

*Orest Kuntiyi and Galyna Zozulya*MORPHOLOGY OF ZINC DEPOSITED VIA CEMENTATION OVER MAGNESIUM ROTARY DISC IN $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ AQUEOUS SOLUTIONS

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Abstract. Zinc cementation by magnesium from $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ aqueous solutions has been investigated. The amount of magnesium has been established as 0.8–2.0 g per 1 g of conditioned zinc to obtain recovery degree $\geq 99\%$. At low concentrations of Zn^{2+} ions (0.025–0.1 M ZnCl_2) dispersed deposit is formed with nanoparticles of reduced metal; at high concentrations (0.25–0.5 M) coarse-crystalline and fern-shaped deposit is formed.

Keywords: cementation, zinc, magnesium, morphology.

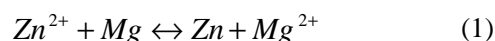
1. Introduction

One of the methods of obtaining non-ferrous metals, including zinc, from spent electrolytes and rinsing technological water is cementation [1]. However, in practice, zinc cementation is complicated owing to its considerable electronegativity ($E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76\text{V}$).

Therefore, only metals with $E_{\text{Me}^{n+}/\text{Me}}^0 < E_{\text{Zn}^{2+}/\text{Zn}}^0$ value may be used as its reducing agents. Contact deposition of zinc has been investigated only by aluminum in aqueous solutions [2]. The dense oxide film over its surface is soluble only in alkali medium; therefore aluminum may be used as an effective cementation agent only at $\text{pH} \geq 12$. Zinc, especially dispersive one, is soluble in such medium. Also taking into account that field waste water has $\text{pH} < 12$, the full deposition of zinc by aluminum is unlikely.

Previously we have shown effective cementation by magnesium taking as an example recovery of non-ferrous [3, 4] and precious [5, 6] metals from leaching solutions of ore and secondary raw materials. Magnesium electronegativity ($E_{\text{Mg}^{2+}/\text{Mg}}^0 = -2.36\text{V}$) ensures great

values of electromotive force (EMF) between microelectrodes, as well as relatively high cementation rate and completeness of metal deposition. Since cementation is equilibrium process (Eqs. 1 and 2), the zinc deposition by magnesium ought to be complete (Eq. 3). The ecological compatibility of the process also should be noted since Mg^{2+} ions in the solution are non-toxic (Eq. 1).



$$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Mg}^{2+}/\text{Mg}}, \text{ or } E_{\text{Zn}^{2+}/\text{Zn}}^0 + \frac{RT}{2F} \ln a_{\text{Zn}^{2+}} = E_{\text{Mg}^{2+}/\text{Mg}}^0 + \frac{RT}{2F} \ln a_{\text{Mg}^{2+}} \quad (2)$$

After corresponding transformations:

$$\lg \frac{(a_{\text{Zn}^{2+}})^{1/2}}{(a_{\text{Mg}^{2+}})^{1/2}} = -\frac{E_{\text{Zn}^{2+}}^0 - E_{\text{Mg}^{2+}}^0}{0.059};$$

$$\lg(a_{\text{Zn}^{2+}})^{1/2} = -\frac{E_{\text{Zn}^{2+}}^0 - E_{\text{Mg}^{2+}}^0}{0.059};$$

$$a_{\text{Zn}^{2+}}^{1/2} = 10^{\frac{-(E_{\text{Zn}^{2+}}^0 - E_{\text{Mg}^{2+}}^0)}{0.059}} = 10^{-16.95\Delta E^0},$$

$$\text{or } a_{\text{Zn}^{2+}} = 10^{-33.9\Delta E^0} \text{ mol}\cdot\text{dm}^{-3} \quad (3)$$

The cementation rate depends upon morphology of the reduced metal. G. Sulka and co-workers [7] show that microanodic zones are blocked over zinc surface at the formation of argenticum dense deposit. The result is the interruption of metal reduction. Hence, it is important to

determine the metal morphology for the prediction of cementation with reference to process rate and completeness of metal recovery [7-9]. This work deals with the morphology of reduced zinc deposit over magnesium surface and continues systematic studies on metal cementation by magnesium from aqueous solutions [3-6].

