

ELECTROCHEMICAL EXTRACTION OF ZINC FROM ACID AND NEUTRAL REGENERATION SOLUTIONS

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Received: 06.09.2018

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Abstract. The results of the electrochemical separation of sulfate and zinc chloride regeneration solutions; the pH influence on the electrolysis process and the extracting efficiency of metallic zinc are presented in the work. It has been established that electrolysis should be carried out in a two-cell electrolyzer to remove metals effectively.

Key words: heavy metal, electrolysis, current density, cathode, sewage treatment.

1. Introduction

The main sources of formation of the wastewater contaminated with salts of metals, alkalis, acids by the enterprises of mechanical engineering and metalworking are galvanic and other production related to the chemical and electrochemical treatment of metal, cold cutting of metal, casting and painting. Concentrated or diluted wastewater is generated by contaminating ecosystems in the environment.

The wastewater of galvanic production largely contains heavy metal ions, which are not only highly toxic but also valuable components. Indeed, nowadays the loss of valuable metals and their removal from the sewage of galvanic production become an urgent issue not only in Ukraine but worldwide. Therefore, one of the main tasks is the development of new methods of purification, disinfection, neutralization, and recycling of contaminated wastewater at galvanic enterprises. Creation of closed water cycles in galvanic industries can solve this problem by using wastewater repeatedly, obtaining metals in a pure form and without contaminating the environment.

There are a lot of methods of extracting heavy metals from sewage, but every method has both advantages and disadvantages. In our opinion, some of the perspective methods are ion exchange and electrolysis. A combination of these methods allows concentrating metals on ion exchangers, and later easily regenerating them with acids. The obtained regeneration solutions can be recycled by electrolysis equipment to get acids and metals in a pure form, herewith acid can be reused by ion-exchange equipment.

Nowadays, there are many techniques under study that can separate the acid from the salts or concentrate the zinc content of the spent pickling baths [1-3]. Previously, in [4], the removal of heavy metals during electrolysis from neutral and weakly alkaline solutions, including zinc ions, was investigated [5]. In [6] the effect of applied potential, agitation rate, and reaction temperature on the efficiency of chlorine removal was investigated and dechlorination mechanism was explored. It is shown that the process of formation of chlorine gases depends on the parameters of the applied potential, reaction temperature and agitation rate.

In our previous work [7], a series of experiments was carried out on the extraction and regeneration of copper ions and zinc by cation exchanger KU-2-8 and the electrochemical separation of the obtained regeneration solutions. The results have shown high efficiency of copper extraction on the cathode in the presence of zinc ions, while zinc remains in the solution. Therefore, the next step in extracting metals from regeneration solutions was the experiment of depositing zinc ions in a single-cell electrolyzer with and without an excess of sulfuric acid to determine when the electrolysis process stops as well as to conduct

electrolysis of zinc chloride in a single-cell electrolyzer and compare the best conditions for zinc precipitation.

2. Experimental part

Electrolysis of model solutions of zinc sulfate and zinc chloride was carried out in a single-cell electrolyzer (Fig. 1).

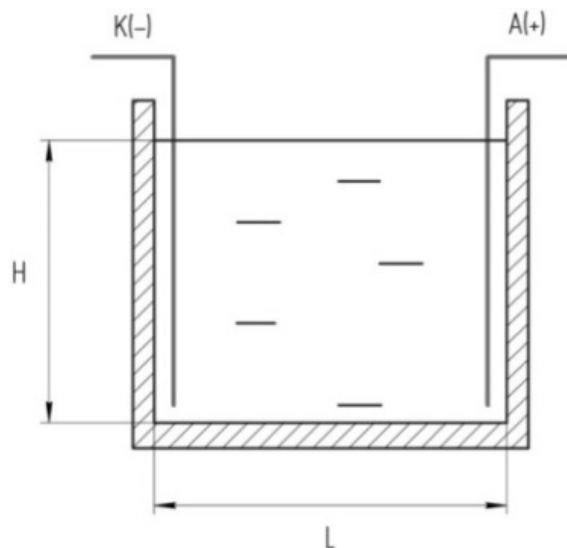


Fig. 1. A single-cell electrolyzer: H – height, L – width, K (-) – the cathode, A (+) – the anode

Zinc sulfate concentration was 500 mg-eq/dm³ and sulfuric acid – 0–200 mg-eq/dm³; zinc chloride concentration – 100, 500 mg-eq/dm³.

