hydrogen evolution and zinc deposition at the cathode, together with oxygen evolution at the anode, can alter the local and bulk acid–base balance of the electrolyte. Nevertheless, the electrolyte remained strongly alkaline throughout all electrowinning experiments.

A 316-grade stainless-steel plate with dimensions of 2 cm × 2 cm × 2 mm was used as the cathode, and a mixed-metal oxide (MMO) coated electrode was used as the anode. The rear surface and edges of the cathode were not masked during electrowinning, and the active cathode area of 9.2 cm^2 represents the total submerged surface area including both faces and three edges (bottom and two sides), with the top edge excluded as it was connected to the power supply. The inter-electrode distance was fixed at 2 cm throughout all experiments. The electrolyte was stirred throughout all electrowinning experiments using a magnetic stirrer at approximately 150 rpm.

Prior to each experiment, the stainless-steel cathode was sequentially polished using SiC abrasive papers with grit sizes of 120, 240, 400, 800, and 1200, then cleaned with distilled water and acetone. After electrowinning, the zinc deposits were carefully rinsed with distilled water without stripping from the substrate using a funnel with filter paper, then dried in an oven at 60 °C with the filter paper and weighed to include any zinc particles collected during washing in the final deposit mass. Under additive-free and single-additive conditions at elevated current densities, dendritic zinc formations detached from the cathode surface upon switching off the power supply and were collected by filtering the electrolyte solution through filter paper, drying, and including their mass in the total deposit mass to ensure accurate gravimetric determination of ΔW. Under the combined additive condition, no dendritic formation was observed even after 4 hours of electrowinning, and filtration of the electrolyte was not necessary. All electrowinning experiments were conducted in duplicate, and results are presented as mean values.

Additive-free electrowinning experiments were conducted at current densities ranging from 100 to 1000 A/m^2 for 1 hour. Subsequently, organic additives were introduced to the PLS to investigate their effects on deposit morphology and electrowinning efficiency. PEG 2000 was added at concentrations of 0.5, 1, and 2 g/dm^3, while thiourea was used at 100 mg/dm^3, each tested over the same current density range for 1 hour. Finally, combined addition experiments were performed by first adding thiourea at 100 mg/dm^3. Then, 1 g/dm^3 PEG 2000 was introduced. This combination of 1 g/dm^3 PEG 2000 and 100 mg/dm^3 thiourea was then tested at a current density of 100 A/m^2 for electrowinning durations of 1, 2, and 4 hours.

In the ammoniacal PLS at pH 11–12, zinc exists predominantly as the tetrammine zinc complex, $Zn(NH_3)_4^{2+}$. The electrowinning process involves the cathodic reduction of these zinc-ammine complexes and the competing hydrogen evolution reaction at the cathode, as well as oxygen evolution at the MMO anode, according to the following reactions (Gu et al., 2018; Ehsani et al., 2021):

$$Zn(NH_3)_4^{2+} + 2e^- \rightarrow Zn + 4NH_3 \quad (2)$$

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad (3)$$

$$4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^- \quad (4)$$

The mass of zinc deposited (ΔW) was determined gravimetrically as the difference between the final (W_f) and initial (W_i) masses of the cathode ($\Delta W = W_f - W_i$). The theoretical mass deposited (W_t), current efficiency (CE), and specific energy consumption (EC) were calculated according to Faraday's First and Second Laws of Electrolysis, Eqs. (5)– (7):

$$W_t = \frac{I\,t\,M}{nF} \quad (5)$$

$$CE = \frac{\Delta W}{W_t} \times 100 \quad (6)$$

$$EC = \frac{VIt}{\Delta W} \quad (7)$$

where ΔW is the experimentally measured mass of zinc deposited (i.e., gravimetric cathode mass gain) (g), W_f and W_i are the final and initial cathode masses (g), respectively, W_t is the theoretical mass of zinc deposited calculated according to Faraday's law (g), I is the applied current (A), t is the electrowinning time in Eq. (5) expressed in seconds (s) and in Eq. (7) expressed in hours (h), M is the molar mass of zinc

(65.38 g/mol), n is the number of electrons transferred per zinc ion (n = 2), F is Faraday's constant (96,500 C/mol), V is the average cell voltage (V), and EC is expressed in Wh/g, which is numerically equivalent to kWh/kg.

The current efficiency values reported in this work were calculated from the total gravimetric cathode weight gain. Because the deposits contained minor amounts of Cd and oxygen-containing species, the calculated values should be interpreted as gravimetric (apparent) current efficiencies rather than Zn-specific current efficiencies.

2.2.3. Characterization

The chemical composition of the ore sample was determined by X-ray fluorescence (XRF; Rigaku ZSX Primus II). The phase composition of the zinc deposits obtained on the stainless-steel cathodes was analyzed by X-ray diffraction (XRD; Rigaku MiniFlex 600, Cu Kα radiation, λ=1.5406 Å). Diffraction patterns were collected over a 2θ range of 20°–90° at a scanning rate of 2° min^{-1}. The surface morphology and elemental composition of the zinc deposits were examined using field-emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (FE-SEM/EDS; FEI Quanta 650 FEG).

3. Results and discussion

3.1. Surface characterization

3.1.1. XRD analysis

The XRD patterns of zinc deposits obtained under additive-free conditions and in the presence of PEG 2000, thiourea, and their combined addition are presented in Fig. 1. It can be seen from Fig. 1 that the diffraction patterns that the additive-free and additive-containing electrowon deposits are similar in terms of the phases. Zinc (Zn) is the dominant phase, indicated by the characteristic reflections at 2θ ≈ 36.3°, 38.9°, 43.1°, 54.3°, 70.0°, 74.5°, 82.0°, and 86.4°, consistent with the hexagonal close-packed crystal structure of zinc (COD 9011599; COD 9008522; COD 9012435) in all electrowinning conditions. However, the relative peak intensities differ depending on the additive introduced.