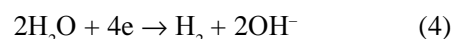
2. Experimental

Zinc cementation was carried out in $n\text{ZnCl}_2 + n\text{NH}_4\text{Cl}$ ($n = 0.025\text{--}0.5$) solutions simulating leaching solutions of secondary raw materials. The process was carried out at rotary magnesium disk (1000 rpm) with diameter of 30 mm (Fig. 1). The process temperature was 293 K, solution volume was 100 cm³. Solution pH was 5.0–6.0 due to the addition of chloride acid. Before each experiment the disk surface was scraped by fine-grained emery, cleaned by alcohol and side face was insulated by teflon tape. The deposit formed at the surface in the result of the cementation was rinsed by water and acetone and dried at 333 K at the air. The morphology of the reduced zinc without removing from magnesium surface was investigated using scanning electron microscope REMMA-102-02. The surface image was obtained as registration of secondary electrons by means of cathode beam scanning over the surface. Secondary radiation was excited using sample radiation by means of cathode beam with the energy of 12–20 keV. The surface phase composition (COMPO mode) and its elementary composition were determined using the same device. After

separation of sprinkled zinc deposit the solution was analyzed by means of trilonometry for the presence of zinc and magnesium ions. On the basis of obtained data magnesium specific consumption necessary for zinc cementation was calculated.

3. Results and Discussion

Within a wide range of zinc ions concentration (0.025–0.5 M) formation of solid zinc deposit was not observed (Figs. 2 and 3). This fact may be explained, first of all, by the great difference between magnesium and zinc standard electrode potentials: $\Delta E = -0.76 - (-2.36) = 1.6$ V, which results in high value of cementation current over microcathodes. Negligible cathode polarization of $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ aqueous solutions also favors the forming of zinc deposit with developed surface. Under cementation hydrodynamic conditions caused by disk rotation and side microcathode reaction (Eq. 4) the deposit sloughs and releases magnesium surface. Therefore, a high part of microanode surface with corresponding high current density at microcathode zones is ensured.



It is known [10] that dispersed metal deposit is formed at values of cathode current density (i_c) higher than limited values (i_{lm}). Therefore, according to zinc morphology over magnesium disk surwashing, drying, and mesh analysis. At the same time the thickness of the structural dendrites is less than 0.5–1 μm (Figs. 2b, c, e, f).

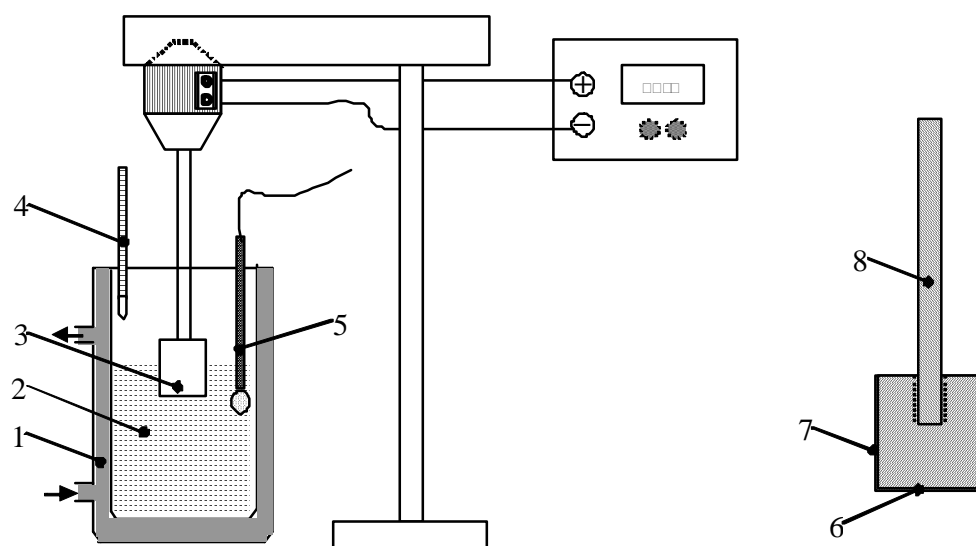


Fig. 1. Scheme of laboratory plant: glass reactor with water-jacket (1); investigated solution (2); magnesium disk (3); burette (4); electrode of pH-meter (5); disk work surface (6); teflon tape (7), and pivot for disk fastening (8)

