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Features of the discharge of zinc in the background solution of sodium sulphate under stirring conditions

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Abstract

The production technology of hydrometallurgical zinc uses various surfactants to thicken pulps, stabilise the electrolysis process, and obtain high-quality cathode deposits. Numerous researches were conducted to study the cathodic and anodic processes in a wide range of the composition of aqueous solutions using various solid electrodes in the absence of intense stirring of the electrolyte and with a high contribution of the migration component of the discharge of metals. This approach to the study of the surfactants' influence rarely provided a high degree of statistical reliability in observing the effect of differently charged surfactants on electrode processes, which is of great importance in the hydrometallurgical production of zinc. In this work, the task was to practically eliminate the contribution of the migration component due to the following factors: conducting electrolysis in a background solution of sodium sulphate, organising electrolyte stirring, performing calculations of current densities at the beginning of electrolysis, and establishing polarisation curves at an increased potential sweep rate from 20 to 100 mV/s. This approach provided a greater degree of statistical reliability in presenting the mechanism of the effect of additions of cationic and anionic surfactants during the stage of zinc discharge on a solid electrode, which was the purpose of the article.

Electrolysis was conducted in the potential range from -1050 to -1250 mV relative to the silver chloride electrode (AgCl/Ag) in the presence of a background sodium sulphate solution (0.5 M of Na₂SO₄ solution) containing 0.005, 0.0125, and 0.025 M ZnSO₄ with the introduction of high-molecular surfactants: cationic and anionic coagulants (floculants) and foaming agents (lignosulphonate – LSTP).

During the electrolysis in a background solution of sodium sulphate with stirring, it was found that the process of discharge of zinc ions on a solid electrode occurs in a mixed-kinetic mode. It was shown that positively charged additives, such as lignosulphonate and cationic coagulant (floculant) Besfloc K6645, have a negative effect on the dynamics of zinc cation discharge, while negatively charged Besfloc K4034 has practically no effect. The approach proposed in this work allows evaluating the influence of additions of cationic and anionic surfactants on the stage of zinc discharge on a solid electrode, which was the practical and scientific value of this work.

Keywords: Zinc, Current density, Potential, Polarisation, Coagulant, Lignosulphonate, Sodium sulphate, Electrode

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1. Introduction

As we know, different surfactants present in hydrometallurgical production solutions influence the process of the cathodic reduction of zinc [1–9]. Among surfactants are foaming agents used for zinc electrolysis and coagulants (flocculants) which are added to solutions to increase the settling rate of pulps and separate the solution from the insoluble mass (zinc cake) under the leaching of heat treatment products.

Numerous researches were conducted to study the cathodic and anodic processes in a wide range of the composition of aqueous solutions using various electrodes [10–17] in the absence of intense stirring of the electrolyte and with a high contribution of the migration component of the discharge of metals. This approach to the study of the influence of surfactants rarely provided a high degree of statistical reliability in observing the effect of differently charged surfactants on electrode processes, which is of great importance in the hydrometallurgical production of zinc. To eliminate the possibility of migration transport, a background electrolyte was introduced in the studied solution with a concentration exceeding the depolariser concentration by at least one hundred times [18, 19, 21]. The elimination of migration transport from the process of electrolysis allows increasing the contribution of the charge transfer stage into the dynamics of the reduction of cations through the “metal – electrolyte” interphase.

In this work, the task was to increase the contribution of the electrochemical stage into the dynamics of zinc discharge due to the following factors:

- Conducting electrolysis in a background solution of sodium sulphate.
- Organising electrolyte stirring (the Reynolds number Re was 1500).
- Performing calculations of current densities at the beginning of electrolysis.
- Establishing polarisation curves at an increased potential sweep rate.

This approach provided a greater degree of statistical reliability in evaluating the effect of additions of cationic and anionic surfactants during the stage of zinc discharge on a solid electrode, which was the purpose and the novelty of this study.