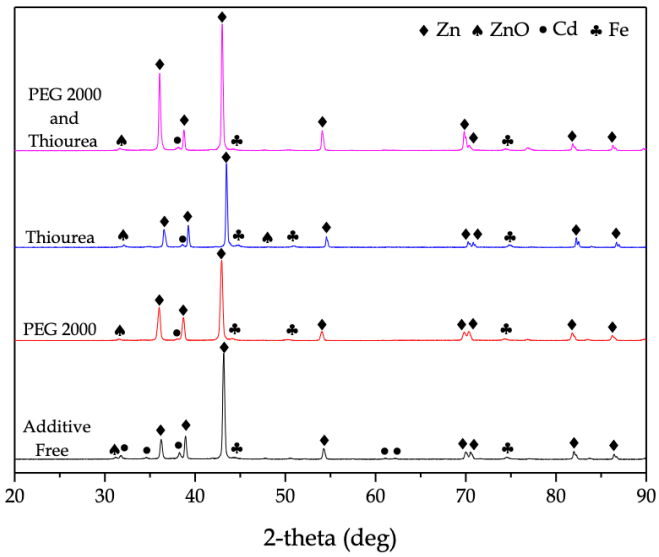

Fig. 1. XRD patterns of zinc deposits obtained by electrowinning under different conditions: additive-free at 100 A/m^2, 1 g/dm^3 PEG 2000 at 200 A/m^2, 100 mg/dm^3 thiourea at 100 A/m^2, and combined addition of 1 g/dm^3 PEG 2000 and 100 mg/dm^3 thiourea at 100 A/m^2 for 2 hours

In the additive-free deposit obtained at 100 A/m^2, reflections corresponding to zinc oxide (ZnO; COD 2300113; COD 9004181), cadmium (Cd; COD 9008490), and iron (Fe; COD 9013474) are detected in addition to the dominant Zn peaks. The presence of ZnO indicates partial surface oxidation of the zinc deposit, which may have occurred either through reaction of deposited zinc with hydroxyl ions in the alkaline ammoniacal electrolyte or upon exposure to air before XRD analysis (Gu et al., 2018). The

co-deposition of Cd is attributed to the reduction of Cd^{2+} ions present in the pregnant leach solution, originating from the dissolution of cadmium-bearing phases in the smithsonite ore during ammoniacal leaching. Since the standard reduction potential of cadmium (E° = -0.403 V) is considerably more positive than that of zinc (E° = -0.763 V), cadmium ions are preferentially reduced at the cathode surface during electrowinning, resulting in their incorporation into the zinc deposit (Safarzadeh and Moradkhani, 2010). The Fe reflections detected in all four XRD patterns are attributed to contributions from the stainless-steel cathode substrate rather than to iron co-deposition from the leach solution, as the X-ray beam penetrates through the relatively thin zinc deposit and diffracts from the underlying steel substrate (COD 9013474; COD 9013481; COD 9008469; COD 9013414). This interpretation is consistent with the absence of iron in the EDS elemental analysis of the deposits (Table 2).

In the deposit obtained with 1 g/dm^3 PEG 2000 at 200 A/m^2, the XRD pattern shows Zn (COD 9012435) as the dominant phase, with ZnO (COD 9004178) and Fe substrate reflections (COD 9013481) also detected. While minor peaks consistent with cadmium reflections are visually observable in the pattern, they could not be reliably matched to a reference card by the XRD analysis software, indicating that cadmium is present at lower levels than in the additive-free deposit, below the diffractometer's reliable phase identification threshold. PEG 2000 adsorption on the cathode surface partially suppresses cadmium co-deposition by blocking active cathode sites available for Cd^{2+} reduction (Trejo et al., 2001; Ballesteros et al., 2007).

In the thiourea deposit obtained at 100 A·m^{-2}, the XRD pattern similarly shows Zn (COD 9008522) as the dominant phase, with ZnO (COD 2300113) and Fe substrate reflections (COD 9008469; COD 9013414) detected. As observed for the deposit obtained with the PEG 2000 additive, minor, unmatched peaks consistent with cadmium reflections are visually present. However, the software could not reliably identify them, confirming that thiourea also reduces cadmium co-deposition through selective adsorption at high-energy crystal-growth sites on the cathode surface (Zhong et al., 2025).

The combined addition of 1 g/dm^3 PEG 2000 and 100 mg/dm^3 thiourea yields the most Zn-rich deposit among all conditions investigated. The XRD pattern shows Zn (COD 9008522) as the dominant phase, with ZnO (COD 9004181) and Fe substrate reflections (COD 9008469) detected. Minor unmatched peaks consistent with cadmium reflections are also visually observable but below the software matching threshold, consistent with the other additive conditions. The relative intensities of the ZnO peaks in the combined additive deposit are reduced compared to the single-additive and additive-free conditions, suggesting that the combined additive system also partially suppresses surface oxidation of the zinc deposit.

3.1.2. Surface morphology and EDS analysis

The surface morphologies of zinc deposits obtained under additive-free conditions and in the presence of PEG 2000, thiourea, and their combined addition were examined by SEM and are shown in Figs. 2–5. The elemental compositions of the deposits determined by EDS analysis are summarized in Table 2.

Table 2. Elemental composition of zinc deposits obtained with and without organic additives determined by EDS analysis

Element	Additive-free (wt%)	PEG 2000 (wt%)	Thiourea (wt%)	PEG 2000 + Thiourea (wt%)
Zn	89.02	89.32	88.62	91.11
O	5.54	7.02	4.59	1.23
Cd	5.43	3.65	6.79	7.66

The SEM images of the additive-free zinc deposit obtained at current densities of 100 and 400 A/m^2 are shown in Fig. 2. At 100 A/m^2, a relatively uniform and compact morphology composed of fine, plate-like deposits was formed, distributed homogeneously over the cathode surface (Fig. 2a). As the current density is increased to 400 A/m^2, a noticeable coarsening of the surface morphology is observed, with larger plate-like deposits (Fig. 2b). This morphological coarsening is likely due to higher nucleation rate and faster crystal growth kinetics at elevated current densities, which promote the formation of larger grains at the expense of surface uniformity (Wang, 2020). At current densities above 400 A/m^2,

dendritic growth becomes increasingly predominant, particularly near the edges of the stainless-steel cathode. Because these geometric discontinuities enhance the local electric field, the local current density is amplified relative to the nominal applied current density at these sites (Bengoa et al., 2014). EDS analysis of the additive-free deposit confirms zinc as the dominant element at 89.02 wt%, with oxygen and cadmium also detected at 5.54 wt% and 5.43 wt%, respectively (Table 2). The oxygen content is consistent with the ZnO phase identified by XRD. In contrast, the cadmium content confirms the co-deposition of Cd^{2+} ions from the pregnant leach solution in the absence of any additives to suppress impurity reduction.