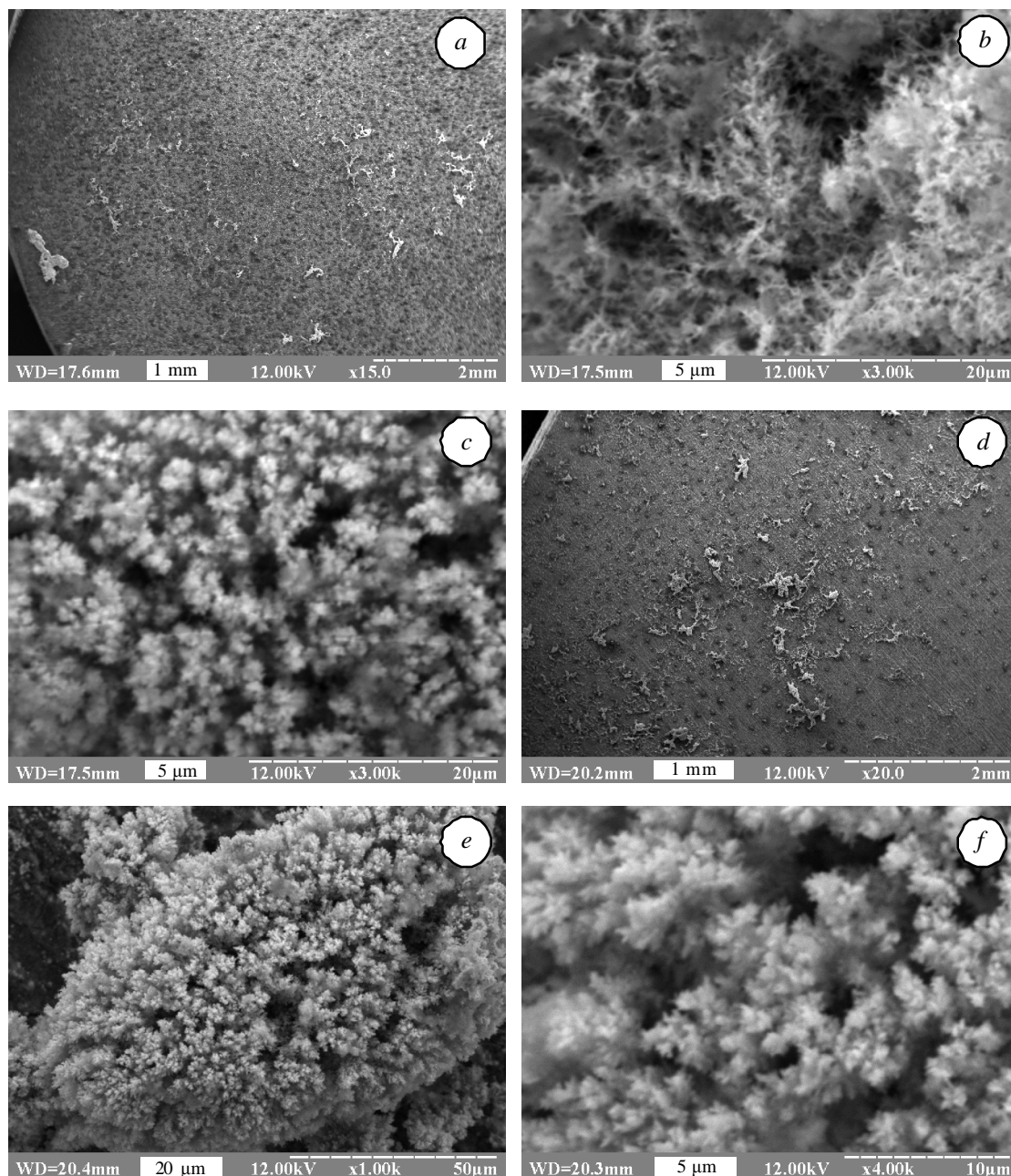


Fig. 2. REM image of magnesium disk with zinc deposited from $n\text{M ZnCl}_2 + n\text{M NH}_4\text{Cl}$ solutions: $n = 0.025$ (a–c) and 0.1 (d–f)

