INTENSIFICATION OF ZINC DISSOLUTION PROCESS IN SULPHURIC ACID

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Abstract

Many high purity salts are produced by dissolving pure metal in non-oxidizing mineral acids. If hydrogen overpotential on the given metal is high, then the rate of overall process is defined by reaction of hydrogen ion reduction. This study investigated the possibility of accelerated dissolving of metal zinc in sulphuric acid by introducing copper cathode on which evolving hydrogen is much easier than on zinc. It was found out that the acceleration of zinc dissolving is possible and, at constant surface of copper cathode, depends on the quality of electrical contact between copper electrode and zinc.

1. Introduction

In the process of zinc sulphate industrial production by the influence of sulphuric acid to the grains of chemically clean zinc, it is observed that

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process of the grain dissolution is relatively slow. To increase the efficiency of production plant, there is an interest to accelerate the process of metal dissolution, because in the total process of zinc salts production (chrystalohydrates), which consists of several successive processes, zinc dissolution is the slowest process and limits the capacity of production plant.

Basically, the problem of slow dissolution of metals in non-oxide acid solutions is substantially connected with the process of hydrogen evolution that follows. In fact, because of the nature of some metals, and there especially stand out zinc, cadmium, tin etc, the process of hydrogen evolution goes with great overpotential that is very slow [1].

2. Theoretical consideration

2.1. Dissolution of zinc as corrosion process

The dissolution of two valence metal more electronegative than hydrogen (in this case it is zinc), in sulphuric acid solution, represents the complex reaction consisting of several degrees, some developing successively and some simultaneously. Having in mind that the process of metal dissolution is followed by hydrogen evolution (the reduction of hydrogen ion), this process can be treated as zinc corrosion with hydrogen evolution [2].

The reaction of zinc dissolution in sulphuric acid solution can be represented by the equation [1]:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

(1)

or the equation (2):

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \tag{2}$$

If these two reactions are observed separately in the process of corrosion, then, by the consistent appliance of regularities on which corrosion processes in electrolytes are based, each of the reactions can be represented by Tafel lines in the system of potential-logarithm current density.

Such a case is shown in the Fig. 1 where instead of metal M, zinc can be observed [3].
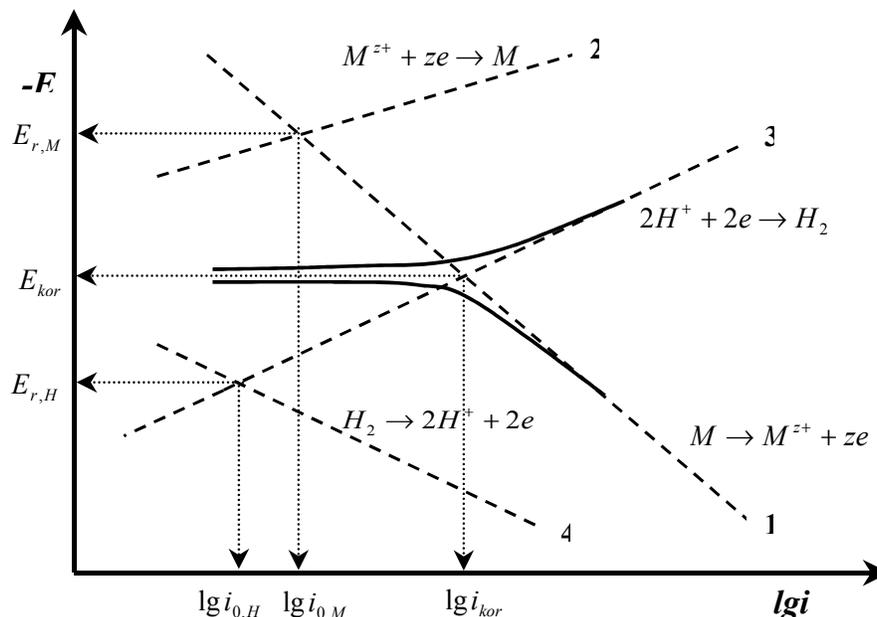
Fig. 1. The process of zinc dissolution followed by hydrogen evolution is shown as corrosion process (dashed lines represent Tafel lines for separate processes and full line represent the curve of total reaction

In Fig. 1 diagram shows: potential (E) – log of current density (log i), the equilibrium process of deposition and dissolution of metal M.