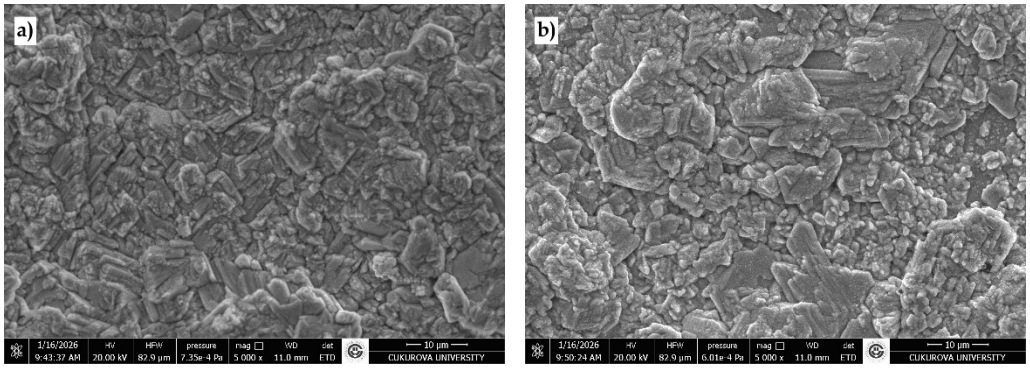

Fig. 2. SEM images of zinc deposits obtained by additive-free electrowinning at current densities of (a) 100 A/m^2 and (b) 400 A/m^2, each at ×5000 magnification

The SEM images of zinc deposits obtained only in the presence of PEG 2000, at concentrations of 0.5, 1, and 2 g/dm^3 at a current density of 200 A/m^2 are presented in Fig. 3. At 0.5 g/dm^3 PEG 2000, the deposit exhibits a rough and heterogeneous surface morphology characterized by irregular plate-like crystallites and localized agglomeration (Fig. 3a), indicating that this concentration is insufficient to provide uniform cathode surface coverage. At 1 g/dm^3 PEG 2000, the surface morphology of the deposit becomes noticeably more compact and fine-grained with reduced surface roughness and porosity (Fig. 3b). The improvement in deposit morphology at this concentration is attributed to the more effective adsorption of PEG 2000 molecules on the cathode surface, where they act as a leveling agent that moderates overall crystal growth and promotes more uniform zinc nucleation (Ballesteros et al., 2007). At 2 g/dm^3 PEG 2000, the surface morphology shows the formation of larger clustered structures composed of fine plate-like deposits (Fig. 3c), suggesting that over-adsorption of PEG 2000 at higher concentrations hinders zinc ion transport to the cathode surface and locally suppresses deposition, leading to uneven growth and agglomeration (Trejo et al., 2001; Ballesteros et al., 2007). EDS analysis shows a slight increase in zinc content to 89.32 wt% and a reduction in cadmium content to 3.65 wt% compared to the additive-free deposit (Table 2), confirming that PEG 2000 adsorption partially suppresses cadmium co-deposition by blocking active cathode sites. The oxygen content increases to 7.02 wt%, which may be attributed to the incorporation of oxygen-containing PEG molecules at the deposit surface or to enhanced surface oxidation associated with the deposit microstructure at certain PEG 2000 concentrations.

The SEM images of zinc deposits obtained in the presence of 100 mg/dm^3 thiourea at current densities of 100 and 400 A/m^2 are presented in Fig. 4. At 100 A/m^2, the deposit exhibits a compact and comparatively fine-grained surface morphology with reduced roughness relative to the additive-free deposit obtained at the same current density (Fig. 4a). This improvement is consistent with the selective adsorption of thiourea molecules at high-energy crystal-growth sites on the cathode surface, where they act as anisotropic growth inhibitors that suppress the preferential development of plate-like crystallites and promote more isotropic nucleation (Zhong et al., 2025). At 400 A/m^2, the thiourea deposit shows a more homogeneous and refined morphology compared to the additive-free deposit at the same current density (Fig. 4b), confirming the stabilizing role of thiourea across a wide current density range. EDS analysis shows zinc at 88.62 wt%, oxygen at 4.59 wt%, and cadmium at 6.79 wt% (Table 2). The lower oxygen content than in the PEG 2000 deposit is consistent with the more compact deposit morphology produced by thiourea, which reduces the available surface area for oxidation.