The increase of zinc ion concentrations increases the percentage of filling of magnesium surface by reduced metal deposit. Thus, while in $0.025\text{--}0.1\text{ M ZnCl}_2$ fragments of dispersed zinc do not exceed $5\text{--}10\%$ of the total surface of magnesium disc (Figs. 2a, d), in 0.5 M solution the covering achieves 30% and more (Fig. 3a). The reason is the increased adhesion of reduced zinc with the support surface of cementation agent due to the formation of less dispersive deposit (Fig. 3). Thus, in 0.25 M ZnCl_2 dendritic

agglomerates are formed from large dendrites (fragments b, c) and in 0.5 M – agglomerates are intermediate between dispersed and compact metal (fragments d–f).

Regardless of ZnCl_2 concentration and zinc recovery degree the latter does not contain impurities of magnesium. It is caused first of all by the great difference between

$E_{\text{Zn}^{2+}/\text{Zn}}^0$ and $E_{\text{Mg}^{2+}/\text{Mg}}^0$. Therefore magnesium impurities, which detach from the surface together with zinc deposit in the result of the anodic reaction (5), are ionized. Owing

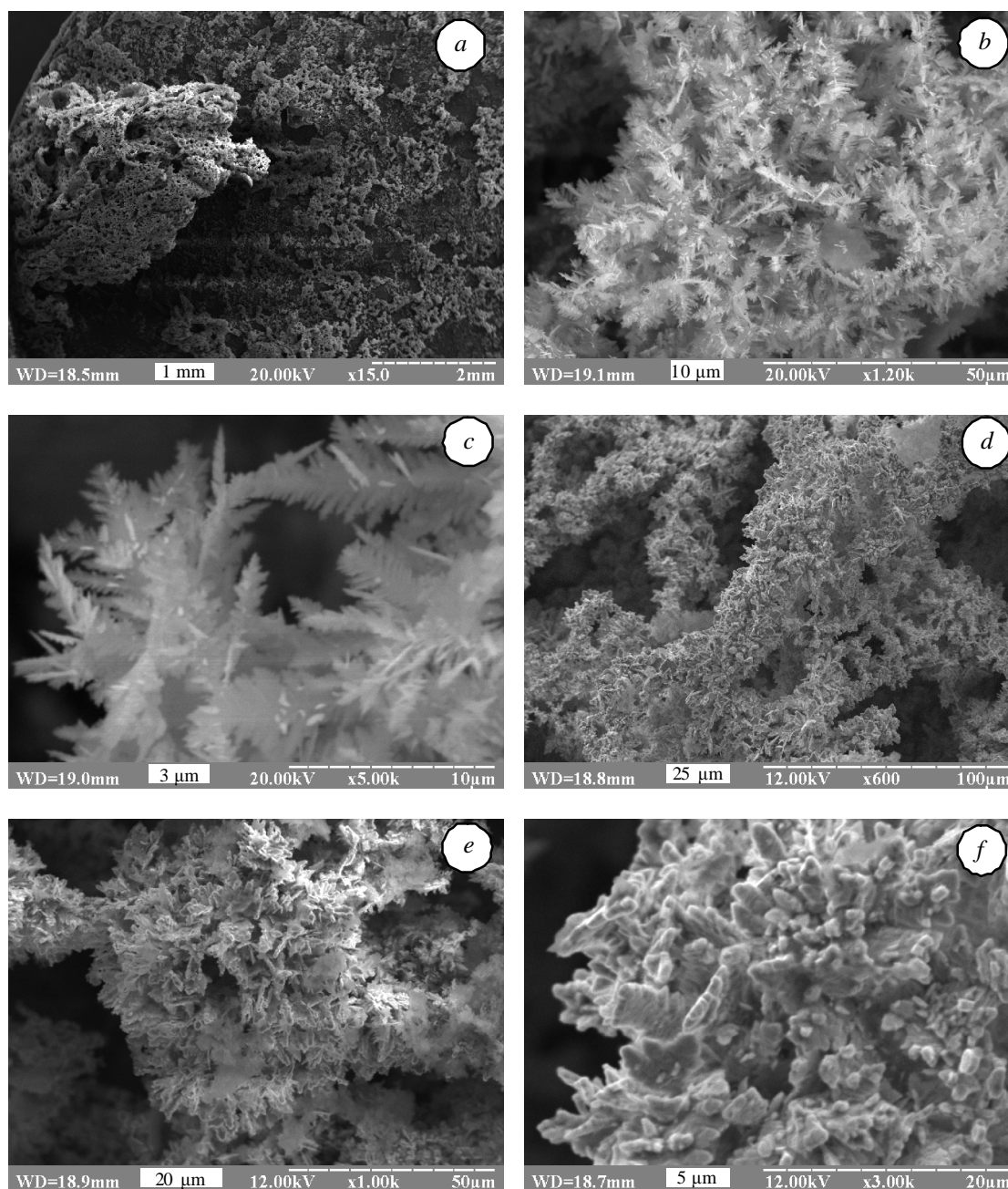
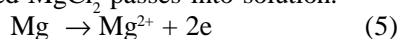