$$M^{Z+} \pm ze \Leftrightarrow M \qquad (3)$$

where M can be zinc, analogically, equilibrium potential on hydrogen electrode:

$$2H^+ \pm 2e \Leftrightarrow H_2 \qquad (4)$$

The balanced process on metal M (that is zinc), is shown by anodic Tafel line 1 and cathodic Tafel line 2, where section presents the equilibrium potential of the process $E_{r,M}$, i.e. the exchange current density of process $i_{o,M}$, while corresponding processes on hydrogen electrode are represented by the curves 4 and 3, i.e. by equilibrium potential $E_{r,H}$ and exchange current density $i_{o,H}$.

According to reaction properties in corrosion couple follows that the speed (current density) of anodic reaction (here zinc dissolution) must be equal to the speed (current density) of cathodic reaction – hydrogen evolution.

To accelerate the process of zinc dissolution, it is necessary to accelerate the process of hydrogen evolution [4] (in the same extent because of the conditions of current equality on corrosion potential). However, hydrogen evolution on zinc surface is a slow process controlled by overpotential of this reaction, it controls the speed of zinc dissolution, so the problem of acceleration zinc dissolution can be solved by examining the ways of acceleration hydrogen evolution during this process [5].

The above mentioned analysis, influence of dissolved oxygen on zinc dissolution was not included, having in mind vigorous hydrogen evolution during zinc dissolving, and oxygen elimination from solution in such a way.

2.2. Electrochemical evolution of hydrogen

The reaction of hydrogen ion, presented by the equation (4), tells nothing about the real mechanism of its developing, overpotential of its developing, the influence of a kind of metal on which the reaction appears, kinetic reaction etc. Namely, no matter if the reaction of hydrogen ion comes in the electrolytic process or during the corrosion, hydrogen appears, in any case, on the limit surface on which H^+ ion receives an electron. It is either the surface of a cathode made of some metal (or non-metal), or the surface of metal that corrodes (dissolutes). As the catalytic influence of metal, on which appears the reduction of hydrogen ion, is very significant (exchange current density i_o for this reaction on platinum is 10^{-3} A/cm^2 while on mercury is 10^{-13} A/cm^2), it is essentially important and that should be kept in mind because, watching macroscopically, they may have the key influence on the speed of reaction (4) [3, 6].

Not dealing with the possible mechanisms of hydrogen ion reduction and hydrogen evolution that clearly indicate the absorption influence of an electrode material [7], the influence of metal on which hydrogen ion reduction appears can be seen in Tafel equations (5) and (6).

Table 1. gives the values of Tafel constants *a* and *b*, defined by two independent methods for different metals at 20°C [3].

$$\eta = a + b \log i \qquad\qquad (5)$$

Where:

$$a = \frac{2.3 \cdot R \cdot T}{\beta \cdot z \cdot F} \cdot \log i_O \qquad b = \frac{- 2.3 \cdot R \cdot T}{\beta \cdot z \cdot F} \qquad\qquad (6)$$

Terms a and b stand for values i_o, R, T, β, z, F, all indicating the constants:

i_o – exchange current density, depending on metal nature;
R – universal (gas) constant;
T – the absolute temperature;
β - constant, so called "symmetry factor";
z – the number of exchanged electrons;
F – Faraday constant,

Where the variables are:
i – current density, and
η - cathodic overpotential.

Tafel equation in E–$log\ i$ diagram represents the line forming a section on ordinate equal to the constant a, while direction coefficient is given by the constant b (equation (6)). Comparing the values of a and b for certain metals in Table 1, it is observed that hydrogen, on a specific metal evolutes harder as the values of the coefficients a and b are higher, that is, if overpotential of hydrogen evolution is higher.

Table 2 gives the values of hydrogen separation overpotential (mV) on different metals under the low current density (1 mV/cm^2), the concentration of sulphuric acid 1,0 mol/dm^3, temperature 25°C [9].