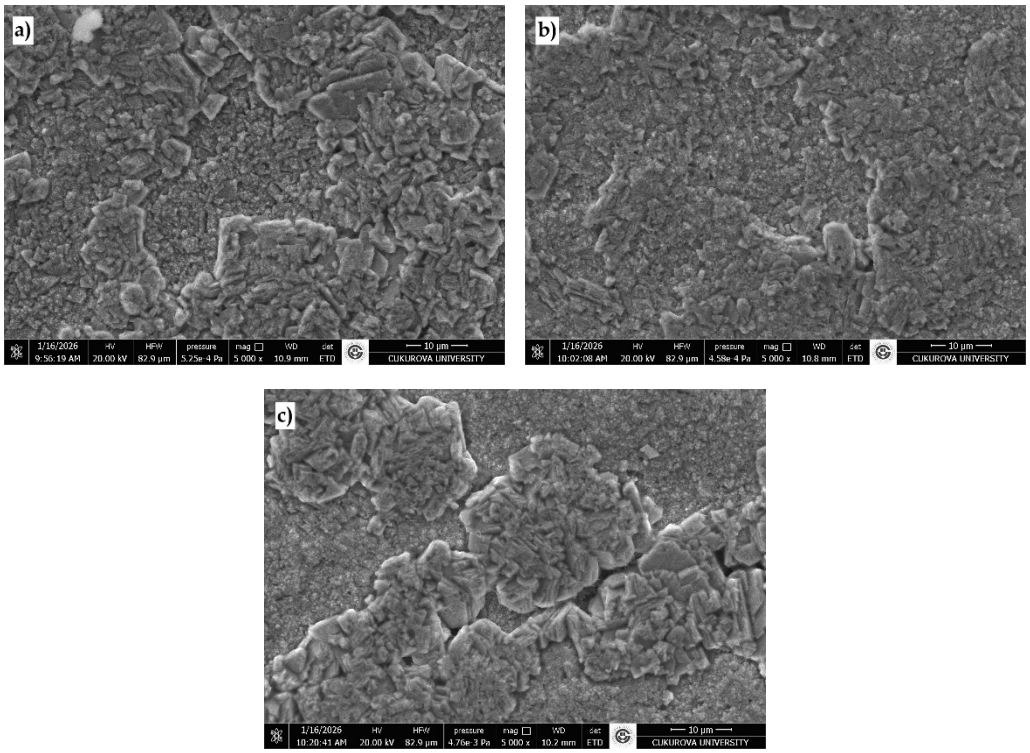

Fig. 3. SEM images of zinc deposits obtained by electrowinning at a current density of 200 A/m² in the presence of PEG 2000 at concentrations of (a) 0.5 g/dm³, (b) 1 g/dm³, and (c) 2 g/dm³; all images taken at ×5000 magnification

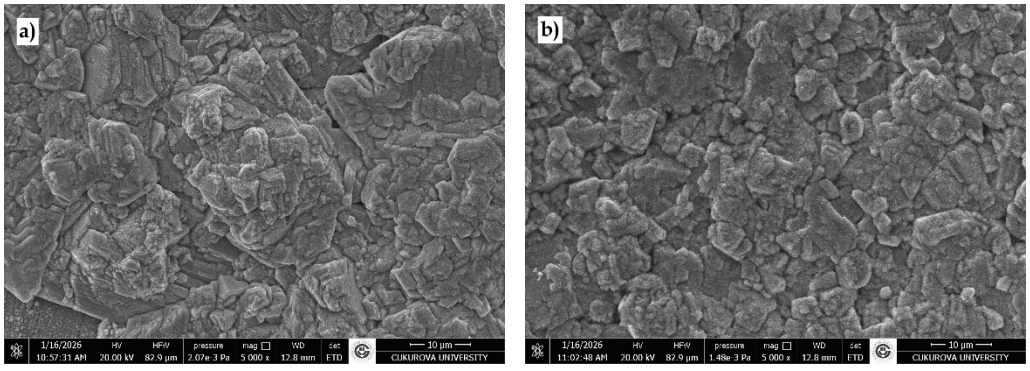

Fig. 4. SEM images of zinc deposits obtained by electrowinning with the addition of 100 mg/dm³ thiourea at current densities of (a) 100 A/m² and (b) 400 A/m² each at ×5000 magnification

The SEM images of the zinc deposit obtained with the combined addition of 1 g/dm³ PEG 2000 and 100 mg/dm³ thiourea at 100 A/m² after 2 hours of electrowinning are presented in Fig. 5. At low magnification (×5000), the deposit exhibits a highly compact and uniform surface morphology with near-complete suppression of the large plate-like crystallites typically observed in additive-free or single additive systems (Fig. 5a). At high magnification (×50,000), the deposit reveals a fine nodular structure consisting of densely packed, nearly spherical grains, indicating enhanced nucleation density and effective suppression of anisotropic crystal growth (Fig. 5b). This morphology reflects the complementary action of PEG 2000 and thiourea: PEG 2000 acts as a leveling agent that moderates overall crystal growth and promotes uniform surface coverage, while thiourea selectively adsorbs at high-energy sites and inhibits anisotropic growth (Ballesteros et al., 2007; Zhong et al., 2025), together producing the finest and most homogeneous deposit observed among all conditions investigated. EDS analysis shows the highest zinc content (91.11 wt%) and the lowest oxygen content (1.23 wt%) among

all conditions (Table 2), consistent with the highly compact, dense morphology that minimizes surface oxidation.

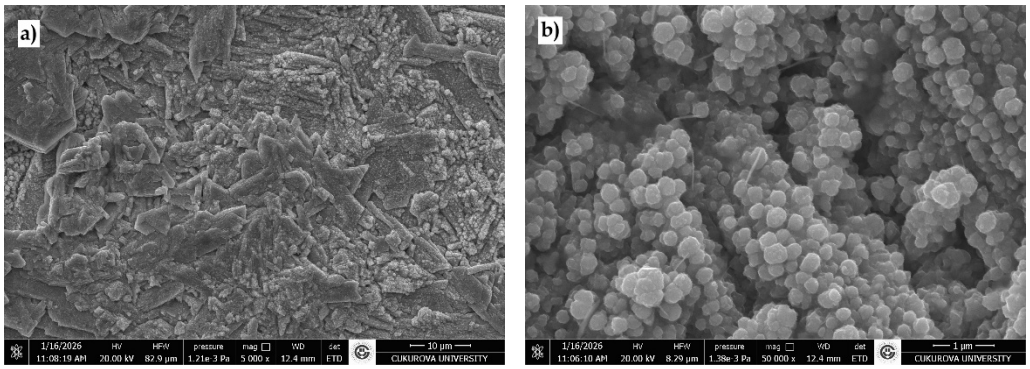

Fig. 5. SEM images of zinc deposits obtained by electrowinning at a current density of 100 A/m² in the presence of 100 mg/dm³ thiourea and 1 g/dm³ PEG 2000 after 2 h, taken at (a) ×5000 and (b) ×50,000 magnifications

Based on the EDS results of the deposits, Cd content decreased from 5.43 wt% in the additive-free deposit to 3.65 wt% in the PEG 2000 deposit. This result is consistent with partial suppression of Cd co-deposition by PEG 2000 adsorption. However, the higher Cd contents detected in the thiourea (6.79 wt%) and combined additive (7.66 wt%) deposits do not necessarily indicate increased bulk Cd co-deposition. The fine, compact morphology obtained with these additives yields deposits with higher surface area per unit volume. Since EDS probes only the near-surface region (~1–2 µm), the apparent Cd enrichment is likely due to surface segregation rather than increased bulk incorporation.