2. Experimental

Electrochemical studies were conducted in a sulphate electrolyte containing 0.005, 0.0125, and 0.025 M $ZnSO_4$ in the background 0.5 M solution of Na_2SO_4 with the introduction of high-molecular surfactants: 50 mg/l of cationic and anionic coagulants (flocculants) with the trade names Besfloc K6645 and Besfloc K4034, as well as 80 mg/l of a foaming agent (lignosulphonate – LSTP). Potentiostatic and galvanostatic measurements and establishing polarisation curves in the dynamic mode were conducted on a PotentiostatP-30Jcom (Elins) using a three-electrode cell [1]. The working electrode (cathode) was made of copper with an area of 0.1 cm², the auxiliary electrode (anode) was made of a platinum plate with an area of 0.2 cm², and the reference electrode was silver chloride (AgCl/Ag). The working copper electrode was polished, degreased in ethanol, and washed with water. The auxiliary electrode was etched in a nitric acid solution (1 : 2 = acid : water) for 5 seconds and washed with distilled water. The measurements were performed at room temperature with and without stirring. At first, before establishing the experimental curves, zinc was increased on a copper cathode with a constant potential of –1200 mV (AgCl/Ag) for 5 min using an electrolyte with a composition of 0.25 M $ZnSO_4$. The results of potentiostatic measurements are presented in the form of average data obtained over the initial period of 1 s of electrolysis while the results of galvanostatic measurements are presented in the form of average data obtained over the initial period of 5 s of electrolysis. The polarisation curves were obtained using a potentiodynamic method with linear potential sweep in the potential range –1050 ÷ –1250. Maximum current density was registered on polarisation curves in the potential range from –1200 to –1250 mV.

Confidence intervals were calculated for the experimental data on the figures. With the value $p = 0.05$, the intervals changed in the range from 0.015 to 1.14 mA/cm² (for current densities) and from 6.82 to 8.77 mV (for polarisation) and amounted to 0.11 lg I , μA when plotting the logarithmic dependence of the current value on the concentration of zinc in an electrolyte.

3. Results and discussion

In this work, the following studies were conducted with and without stirring in a background solution of sodium sulphate: the dependences of the current density on time were obtained during the potentiostatic measurements with various cathodic potentials: -1100 , -1150 , -1200 , -1250 mV (AgCl/Ag) (Fig. 1 a,b) and additions of the LSTP foaming agent (Fig. 2 a,b). The dependences of the current density on the concentration of zinc in an electrolyte were

obtained in the potentiodynamic mode with the linear potential sweep of 20 and 100 mV/s (Fig. 3) and on the square root of the linear potential sweep of rate (Fig. 4).

During electrolysis in the presence of a background sodium sulphate solution, zinc deposited on an electrode darkens with cathodic potentials of more than -1150 mV in magnitude. It is related to the oxidation of reduced zinc and possible side reaction of the reduction of sulphate ions on a cathode, as noted in [20, 22],