Table 1. Values of the constants a and b in Tafel equation for the reaction of hydrogen evolution on different metals

metal	acid solutions		alkalic solutions	
	a	*b*	*a*	*b*
Pt	0.10	0.03	0.31	0.10
Pd	0.24	0.03	0.53	0.13
Au	0.40	0.07	-	-
W	0.40	0.1	-	-
Co	0.62	0.14	0.60	0.14
Ni	0.63	0.11	0.65	0.10
Mo	0.66	0.08	0.67	0.14
Fe	0.70	0.12	0.76	0.11
Nb	0.80	0.10	-	-
Ti	0.82	0.14	0.83	0.14
Bi	0.84	0.12	-	-
Cu	0.87	0.12	0.96	0.12
Ag	0.95	0.10	0.73	0.12
Ge	0.97	0.12	-	-
Al	1.0	0.10	0.64	0.14
Be	1.08	0.12	-	-
Sn	1.20	0.13	-	-
Zn	1.24	0.12	1.20	0.12
Cd	1.40	0.12	1.05	0.16
Hg	1.41	0.114	1.54	0.11
Pb	1.56	0.11	1.36	0.25

Table 2. Values of hydrogen overpotential η for certain metals

metal	Pt, platinized	Pd	Au	Fe	Pt, smooth	Ag	Ni	Cu	Cd	Sn	Zn	Hg
η, mv	0	0	20	80	90	150	210	230	480	530	700	780

Analyzing Tables 1 and 2 it can be observed that zinc shows one the highest overpotential of hydrogen evolution, which explains a slow dissolution of zinc in acids with evolution of hydrogen.

Decreasing overpotential hydrogen evolution on a specific metal can be influenced by increasing electrode surface (decreasing current density), increasing temperature, decreasing pH solution value, etc. [4, 5]. Table 2

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shows the influence of increasing surface (smooth and spongy platinized platinum), on overpotential hydrogen evolution.

Hydrogen evolution, being the reaction influenced by the nature of metal where it develops, can be accelerated if the reaction of hydrogen ion reduction can be "removed" on metal of low hydrogen overpotential (e.g.: Pt, Pd, Au etc.) [1,8,9].

The idea to accelerate the process of zinc dissolution during the production of zinc salt by dissolution zinc grains in sulphuric acid, is actually based on the possibility that reaction of hydrogen evolution appears on metal with less hydrogen overpotential reaction. Namely, a metal with low overpotential hydrogen evolution more electropositive than zinc is introduced in the solution of sulphuric acid where grains of zinc dissolute, and if such metal is electrically connected with zinc, the corrosion couple is formed where zinc oxidize and hydrogen ions reduce. In such a system, the reaction of hydrogen ion reduction is mainly "removed" from zinc to an insert metal, which has the role of corrosion couple cathode (well known corrosion effect), [1,2,3]. It enables hydrogen evolution easier resulting accelerated zinc dissolution. Similar solutions have already been used in some electrochemical technologies (amalgam dissolution in electrical production of chorine and hydroxide) [3,5,6,7]. It is, obvious that chosen metal should be more electropositive but zinc, and it would be best to use some of platinum group metals (because of their low hydrogen overpotential).

3. Results and discussion

3.1. Preliminary experiment

The preliminary experiment has been made to check the thesis about accelerated zinc dissolution in sulphuric acid solution in the presence of accessory copper electrode. Two zinc electrodes of cylinder shape have been used, each of about 50 g and about 15 cm^2, with copper conductors (contacts) melted in their basis. These electrodes have been measured and put into two separate glasses contaninig 100 cm^3 20 wt.% sulphuric acid solution, but copper conductors were not sunk in the solution. Copper plate has been put in one of glasses shortly connected with zinc electrode already set in that glass

(through mentioned conductor) while the second glass contained only zinc electrode. The experiments of zinc dissolution, in both glasses, lasted for 30 minutes. After that, zinc electrodes were taken out from the solution, washed, dried and measured. It was noted that the average speed of zinc electrode dissolution connected with the copper plate is about 6 times higher than of zinc electrode itself (1,34 g/h to 0,22 g/h).