Additionally, the 2-hour electrowinning time in the combined addition experiments may have contributed to greater surface Cd accumulation. Given the relatively low cadmium concentration in the pregnant leach solution (~53 mg/dm³ Cd versus ~14.4 g/dm³ Zn), cadmium is more likely incorporated as a highly dispersed solid solution within the zinc deposits. The low peak intensities of the unmatched peaks consistent with crystalline Cd in the thiourea and combined additive deposits support this interpretation, as XRD identifies long-range crystalline order within the bulk deposit and requires higher phase abundance for reliable phase detection (Mourdikoudis et al., 2018). Additionally, similar discrepancies have been observed between surface-sensitive elemental analyses and bulk crystallographic characterization in electrodeposition systems containing trace metallic impurities (Muresan et al., 1996).

3.2. Current efficiency and energy consumption

In the ammoniacal pregnant leach solution at pH 11–12, zinc exists predominantly as the tetrammine zinc complex ion, $Zn(NH_3)_4^{2+}$. This complex is formed when Zn^{2+} ions react with ammonia molecules (Ehsani et al., 2021). As described in section 2.2.2, the electrowinning process involves the cathodic reduction of zinc-ammine complexes (Eq. 2) competing with hydrogen evolution (Eq. 3). In contrast, oxygen evolution occurs at the MMO anode (Eq. 4). The current efficiency of the electrowinning process is therefore determined by the relative rates of zinc deposition and hydrogen evolution at the cathode surface. The competing hydrogen evolution reaction is thermodynamically favored in alkaline ammoniacal electrolytes due to the high pH and the presence of water molecules as proton donors at the cathode surface (Vadlamudi and Chatterjee, 2025; Nikolić et al., 2026). The addition of organic additives such as PEG 2000 and thiourea modifies the cathode surface through selective adsorption. This modification suppresses hydrogen evolution while promoting more uniform zinc nucleation, enhancing current efficiency and improving zinc-deposit quality, as discussed in the following sections.

The average cell voltage recorded during additive-free electrowinning increased progressively from 4.245 V at 100 A/m² to 5.325 V at 200 A/m², 6.820 V at 400 A/m², 11.185 V at 800 A/m², and 15.535 V at 1000 A/m², consistent with increased ohmic resistance and cathodic polarization at higher current densities. Fig. 6 presents the variation of current efficiency (CE) and specific energy consumption (EC) as a function of applied current density for additive-free zinc electrowinning from the ammoniacal pregnant leach solution. At a relatively low current density of 100 A/m², the process exhibits a moderate

CE of 79.7% and a low EC of 4.37 kWh/kg. At 200 A/m², CE improves to 84.1% with a corresponding EC of 5.19 kWh/kg. The maximum CE of 86.4% is achieved at 400 A/m², accompanied by an EC of 6.47 kWh/kg. The increase in CE with current density up to 400 A/m² is consistent with progressive suppression of the hydrogen evolution reaction relative to zinc deposition, as cathodic overpotential rises and zinc ion reduction becomes the dominant cathodic process (Vadlamudi and Chatterjee, 2025).

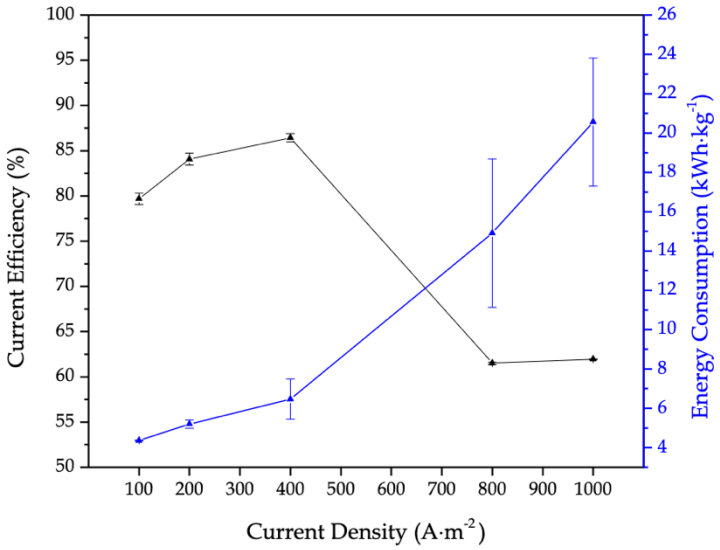

Fig. 6. Current efficiency and specific energy consumption as a function of current density for additive-free zinc electrowinning

At current densities beyond 400 A/m², the electrochemical performance deteriorates sharply. At 800 A/m², CE drops to 61.5%, and EC increases to 14.91 kWh/kg; this trend continues at 1000 A/m², where CE remains at 62.0%, and EC reaches 20.56 kWh/kg. This pronounced deterioration in performance at elevated current densities is attributed to the onset of mass transport limitations, where the rate of zinc ion diffusion to the cathode surface becomes insufficient to sustain uniform deposition at the applied current, leading to increased hydrogen evolution and dendritic growth (St-Pierre and Piron, 1990; Wang, 2020). These results show that while additive-free electrowinning can achieve acceptable CE values within a limited current density range of 100–400 A/m², the process is severely constrained at higher current densities and requires organic additives.