These model solutions were similar in composition to the obtained regeneration solutions with the volume of 0.2 dm³. The stainless steel cathode and the titanium anode coated by ruthenium oxide were used as

electrodes. The area of the electrode was 12 cm². Before the experiment, the steel electrode was polished and washed. The current strength was 0.5 A for all the experiments.

3. Results and discussion

3.1. Electrolysis of the zinc sulfate solutions

The results of electrolysis of zinc sulfate are shown in Fig. 2. From the graphs we can see that electrolysis occurred with extracting metallic zinc on the steel cathode, but for a certain period of time. In all the cases of the experiment the rate of zinc recovery decreases with the increase in the acidity of solutions (Fig. 3).

In case (1) from Fig. 2, 3 shows that the electrolysis was carried out without excess acid, the zinc deposition process stopped during the third hour of the experiment and the concentration of the metal was 320 mg-eq/dm³ and the acidity was 200 mg-eq/dm³. After electrolysis, the temperature = 28 °C, pH = 1.34.

In the following 3 experiments (Fig. 2, 3), the electrolysis process took place for about 5 hours, and then stopped. In the second experiment (2), at the beginning of electrolysis, the acidity of the solution – 50 mg-q/dm³, in the third (3) it was 100 mg-eq/dm³, and in the fourth (4) – 200 mg-eq/dm³. After completion of the electrolysis in the second experiment (2) – $C_{Zn^{2+}} = 240$ mg-eq/dm³, $K = 300$ mg-eq/dm³, $t_{sol} = 28$ °C, pH = 1.24; in the third (3) – $C_{Zn^{2+}} = 250$ mg-eq/dm³, $K = 350$ mg-eq/dm³, $t_{sol} = 26$ °C, pH = 1.12 and in the fourth (4) – $C_{Zn^{2+}} = 340$ mg-eq/dm³, $K = 350$ mg-eq/dm³, $t_{sol} = 23$ °C, pH = 1.10. From the results it can be seen that the increase in the acidity after the experiment led to the decrease in temperature.

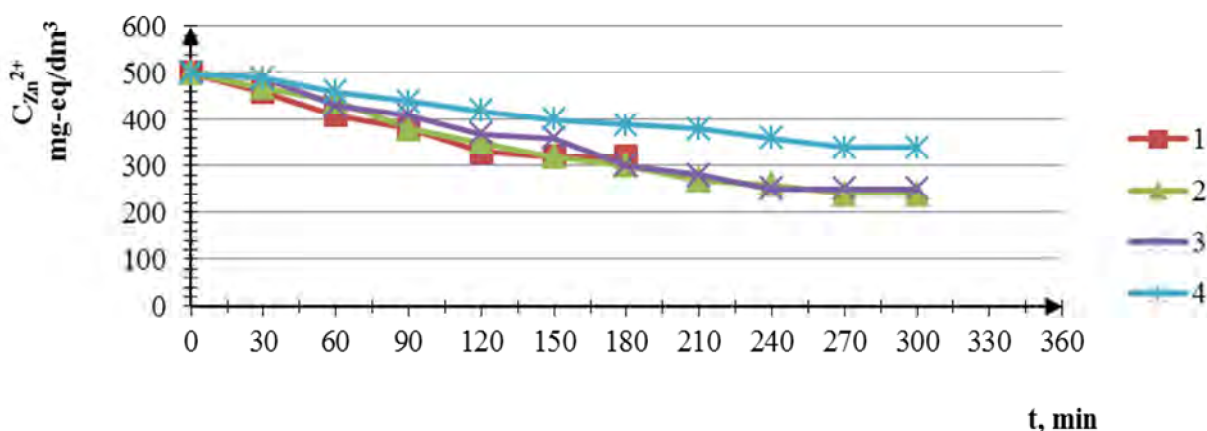


Fig. 2. Dependence of the residual concentration of zinc ions (1, 2, 3, 4) on the time of electrolysis of solutions containing 500 mg-eq/dm³ of zinc ions at the acidity of solutions 0 mg-eq/dm³ (1), 50 mg-eq/dm³ (2), 100 mg-eq/dm³ (3) and 200 mg-eq/dm³ (4), the current density – 3.33 A/dm² (1, 2, 3, 4)