3.1.1. First and second series of zinc grains dissolution experiments

To determine the dynamics of zinc grain dissolution in 20 wt.% of sulphuric acid solution, there have been made two series of experiments: dissolution of grains in the presence, and in the absence of copper electrode. The acid concentration and stehiometric surplus of zinc are chosen according to basic demands of concrete production process, to make the results of the analysis as close to real usage. Each of performed series incuded 13 experiments, lasting 5, 10, 20, 30, 45, and 60 minutes, 2, 3, 5, 8, 12, 18, and 24 hours. Each of the experiments was done by zinc of 18.4 g mass, of 99.995% purity and 115 g 20 wt.%-sulphuric acid solution of analyitical purity). Zinc mass that has been used in the experiments has been 30 mol percent higher than stehiometric amount of used sulphuric acid. These experiments have been done in narrow cylinder glass jars with high walls. Firstly the measured amount of zinc grains was put in such a jar and then the acid solution was added. In the experiments with copper electrode, grains of zinc were lowered on circle copper plate of jar diameter (about 7 cm) that was previously put at the bottom of reaction jar and then the acid solution was added.

After the mentioned time of duration, the experiments have been stopped, and obtained splutions have been put to analysis. In the experiments with copper electrode, the content of zinc, copper, sulphuric acid and pH solution values have been determined, while in experiments where copper electrode has not been used, copper has not been determined in obtained solution.

Fig. 2 gives the results of the series of zinc grain dissolution experiments in sulphuric acid solution, without using copper electrode and Fig. 3 gives the results with using copper electrode.
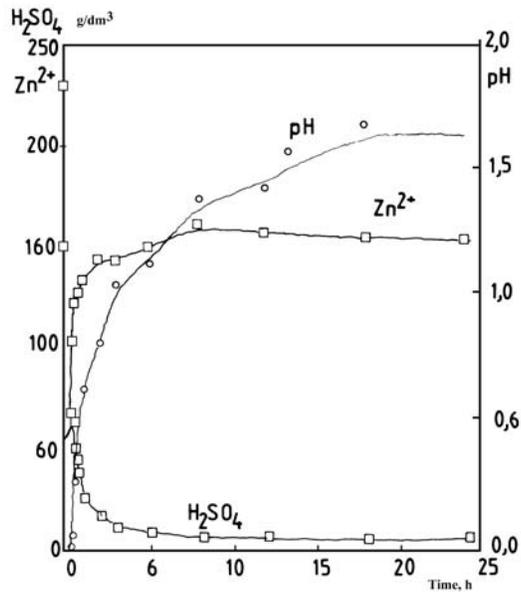
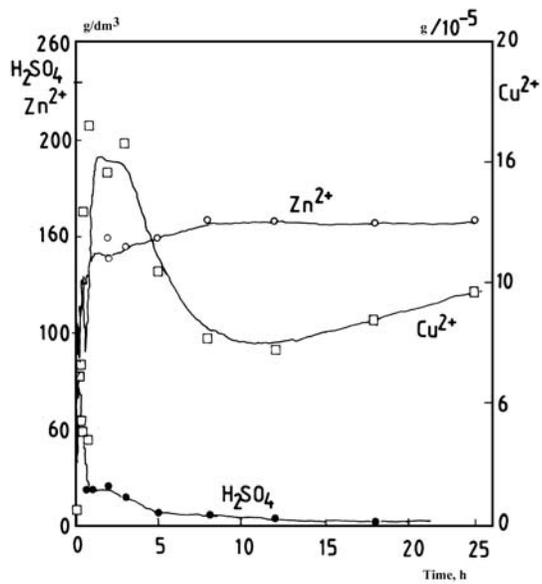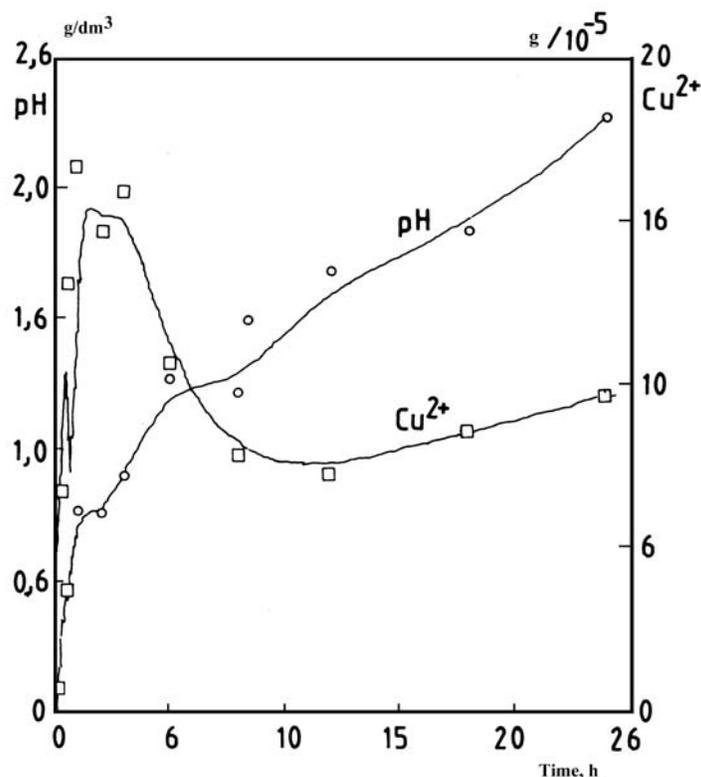*Fig. 2. Zinc dissolution in sulphuric acid in the absence of copper electrode*