Fig. 7 presents the variation of CE and EC as a function of current density for zinc electrowinning in the presence of PEG 2000 at concentrations of 0.5, 1, and 2 g/dm³. At a PEG 2000 concentration of 0.5 g/dm³, the CE increases from ~73% at 100 A/m² to a maximum of ~89% at 200 A/m², then decreases markedly at higher current densities, reaching ~52% at 1000 A·m⁻². The relatively low CE at 100 A/m² and the rapid decrease at higher current densities suggest that 0.5 g/dm³ PEG 2000 provides insufficient surface coverage to stabilize zinc deposition over a wide current-density range, consistent with the rough, heterogeneous deposit morphology observed at this concentration. The EC at 0.5 g/dm³ remains relatively low at lower current densities but increases sharply above 400 A/m², reaching ~28 kWh/kg at 1000 A/m², indicating significant energy losses due to increased hydrogen evolution and irregular deposit formation at elevated current densities. Duan et al. (2023) reported a CE of 99% and EC of 2.391 kWh/kg in a PEG 20,000-assisted ammoniacal system at 400 A/m² and 40°C using a bench-scale cell, which is higher than the CE achieved in the present study at comparable current densities. This difference may result from the higher zinc concentration (40 g/dm³) and optimized flow conditions employed in their study compared to the static electrolyte conditions used here.

At 1 g/dm³ PEG 2000, the CE remains comparatively high over a broader current density range, increasing from ~80% at 100 A/m² to a maximum of ~87% at 400 A/m², before decreasing to ~67% at 800 A/m² and ~52% at 1000 A/m². The EC increases more gradually than at 0.5 g/dm³, reaching ~25 kWh/kg at 1000 A/m². The superior performance at 1 g/dm³ is attributed to the more effective and uniform adsorption of PEG 2000 on the cathode surface at this concentration, which acts as a leveling agent that moderates crystal growth, reduces surface roughness, and suppresses hydrogen evolution

over a wider current density range (Trejo et al., 2001; Ballesteros et al., 2007). Similar improvements in CE and deposit morphology have been reported with PEG-type additives in ammoniacal zinc electrodeposition systems (Gu et al., 2018; Duan et al., 2023).

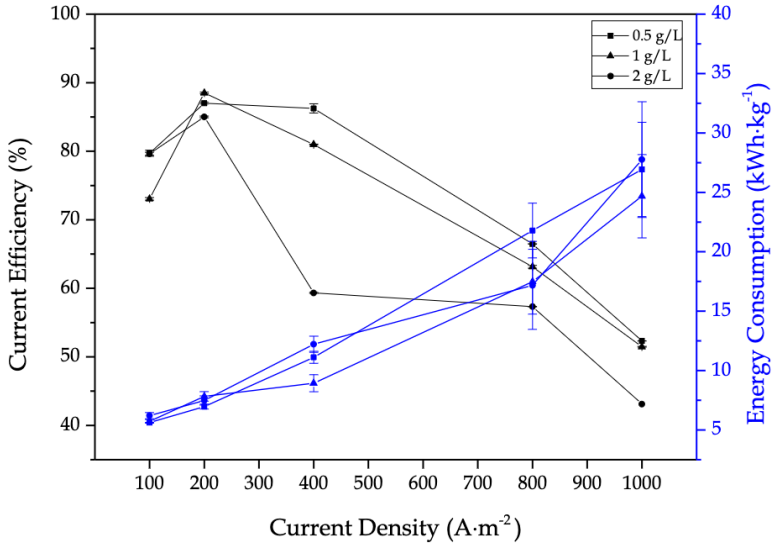

Fig. 7. Current efficiency and specific energy consumption as a function of current density for zinc electrowinning in the presence of PEG 2000 at concentrations of 0.5, 1, and 2 g/dm^3

At the highest PEG 2000 concentration of 2 g/dm^3, the CE peaks at ~80% at 200 A/m^2 and decreases more rapidly with increasing current density compared to the 1 g/dm^3 condition, dropping to ~57% at 800 A/m^2 and ~43% at 1000 A/m^2. Interestingly, the EC at 2 g/dm^3 is the lowest among all PEG 2000 concentrations at high current densities, which may be attributed to the lower cell voltage resulting from the highly inhibited deposit surface at over-adsorption conditions. The rapid decrease in CE at 2 g/dm^3 beyond 200 A/m^2 is consistent with over-adsorption of PEG 2000 molecules, which hinders zinc-ion transport to the cathode surface and locally suppresses deposition, increasing hydrogen evolution and reducing current utilization for zinc deposition (Ballesteros et al., 2007). Based on the combined evaluation of CE, EC, and deposit morphology, 1 g/dm^3 PEG 2000 at 200 A/m^2 represents the optimal condition for single-additive PEG 2000 electrowinning from the ammoniacal pregnant leach solution. The average cell voltages recorded at the optimal PEG 2000 concentration of 1 g/dm^3 were 5.575 V at 100 A/m^2, 8.310 V at 200 A/m^2, 9.405 V at 400 A/m^2, 14.175 V at 800 A/m^2, and 15.750 V at 1000 A/m^2. The higher cell voltages observed with PEG 2000 than in the additive-free condition at equivalent current densities reflect increased cathodic polarization associated with PEG 2000 adsorption on the cathode surface.

Fig. 8 presents the variation of CE and EC as a function of current density for zinc electrowinning in the presence of 100 mg/dm^3 thiourea. The average cell voltages recorded during thiourea electrowinning were 5.175 V at 100 A/m^2, 6.535 V at 200 A/m^2, 9.300 V at 400 A/m^2, and 13.660 V at 800 A/m^2. The cell voltage at 1000 A/m^2 was recorded as 12.815 V, slightly lower than at 800 A/m^2, which may reflect measurement variability associated with the pronounced dendritic growth and deposit instability observed at this current density. Adding thiourea to the pregnant leach solution significantly improves CE across the entire current density range investigated compared with the additive-free system. At 100 A/m^2, CE increases from 79.7% in the additive-free system to approximately 89% with thiourea addition, accompanied by a slightly higher EC of ~4.8 kWh/kg. At 200 A/m^2, CE improves further to ~91%, with EC increasing moderately to ~5.9 kWh/kg. The maximum CE of approximately 94% is achieved at 400 A/m^2, with EC of ~8.1 kWh/kg. The superior CE achieved with thiourea addition compared to the additive-free system could be associated with the selective adsorption of thiourea at high-energy crystal growth sites on the cathode surface, which suppresses anisotropic zinc crystal growth and dendrite formation, thereby maintaining a more compact deposit morphology that limits the active surface area available for hydrogen evolution (Zhong et al., 2025).