Fig. 3. REM image of magnesium disk with zinc deposited from $n\text{M ZnCl}_2 + n\text{M NH}_4\text{Cl}$ solutions:
 $n = 0.25$ (a–c) and 0.5 (d–f)

to good solubility and hydrodynamic conditions of cementation the formed MgCl_2 passes into solution.



Magnesium specific consumption at metal recovery degree $\geq 99\%$ in $0.5\text{--}0.25\text{ M ZnCl}_2$ is ranged from 0.8 to 1.0 g per 1 g of standard zinc and from 1.3 to 2.0 g – in $0.1\text{--}0.025\text{ M}$ solution. Market prices for magnesium and zinc are proportionate. However the price of metal powders is several times higher than the price of corresponding compact metals. Thus cementation of powder zinc by

magnesium is very promising from economic point of view. Taking into account non-toxicity of magnesium ions, another perspective direction of cementation is the ecological one, namely zinc recovery from waste electrolytes and technological zinc-containing solutions.

4. Conclusions

1. Using cementation by magnesium fine zinc in $0.025\text{--}0.25\text{ M ZnCl}_2$ and porous zinc in 0.5 M is formed.

It favors easy release of cementation agent surface from deposited zinc and ensures large specific surface of microanodic zones as well as high process rate.

2. The great difference between and standard electrode potentials and good solubility of magnesium salt ensures high purity of reduced zinc and completeness of its deposition.

3. Magnesium specific consumption in 0.25–0.025 M ZnCl_2 is within the range of 1.0–2.0 g per 1 g of fine zinc resulting in the possibility to use cementation for zinc powder production.

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МОРФОЛОГІЯ ЦИНКУ, ОСАДЖЕНОГО ЦЕМЕНТАЦІЄЮ НА МАГНІЄВОМУ ОБЕРТОВОМУ ДИСКУ У ВОДНИХ РОЗЧИНАХ $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$

Анотація. Досліджено цементацію цинку магнієм з водних розчинів $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$. Встановлено, що за повноти вилучення металу $\approx 99\%$ питомі витрати магнію становлять 0.8–2.0 г на 1 г кондиційного цинку. Показано, що за низьких концентрацій іонів Zn^{2+} (0.025–0.1 M ZnCl_2) формується дисперсний осад із субмікронними розмірами частинок відновленого металу, за високих (0.25–0.5 M) – грубокристалічний дендритоподібний.

Ключові слова: цементація, цинк, магній, морфологія.