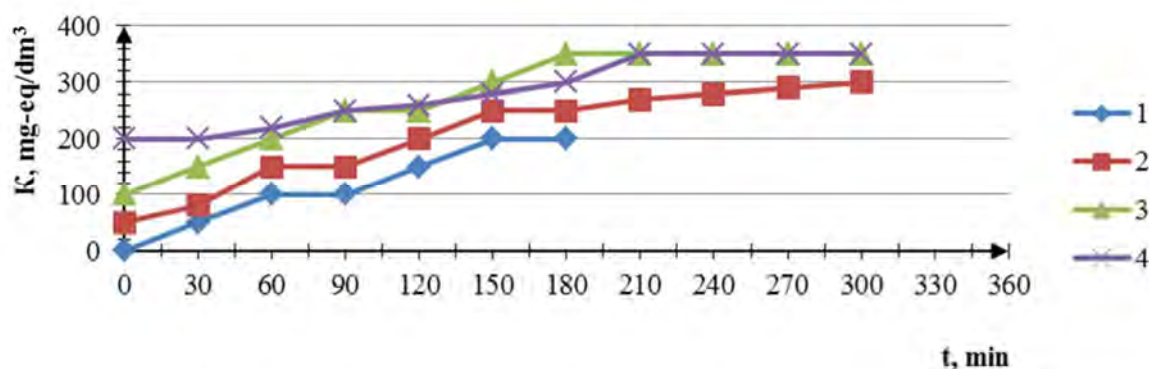
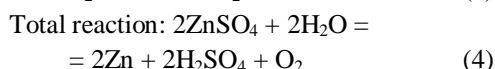
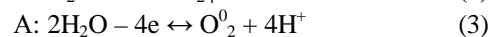
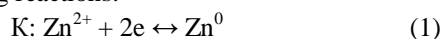


Fig. 3. Changing in the acidity of the zinc sulfate solution ($C_{Zn^{2+}} = 500 \text{ mg-eq/dm}^3$) depending on the time of electrolysis, the initial acidity 0 mg-eq/dm^3 (1), 50 mg-eq/dm^3 (2), 100 mg-eq/dm^3 (3) and 200 mg-eq/dm^3 (4), the current density – 3.33 A/dm^2 (1, 2, 3, 4)

Considering that in a range of voltage zinc is before hydrogen, but after aluminum, it is possible to precipitate it on the cathode and to emit hydrogen. In general, cathode and anode processes can be described by the following reactions:



In general, the process of zinc deposition occurs while there is the over-potential of hydrogen ions discharge on the cathode. With the increase in the amount of hydrogen ions the acidity increases, and the hydrogen over-potential decreases, as its absolute potential increases [8, 9] and the process of extracting zinc stops. It is also known that colloidal substances can be added to the solution in order to increase the hydrogen over-potential [8].

The value of voltage with the decrease in zinc ions concentration was also recorded during the experiments. Fig. 4 shows that the initial voltage in the first experiment (1) was 8.3 V , in the second one (2) it was 5.8 V , in the third (3) – 5.1 V , and in the fourth (4) – 4.1 V . The final voltage of the solutions in the first experiment (1) was 4.3 V , in the second one (2) it was 3.5 V , in the third (3) – 3.4 V , and in the fourth (4) – 3.4 V .

The results of the research showed that the electrolysis process of zinc sulfate in a single-cell electrolyzer is not effective (Fig. 5). This process should be carried out in a two-cell electrolyzer with an anion exchange membrane for separation of the cathode and anode areas [10, 11].

As a result, it is possible to obtain metallic zinc and sulfuric acid, which can be reused to regenerate ion exchangers for the implementation of non-waste processes of purifying sewage from galvanic plants.

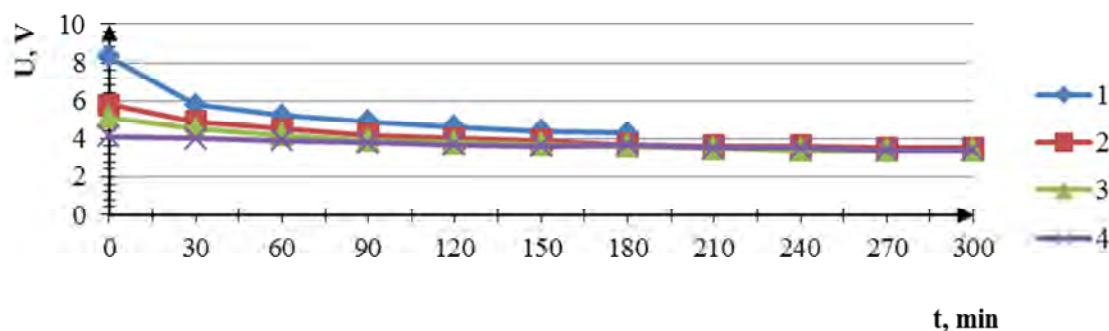


Fig. 4. Changing in the voltage of the zinc sulfate solution ($C_{Zn^{2+}} = 500 \text{ mg-eq/dm}^3$) depending on the time of electrolysis with the initial voltage 8.3 V (1), 5.8 V (2), 5.1 V (3) and 4.1 V (4) and the current density of 3.33 A/dm^2 (1, 2, 3, 4)