Fig. 3. Zinc dissolution in sulphuric acid in the presence of copper electrode

Fig. 4 showes change of pH values and the content of copper in the solution (in the presence of copper electrode), depending on the experiment duration (data are given for the 2nd series of experiments).

Fig. 4. Copper dissolution in sulphuric acid in the presence of copper electrode (during zinc dissolution experiment)

Fig. 5 presents the contents of zinc in the solution during dissolution experiments in the presence (curve 2), and the absence of copper electrode (curve 1), (data are given for 1st and 2nd series of experiments), which enable determination of zinc grain dissolution speed in observed conditions.

Considering the speed of zinc dissolution in presented series of experiments, one apparently unusual phenomenon can be observed, and that is insignificant difference between zinc grain dissolution speed in the preesence and the absence of copper electrode. Zinc grain dissolution is faster

only only first 0.5 – 1 hour of the experiment duration in the presence of copper electrode. As the experiment goes on the difference between zinc grain dissolution speed in the presence and the absence of copper electrode disappears.
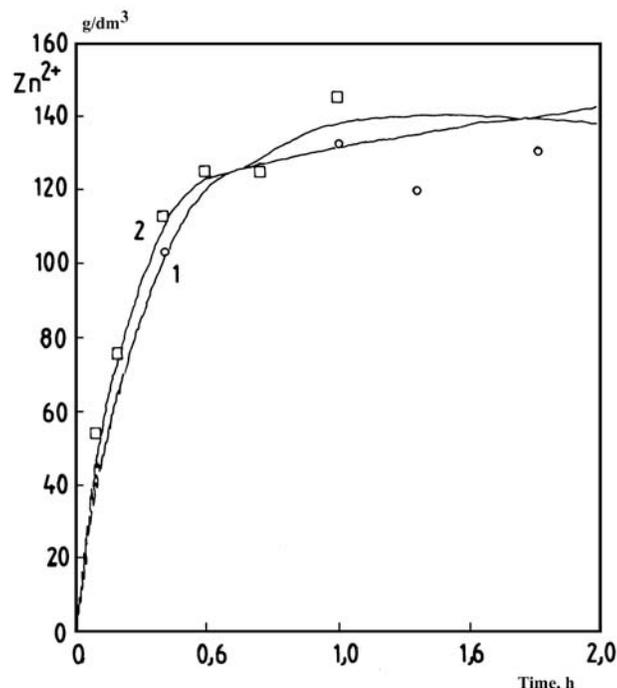

Fig. 5. Dependence of zinc content on the duration time of zinc dissolution

The observed phenomenon, almost having the same zinc grain dissolution speed in the presence and the absence of copper electrode, which appears limiting from the aspect of possibilities of accelerating dissolution process, is different from the results obtained in the preliminary experiment, where the significant increasing of zinc dissolution speed in the presence of copper electrode has been approved [10-14].

According to the conditions of the preliminary experiment and the results of the 1st and 2nd series of experiments, it is possible to presume the reasons for these deviations. Namely, the electrical contact of zinc grains with copper plate (in the experiments of zinc grain dissolution), is incomparable weaker

than the contact between copper electrode and zinc obtained through copper conductor melted in zinc cylinder (in the preliminary experiment). The situation becomes more unfavourable if we have in mind that with decreasing zinc grain mass and their lower pressure on copper electrode, the electrical contact of two metals additionally loses on its efficiency. All that leads to insufficient "remove" of the reduction H^+ ion from zinc to copper reaction, which slows down the process of grain dissolution [15-21]. Here, zinc dissolution speed directly depends on the hydrogen evolution speed, it is obvious why there is no expected acceleration of zinc grain dissolution in the presence of copper electrode.