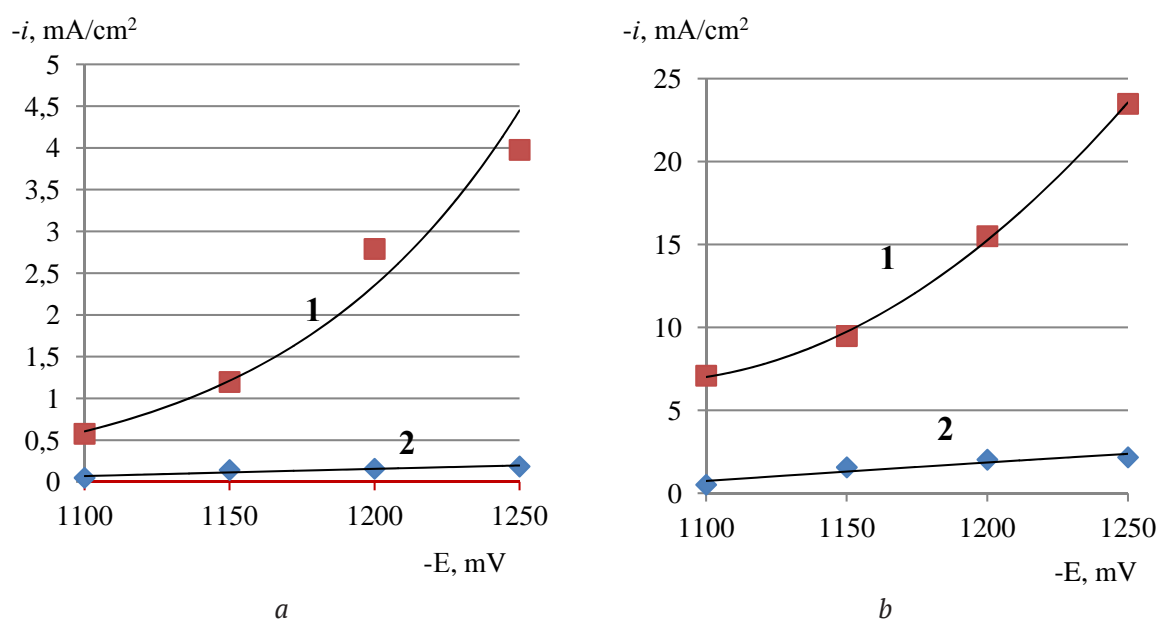


Fig. 1. Dependence of current density (i) on the cathode potential (E): 1 – with stirring; 2 – without stirring. The content of sodium sulphate 0.5 M and zinc sulphate in the electrolyte: a – 0.005 M; b – 0.025 M. The confidence interval at significance levels ($p = 0.05$) was 0.30 mA/cm² (a) and 1.14 mA/cm² (b)

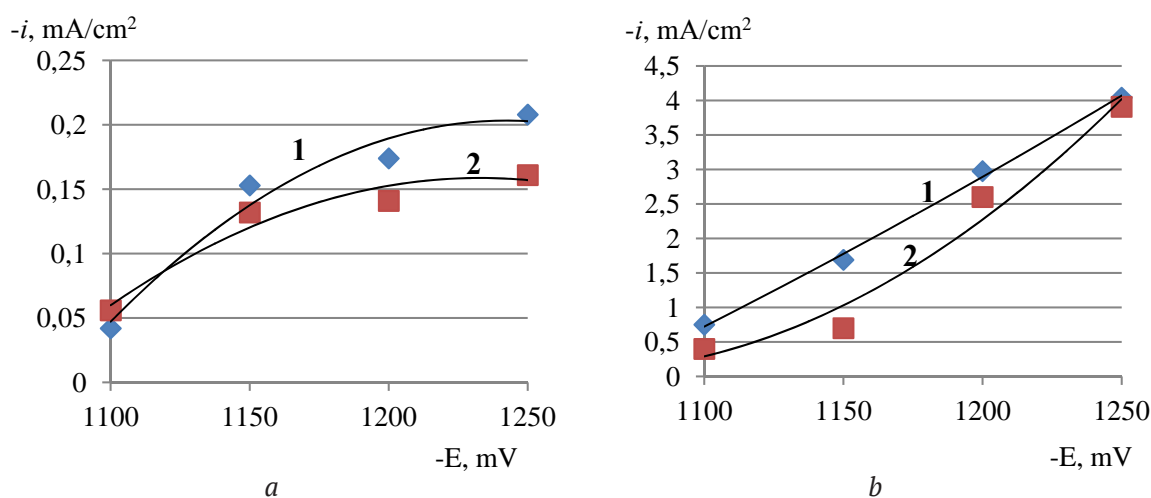


Fig. 2. Dependence of current density (i) on the cathode potential (E) under conditions without stirring (a) and with stirring (b). The content of sodium sulphate in the electrolyte is 0.5 M and the content of zinc sulphate is 0.005 M: 1 – without the addition; 2 – with the addition of 50 mg/l of LSTP. The confidence interval ($p = 0.05$) was 0.015 mA/cm² (2a) and 0.125 mA/cm² (b)