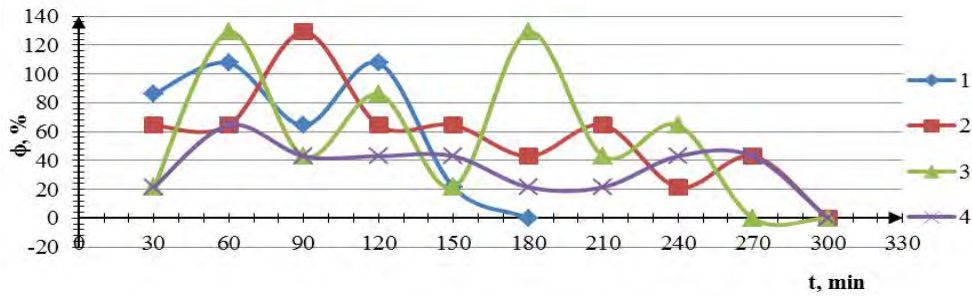


Fig. 5. Changing the current efficiency of recovered zinc with the time of electrolysis, depending on the composition of the solution and the density of the current:

- 1 – $C_{Zn^{2+}} = 500 \text{ mg-eq/mg}^3$, $K = 0 \text{ mg-eq/mg}^3$, $j = 3,33 \text{ A/dm}^2$;
- 2 – $C_{Zn^{2+}} = 500 \text{ mg-eq/mg}^3$, $K = 50 \text{ mg-eq/mg}^3$, $j = 3,33 \text{ A/dm}^2$;
- 3 – $C_{Zn^{2+}} = 500 \text{ mg-eq/mg}^3$, $K = 100 \text{ mg-eq/mg}^3$, $j = 3,33 \text{ A/dm}^2$;
- 4 – $C_{Zn^{2+}} = 500 \text{ mg-eq/mg}^3$, $K = 200 \text{ mg-eq/mg}^3$, $j = 3,33 \text{ A/dm}^2$

3.2. Electrolysis of the zinc chloride solutions

Experiment results are presented in Fig. 6. The graphs show that the reduction of zinc ions from the solution in a single-cell electrolyzer takes place almost completely for 8.5 hours (the current density of 3.33 A/dm^2). In the first experiment (1), the concentration of zinc chloride solution was 501 mg-eq/dm^3 , and at the end of the experiment, the concentration of the metal – 50 mg-eq/dm^3 . In the second experiment (2), the initial concentration of zinc ions was 100 mg-eq/dm^3 , and at the end of this study it was $\sim 0 \text{ mg-eq/dm}^3$. Measurement of

alkalinity is complicated by the presence of active chlorine in the solution. Also, the flakes of metal prevented the flow of electrolysis. Mixing the solution and cleaning the cathode contributed to the normal flow of the experiment.

In general, it was possible to reduce the concentration of metal to the minimum values in almost 9 hours, so the process of separation of zinc chloride in a single-cell electrolyzer is more effective than electrolysis of zinc sulfate. Change in the current efficiency of the recovered zinc with the time of electrolysis is presented in Fig. 7.

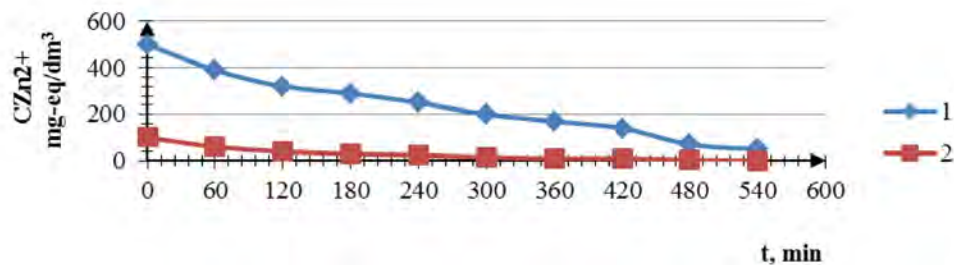


Fig. 6. Dependence of the residual concentration of zinc ions (1, 2) on the time of electrolysis of the solutions containing 500 mg-eq/dm^3 (1) and 100 mg-eq/dm^3 (2) of zinc ions, the current density 3.33 A/dm^2 (1, 2)