From Fig. 3 and 4 it can be observed that in the presence of copper cathode, during the first few hours, increasing of copper content appears, followed by decreasing and finally stabilization of this ion at the value that is higher than the copper content in starting solution of sulphuric acid. This phenomenon can be explained by dissolution of copper(II) oxide from the copper electrode surface, while the amount of dissolute copper decreases by developing cementing processes on zinc, following lower acidity of solution.

The content of copper in the solution obtained at the end of zinc grain dissolution process does not disturb reaching analytical purity of solid zinc sulphate, being produced through several experiments evaporation of obtained solution to zinc sulphates crystals.

3.1.2. Third and fourth series of the experiments

To confirm the hypothesis given above, the third and fouth series of experiments have been taken, with zinc electrodes (cylinders, as in preliminary experiment) used again, examining their dissolution in the presence and the absence of copper plate electrode, this time excellently electrically connected with zinc cylinder, electrical conductor. The experiments were taken in the jars of similar shape as in the previous experiments, and for zinc dissolution it was taken 115 cm^3 of 20 wt.% sulphuric acid solution for each of experiments. The duration of the experiment has been limited in 5, 15, 35, 65, 75, and 120 minutes. In these series of experiments only the content of zinc in solution was examined in the function of time duration experiment.

Fig. 6 shows the results of the series of dissolution zinc cylinders experiment (curve 1), in the presence of copper plate electrode (curve 2).
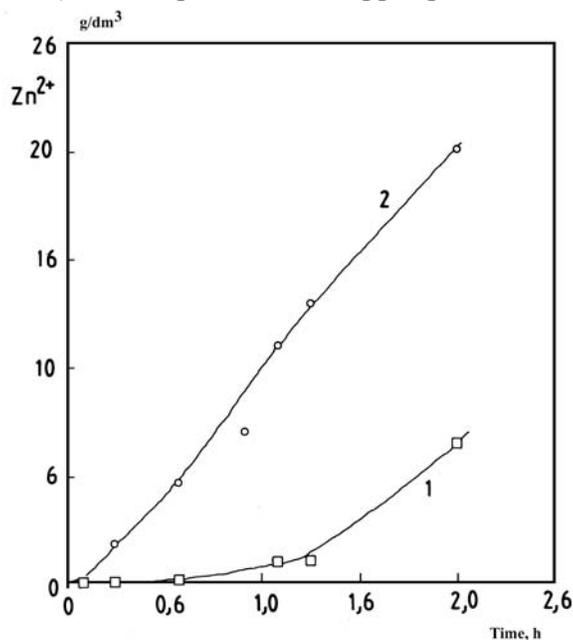

Fig. 6. Dependence of zinc content on zinc electrode dissolution time

Fig. 6 shows the results of the experiments which it can be seen that there obvious exist faster growth of zinc content in solution during zinc dissolution in the presence of copper electrode.

Considering the curves of zinc changing concentration in the solution, as the function of dissolution zinc cylinder time duration in the presence and absence of copper anodes, it can be observed that the difference in zinc dissolution speed in the presence and absence of a copper electrode is significant again, confirming the hypothesis given previously. The effects of acceleration zinc dissolution in this series of experiments are comparable with preliminary experiment, which confirms the significance of better zinc and accessory copper cathode contact.

3.1.3. Fifth series of experiments

In the fifth series of experiments, zinc grains were disoluted in the presence

of copper sawdust in the shape of sticks, dimension 40x1x1 mm, curved into an arch. This series of experiments has been taken to determine if this shape of copper electrode, trough copper and zinc electrical contact quality, has influence on zinc grain dissolution speed if other experiment conditions are constant. Namely, the contact of such pieces of copper with zinc is, according to the visual judgement, better than the contact when zinc grains are on copper plate.