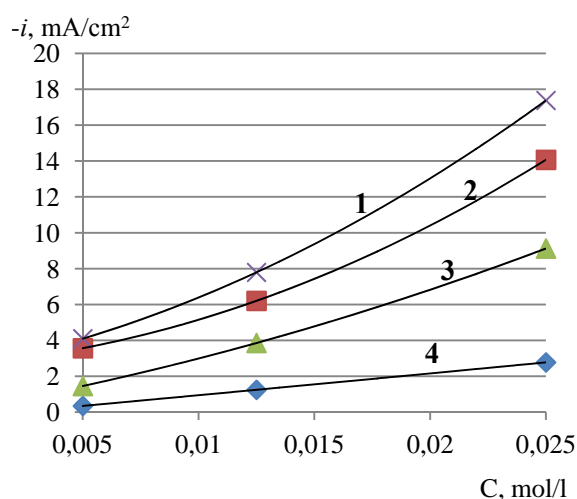


Fig. 3. The dependence of the maximum current density (i) on the concentration of zinc sulphate (C) in the background solution of 0.5 M sodium sulphate under the linear potential sweep in the potential range from -1050 to -1250 mV at a speed of 100 mV/s (1 – with stirring; 3 – without stirring) and with a sweep rate of 20 mV/s (2 – with stirring; 4 – without stirring). The confidence interval ($p = 0.05$) was 0.85 mA/cm^2

and justified by the conducted thermodynamic calculations and the obtained experimental data.

If we compare the polarisation curves (Fig. 1 a,b), a considerable increase in current densities (by ten times and more) can be observed under stirring with all potentials. Without stirring, the polarisation curves have linear dependence, while with stirring, the dependence of the current density change on the potential can be identified as a quadratic dependence. The obtained experimental data allow making an assumption about the increased contribution of the electrochemical stage into the overall rate of the zinc discharge process under stirring. Similar data were obtained when establishing polarisation curves using a potentiodynamic method with linear potential sweep in the potential range of $-1050 \div -1250$ mV (Fig. 4). When building the dependences of the current values on the square root of the linear potential sweep, it can be noted that the straight lines do not pass through the origin of coordinates. In this case, in [23] a conclusion is made that the process occurs in the mixed mode.

Without stirring, the effect of LSTP addition is not really seen at low cathodic potentials ($-1100, -1150$ mV) and the concentration of zinc in the solution 0.005 M. At the same time, under intense stirring we can observe a decrease in the

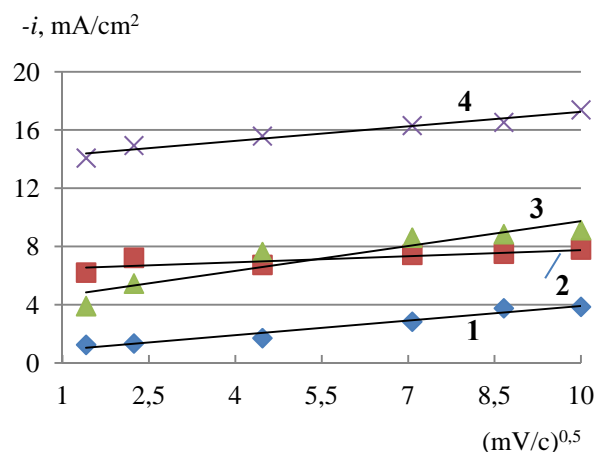


Fig. 4. Dependence of the maximum current density value (i) in a background solution of 0.5 M sodium sulphate on the square root of the linear potential sweep of rate in the potential range from -1050 to -1250 mV. 1 – zinc concentration (C) = 0.0125 M without stirring, 2 – $C = 0.0125$ M with stirring; 3 – $C = 0.025$ M without stirring, 4 – $C = 0.025$ M with stirring. The confidence interval ($p = 0.05$) was 0.85 mA/cm^2

current density in the above-mentioned potential range if we add 50 mg/l of LSTP (Fig. 2b). Based on the obtained data, we can make a conclusion that under stirring the LSTP foaming agent has greater influence on the stage of charge transfer through the “metal – electrolyte” interphase. Also, we assume that the addition of 50 mg/l of LSTP should not greatly influence the transport stage of zinc discharge process.