At current densities above 400 A/m², the CE decreases, dropping to approximately 82% at 800 A/m² and ~58% at 1000 A/m², while the EC increases to ~13.8 and ~18.5 kWh/kg, respectively. Despite this decrease at high current densities, the CE values achieved with thiourea remain higher than those of the additive-free system across the entire current density range, demonstrating its effectiveness as a stabilizing agent for zinc electrowinning from ammoniacal solutions. The decrease in CE at very high current densities is attributed to the increasing dominance of mass transport limitations and hydrogen evolution, which eventually overcome the stabilizing effect of thiourea adsorption at the cathode surface (Kim et al., 2019).

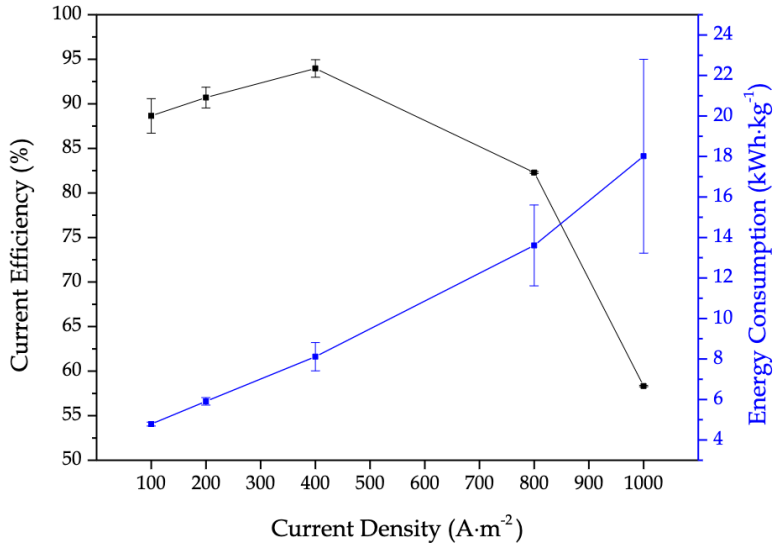

Fig. 8. Current efficiency and specific energy consumption as a function of current density for zinc electrowinning in the presence of 100 mg/dm³ thiourea

The concentrations of 1 g/dm³ PEG 2000 and 100 mg/dm³ thiourea selected for the combined addition study were identified as the optimum concentrations for each additive when used alone, based on their individual performance in current efficiency and deposit morphology, as discussed in the preceding sections. The combined addition experiments therefore used the individually optimized additive concentrations, providing a rigorous basis for evaluating the combined additive effect under the investigated conditions. Fig. 9 presents the variation of CE and EC as a function of electrowinning time for the combined addition of 1 g/dm³ PEG 2000 and 100 mg/dm³ thiourea at 100 A/m². The average cell voltages recorded under the combined additive condition at 100 A/m² were 6.030 V at 1 hour, 5.785 V at 2 hours, and 6.450 V at 4 hours. The process exhibits a CE of about 80% and an EC of ~6.2 kWh/kg over 1 hour of electrowinning, corresponding to the formation of a compact surface morphology on the cathode. The lowest cell voltage at 2 hours coincides with the maximum CE of approximately 95%, reflecting the formation of the most compact and uniform deposit morphology at this duration, which minimizes ohmic losses at the cathode surface. The CE increases to approximately 95% while the EC decreases to its lowest value of ~5.0 kWh/kg after the electrowinning time is increased to 2 hours. This optimum performance at 2 hours coincides with the development of the most compact and homogeneous zinc deposit, as indicated by SEM analysis (Fig. 5), reflecting the complementary action of PEG 2000 as a leveling agent and thiourea as an anisotropic growth inhibitor, which together promote uniform zinc nucleation and suppress hydrogen evolution over the entire cathode surface.

At the prolonged electrowinning time of 4 hours, the CE decreases slightly to approximately 93%, accompanied by a moderate increase in EC to ~5.6 kWh/kg. This is attributed to the gradual thickening of the zinc deposit, which increases electrical resistance and limits ion transport. The slight increase in cell voltage at 4 hours is consistent with the gradual thickening of the zinc deposit, which increases electrical resistance at the cathode. Therefore, current efficiency in zinc electrowinning decreases slightly with longer electrowinning times (Lu et al., 2013). However, the CE remained above 90% even at 4 hours, indicating that the combined additive system maintains favorable electrowinning stability

over prolonged durations, unlike additive-free or single-additive systems where efficiency deteriorates rapidly due to dendritic growth and increased hydrogen evolution.

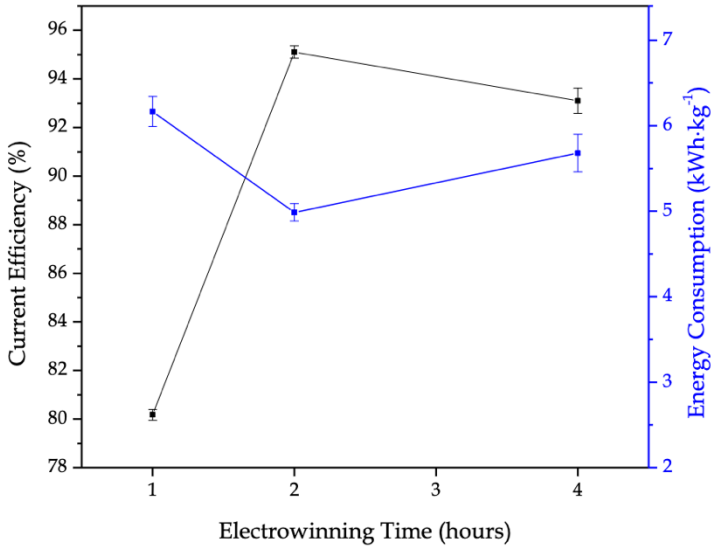

Fig. 9. Current efficiency and specific energy consumption as a function of electrowinning time for zinc electrowinning with the combined addition of 1 g/dm³ PEG 2000 and 100 mg/dm³ thiourea at 100 A/m²