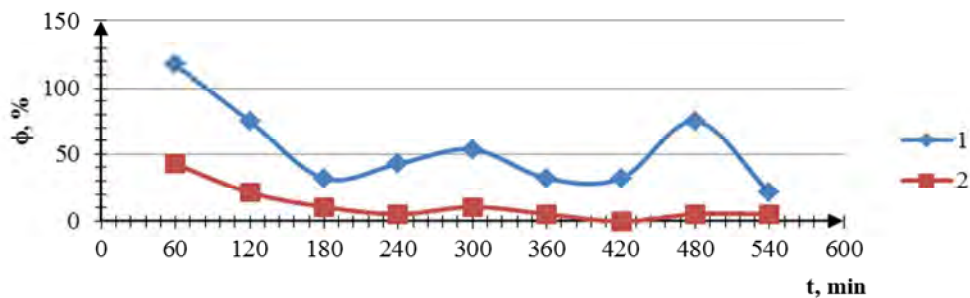


Fig. 7. Changing in the current efficiency of the recovered zinc with the time of electrolysis, depending on the composition of the solution and the current density:

- 1 – $C_{Zn^{2+}} = 500 \text{ mg-eq/dm}^3$, $j = 3.33 \text{ A/dm}^2$;
- 2 – $C_{Zn^{2+}} = 100 \text{ mg-eq/dm}^3$, $j = 3.33 \text{ A/dm}^2$

Also, during the research, the value of the voltage of the zinc chloride solution was fixed (Fig. 8). Graphs show that in the first experiment (1) the initial voltage

was 4.8 V, and at the end of this experiment it was 4.3 V; and in second experiment (2) the initial voltage was 11.7 V and the final voltage was 8.0 V, respectively.

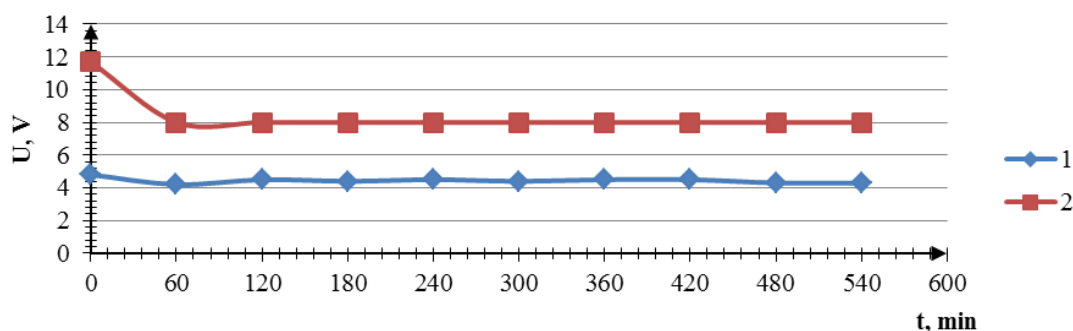
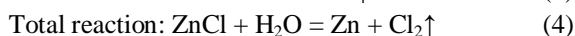
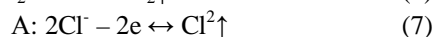
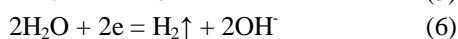
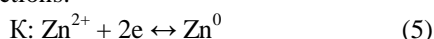


Fig. 8. Changing in the voltage of the zinc sulfate solution ($C_{Zn^{2+}} = 500$ and 100 mg-eq/dm³) depending on the time of electrolysis with the initial voltage 4.8 V (1), 11.7 V (2), the current density – 3.3 A/dm² (1, 2)

In general, processes occurring on electrodes can be described by reactions:



Reduction in zinc concentrations up to ~ 0–0.05 mg-eq/dm³ can be explained by the fact that the solution was not acidified during electrolysis, in the cathode sheath there was continuous hydrogen over-potential, and chlorine gas was evolved on the anode. The evolved chlorine gas can be disposed and used to disinfect water.

Conclusions

Electrochemical extraction of zinc ions from regeneration solutions with previously removed copper ions containing sulfates and chlorides in the single-cell electrolyzer with current density 3.3 A/dm² was carried out.

It was found that the electrolysis process of zinc sulfate is carried out until the solution is acidified and there is a competing reaction (2) on the steel cathode. It was also determined that electrolysis of zinc chloride can be carried out in a single-cell electrolyzer, reducing the concentration of metal to a minimum concentration in 9 hours.

In general, the electrochemical process of zinc deposition is expedient to be carried out in two-cell electrolyzers with an anion exchange membrane, for separating the cathode and anode areas. In this case, it is possible to concentrate the acid and return it to the regeneration processes, which makes it possible to create closed cycles of sewage treatment of galvanic production.

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