To study the mechanism of zinc electrolysis in a background solution of sodium sulphate under intense stirring, the reaction order was calculated by zinc ion with four potentials. The data of the discharge current values determined using the potentiostatic method [24] during the first second of the beginning of the process were used for the calculations. The calculations which were performed using the equation of the logarithmic dependence of the current values on the concentration of zinc in a solution are presented below:

$$I = K \cdot (C_{\text{Zn}^{2+}})^z$$

$$\lg I = \lg K + z \lg C_{\text{Zn}^{2+}},$$

where I is discharge current, μA , z is the reaction order for zinc ion, and K is a constant. The results are presented in Figs. 5 and 6.

Figs. 5 and 6 show that all dependences with high correlation coefficients ($R^2 = 0.98–0.99$ and higher) are described by straight lines. With the addition of the foaming agent, the reaction order for zinc for the studied system increases on average with 4 potentials from 1.224 ± 0.059 (without the addition) to 1.475 ± 0.126 . We believe that the increase of the reaction order over one in the concentration of zinc in an electrolyte in the system with stirring is related to the transition of the process from the diffusion to the mixed mode.

As the data obtained in galvanostatic mode showed, polarisation of the electrode in the presence and in the absence of the additives decreases under intense stirring. For example, with the current density of 1.7 mA/cm^2 (Fig. 7 a,b) polarisation decreases by 1.6 times with the addition of a cationic coagulant and almost by 3 times in the presence of the anionic coagulant without the addition. The obtained data showed a change in the mechanism of zinc electrolysis under stirring conditions, when the mass transfer

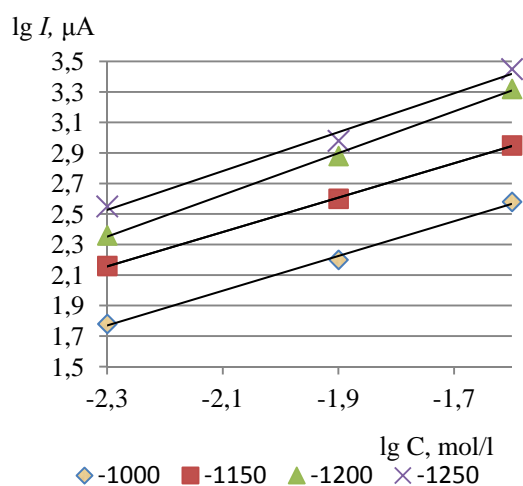


Fig. 5. The logarithmic dependence of the initial current density ($\lg I$) (for 1 s) on the concentration of zinc ($\lg C$) in the electrolyte with the Na_2SO_4 background (0.5 mol/l) at different potentials (-1100; -1150; -1200; -1250) mV according to (Ag/AgCl). Solution without foaming agent. Under stirring. The confidence interval ($p = 0.05$) was 0.11 ($\lg I$, μA)

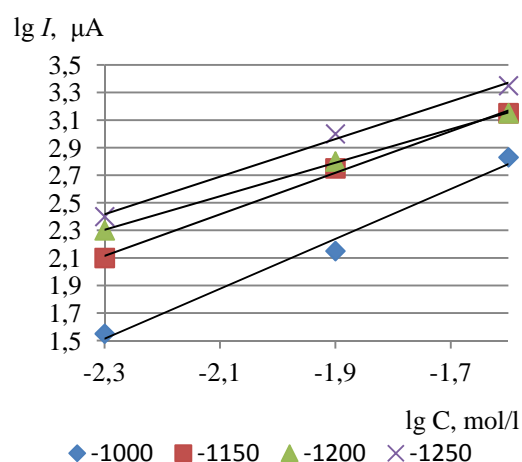


Fig. 6. The logarithmic dependence of the initial current ($\lg I$) (for 1 s) on the concentration of zinc ($\lg C$) in the electrolyte with the Na_2SO_4 background (0.5 mol/l) at different potentials (-1100; -1150; -1200; -1250) mV according to (Ag/AgCl). Solution with the addition of 80 mg/l of foaming agent. Under stirring. The confidence interval ($p = 0.05$) was 0.11 ($\lg I$, μA)