18.4 g zinc grains, used in the first two series of experiments, are mixed with 15.0 g of copper sawdust. The solution of sulphuric acid has been added in that mixture (115 g 20 wt.% solution) in a glass jar with high walls, and the series of experiments has been done, in lasting of: 5, 10, 20, 40 minutes, 1 and 2 hours. These durations of the experiments have been chosen becacuse in the previous series of experiments, the differences dissolution speed have been observed exactly in that first 1 to 2 hours of experiment duration. The content of Zn^{2+}, H_2SO_4 and Cu^{2+} has been examined in obtained solutions. Fig. 7 shows the results of zinc grain dissolution obteined in the fifth series of experiments.
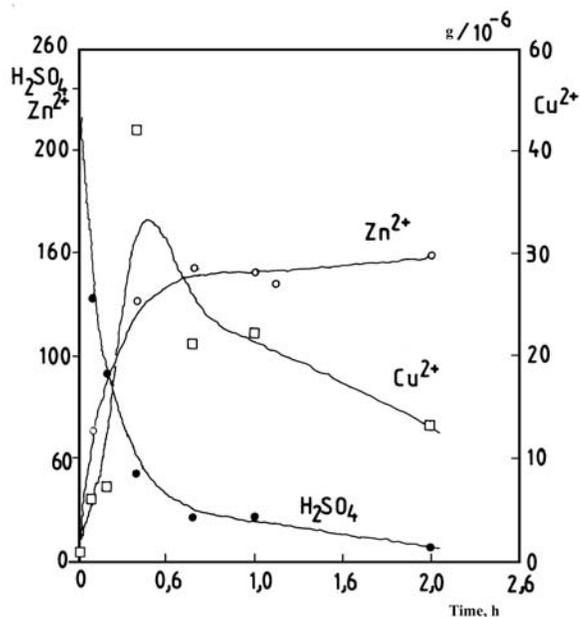

Fig. 7. Zinc dissolution in sulphuric acid in the presence of copper sawdust

In order to compare the efficiency of zinc grain dissolution, in the presence of copper plate electrodes that is copper sawdust. Fig. 8 shows the results of zinc concentration change from the fifth series of experiments (copper sawdust, curve 2) and the second series of experiments (copper plates, curve 1).
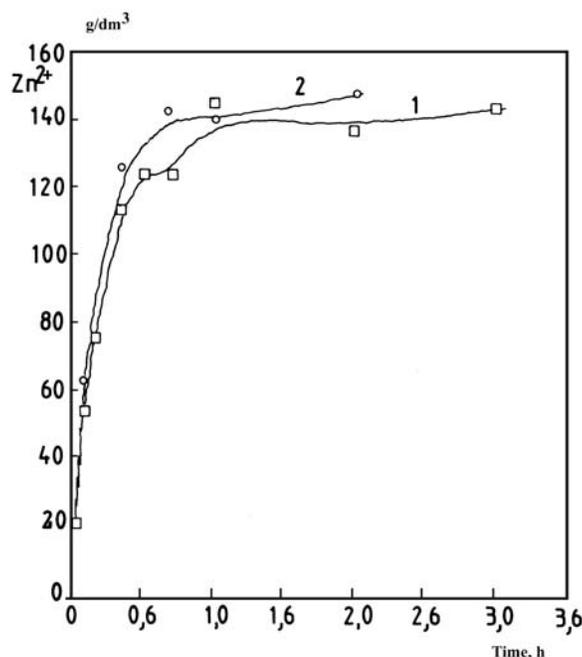

Fig. 8. Zinc dissolution in sulphuric acid in the presence of different shapes (copper electrode)

Considering the results of the fifth series of experiments shown in Fig. 7, it can be observed that by using copper in the form of sawdust, as an electrode, certain accelerated dissolution was observed comparing with the experiments in which copper plates have been used (as shown in Fig. 3). Zinc grain dissolution speed in the presence of copper plate and copper sawdust are shown together in Fig. 8 where they can be compared.

At the begining, the content of copper in this series of experiments grows but then starts to decrease, as in the second series of experiments, so it can be

assumed that the causes of this phenomen are the same in both cases.

The complete results of the fifth series of experiments of zinc grain dissolution show that the shape of copper electrode, through the contact quality at almost equal surface of copper in both experiments, influences the speed of grain dissolution.