The combined addition of 1 g/dm³ PEG 2000 and 100 mg/dm³ thiourea achieved the highest CE of approximately 95% with a low EC of ~5.0 kWh/kg at the optimal condition of 100 A/m² for 2 hours in comparison to additive-free electrowinning (highest CE ~86.4% at 400 A/m², lowest EC ~4.37 kWh/kg at 100 A/m²) and single-additive systems (highest CE ~94% with thiourea at 400 A/m², highest CE ~87% with 1 g/dm³ PEG 2000 at 400 A/m²). The complete suppression of dendritic growth, stable electrowinning for up to 4 hours, and a maximum CE of ~95%, exceeding the values obtained with PEG 2000 (~87%) and thiourea (~94%) alone, indicate an apparent synergistic behavior between the two additives under the investigated conditions. These results indicate that the combined additive system improves current efficiency while maintaining favorable energy consumption under the investigated conditions for zinc electrowinning from ammoniacal pregnant leach solutions derived from smithsonite ore. In contrast, zinc electrowinning from ZnO dissolved in 2:1 urea/choline chloride ionic liquid at 363 K, which achieved CE values of 78.5–88.9% with EC of 3.04–3.66 kWh/kg (Yang and Reddy, 2015), requires elevated temperatures and specialized electrolyte preparation compared to the ambient-temperature ammoniacal system employed in the present study.

The current efficiency and specific energy consumption obtained in the present study should be considered together when evaluating the effect of the additives on electrowinning performance. This approach is consistent with previous zinc electrowinning studies that jointly use current efficiency, energy consumption, and deposit morphology to assess the electrochemical performance of different electrolyte compositions and additives (Xu et al., 2020; Duan et al., 2023). Previous studies have also shown that organic additives can either improve or deteriorate current efficiency and energy consumption depending on their chemical nature and concentration. For instance, thiourea has been reported to adversely affect current efficiency and increase energy consumption under some zinc electrowinning conditions, whereas PEG-assisted ammoniacal systems have improved both current efficiency and deposit morphology, highlighting the importance of evaluating these parameters together (Xu et al., 2020; Duan et al., 2023).

In addition, the present study established the Zn dissolution during the leaching stage using an XRF-based mass balance between the initial ore and the leaching residue rather than direct PLS analysis. However, a complete Zn mass balance for the electrowinning stage was not established, as the Zn concentration remaining in the electrolyte after electrowinning, potential washing losses, and any precipitate or sludge were not quantitatively determined. Moreover, chemical analysis did not independently determine bulk deposit composition; therefore, Zn-specific current efficiency could not be determined. Accordingly, the reported electrowinning performance focused primarily on cathodic

deposition behavior, apparent current efficiency, and specific energy consumption rather than complete process-level Zn recovery.

4. Conclusions

In this study, zinc electrowinning from ammoniacal pregnant leach solution obtained by selective alkaline leaching of carbonate-containing smithsonite ore from Yahyalı, Kayseri, Türkiye, was investigated under additive-free conditions and in the presence of PEG 2000, thiourea, and their combined addition. The study systematically evaluated how additive type, concentration, and current density affected deposit phase composition, surface morphology, current efficiency, and specific energy consumption. The following conclusions can be drawn:

1. Additive-free electrowinning achieved a maximum current efficiency of 86.4% at 400 A/m^2. However, the electrowinning performance deteriorated at higher current densities due to dendritic growth and increased hydrogen evolution. XRD and EDS analyses showed that cadmium (5.43 wt%) co-deposited and that ZnO formed as a secondary phase.
2. The addition of PEG 2000 at an optimal concentration of 1 g/dm^3 improved deposit compactness and grain uniformity through its leveling action on the cathode surface, and partially suppressed cadmium co-deposition, as evidenced by a reduction in EDS Cd content to 3.65 wt% and the low intensities of Cd peaks in the XRD pattern. However, over-adsorption at 2 g/dm^3 led to reduced deposit uniformity and decreased current efficiency at elevated current densities.
3. Adding 100 mg/dm^3 thiourea served as an effective stabilizing agent for zinc electrowinning over a wide current-density range, achieving a maximum current efficiency of approximately 94% at 400 A/m^2. It was also concluded that thiourea is more effective than PEG 2000 at improving current efficiency at elevated current densities.
4. The combined addition of 1 g/dm^3 PEG 2000 and 100 mg/dm^3 thiourea exhibited apparent synergistic behavior under the investigated conditions, as evidenced by the complete suppression of dendritic growth and enhanced current efficiency beyond that achieved by either additive alone. The optimum condition of 100 A/m^2 for 2 hours yielded a maximum current efficiency of approximately 95% with the lowest specific energy consumption of ~5.0 kWh/kg among the additive-containing conditions investigated. The combined additive deposit exhibited the finest and most homogeneous nodular morphology among all conditions investigated. EDS analysis showed the highest zinc content (91.11 wt%) and the lowest oxygen content (1.23 wt%) among all deposits examined.
5. The higher Cd contents detected by EDS in the thiourea (6.79 wt%) and combined additive system (7.66 wt%) electrowon deposits compared to the additive-free condition can be attributed to surface segregation effects associated with the fine and compact deposit morphology, rather than to increased bulk cadmium co-deposition. The low intensities of the Cd peaks detected by XRD in these deposits support the interpretation that cadmium exists in a highly dispersed or amorphous state below the XRD detection threshold.
6. The combined use of PEG 2000 and thiourea effectively improved current utilization while maintaining favorable energy consumption and stable electrowinning performance for up to 4 hours. These results indicate the potential of the combined PEG 2000 and thiourea additive system for the hydrometallurgical recovery of zinc from carbonate-containing smithsonite ores as zinc-rich deposits.
7. The findings of this study should be interpreted within the investigated experimental conditions and in light of the limitations outlined above. Future studies should include direct PLS and bulk deposit analyses, Zn-specific current efficiency determination, and a complete process-level Zn mass balance.

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