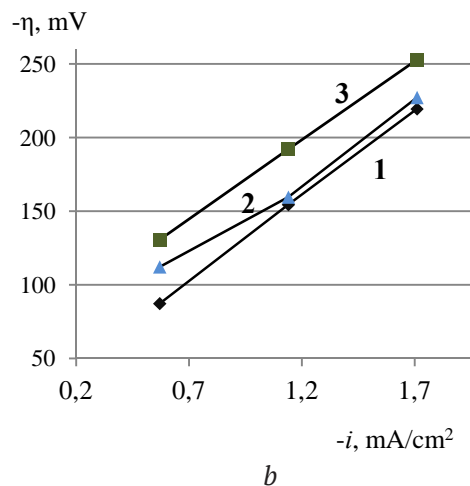
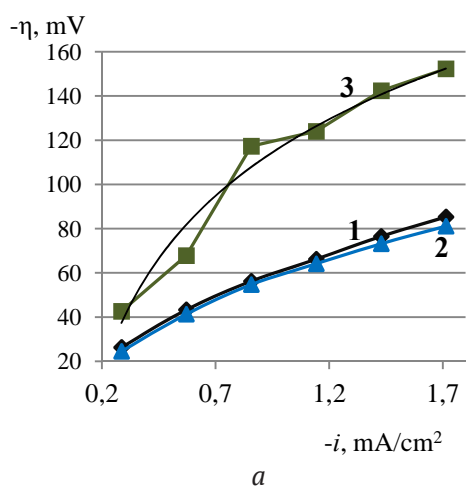


Fig. 7. Dependence of polarisation ($-\eta$) on current density (i) during electrolysis of a solution of $0.025 \text{ M ZnSO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$. 1 – without coagulant; 2 – anionic; 3 – cationic. With stirring, the confidence interval ($p = 0.05$) was 8.77 mV (a). Without stirring, the confidence interval ($p = 0.05$) was 6.82 mV (b)

process greatly accelerated and the contribution to the dynamics of the process of charge transfer stage through the “metal – electrolyte” interphase, the so-called electrochemical stage, started increasing. It was confirmed by the experimental data on the influence of cationic and anionic surfactants on the process of zinc discharge. In our opinion, if the process of zinc discharge was limited only by the transport stage (concentration polarisation), the unequal influence of differently charged coagulants on the cathodic process would be unlikely.

Therefore, the obtained experimental data under intense stirring in the presence of a background sodium sulphate solution, a foaming agent, and cationic and anionic coagulants (flocculants) correspond to the theoretical concepts of electrochemical processes [25–26].

4. Conclusions

The data obtained in this work, including quadratic dependence of current density of zinc discharge on the value of the cathode potential, the fact that the straight lines of dependence of current density of zinc discharge on the square root of the linear potential sweep of rate do not pass through the origin of coordinates, change in the reaction order for zinc electrolysis in the presence of surfactants, and an increase in the influence interval of differently charged surfactants on electrode processes, allow determining that the process of discharge of zinc ions in a background solution on a solid electrode occurs in a mixed-kinetic mode, where it is difficult to identify a significant contribution to the dynamics of the process of the stage of mass-transfer of ions or the charge transfer stage through the “metal – electrolyte” interphase.

Thus, the approach suggested in this work provided a greater degree of statistical reliability in evaluating the effect of additions of cationic and anionic surfactants on the stage of zinc discharge, which is of great importance for hydrometallurgical technologies and outlines further lines of research in this field.

Contribution of the authors

A. V. Kolesnikov – academic advisor, setting tasks, research concept, methodology, conclusions.
E. I. Ageenko – conducting experimental work,

participating in the analysis of the obtained data, text editing.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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