3.2. Appliance of analysis results

The industrial plant for metal grain dissolution where zinc sulphate crystal hydrate [17] has been produced, consists of glass circulation reactor with perforated bottom, changer of heat, reservoirs for acid and demineralize water, storage receiving jars for sulphuric acid, receiving jars for zinc sulphate solution, vacuum filter and system for gases rinsing. The plants works in batch way. The process of zinc dissolution develops under the influence of acid on zinc grains, which are put on the perforated bottom of reactor. The sulphuric acid solution, with the help of a pump, circulates through the layer of zinc grains in the changer of heat, returning to the reactor after releasing gasses. When predominant acid quantity reacts, the rest of the acid is neutralized by the added zinc oxide, and then the solution is filtrated through vacuum filter to release the rest of solid phase. Filtrate, that contains metal salt solution has been brought into a receiving jar, and is further taken to section of evaporation and crystallisation.

To accelerate the process of zinc grain dissolution, according to the results of the analysis given in this paper, it is necessary to bring copper electrode in electrical contact with grains. The efficiency of this contact mostly depends wheter and how much the process of zinc grain dissolution could be accelerated. Although different technical solutions to this problem could be found: copper net where zinc grains are placed, copper perforated bottom of the reactor, copper basket that would be loaded with grainc etc., neither solution has been checked under industrial conditions [16]. Namely, having in mind that the glass reactor is in question with no possible design interventions, many possibilities of the usage of copper electrode must be rejected because of the risk of damaging the reactor or complicated manipulation during the introduction of such an electrode into the reactor.

The effects of accelereted zinc grain dissolution observed in the experimental part of the paper are related to static laboratory conditions for experiments. Real acceleration of zinc grain dissolution in industrial conditions could be observed only through industrial experiments in actual reactor. During the flow of electrolytes through the layer of zinc grains, many negative effects that follows the experiments in static conditions, mainly connected with diffusion phenomenon, disappear or are substantially reduced.

The maximum effects that are expected by the introduction of copper electrode can be obtained after determination and usage of an optimal form, size and type of copper electrode, which will be the subject of further analysis.

4. Conclusion

According to the complete theoretical observations and experimental work, the following may be concluded:

1. Zinc belongs to a group of metals with the highest overpotential of hydrogen evolution.
2. Zinc dissolution in sulphuric acid has all the characteristics of a corrosion process whose speed is controlled by cathodic reaction, that is, reduction of H^+ ion, and can be accelerated if the cathodic reaction accelerate.
3. The acceleration of cathodic reaction (reduction of H^+ ion) is possible if this reaction moves from zinc to a more electropositive metal that has less overpotential of hydrogen separation than zinc, where such metal has the role of cathode. The necessary condition for the appliance of such cathode is its surface as large as possible and best electrical contact with zinc.
4. Of all available metals with lower overstrain of hydrogen separation and lower price, in the analysis copper has been used as economically more accessible in the analysis.
5. The results concerning the acceleration of zinc dissolution in sulphuric acid with the usage of copper cathode showed the positive effects only in the cases when zinc and copper (no matter what their physical forms are) were brought in excellent electrical contact (the preliminary experiment, fourth serial and, partially, fifth series of experiments).
6. Concering the application of the analysis results in industrial plant for

zinc grains dissolution, it is necessary to make a selection of possible shapes and types of copper accessory cathode, in such a way not to imperil the correctness and plant readiness. The results of industrial experiments would give more realistic picture of the possibilities of zinc grain dissolution processes, as well as, the possibility for reduction the plant engaging time for dissolution, which has been the basic aim of this analysis.

Acknowledgements

References

1. S.Mladenović, Korozija materijala, Tehnološko-metalurški fakultet, Beograd, 1978. (In Serbian)
2. S.Mladenović, Corrosion Velocity of Ideal Clean Metals (Zinc) of the Base of Kinetics Theory, Zaštita materijala (Beograd), 40(1) (1999).
3. A.Despić, D.Draž ić, O.Tatić, Osnovi elektrohemije, Naučna knjiga, Beograd, 1970. (In Serbian)
4. S.Mladenović, Tehnička elektrohemija I i II, Tehnološko-metalurški fakultet, Beograd, 1974. (In Serbian)
5. D.Pletcher, Industrial Electrochemistry, Chapman and Hall, London, 1982.
6. C.L.Mantell, Electrochemical Engineering, McGrow Hill Book Company, London, 1960.
7. L.M.Rimenko, Elektrodnii materiali, Moskva, 1977. (In Russian)
8. M.Šušić, Osnovi elektrohemije i elektrohemijske analize, Naučna knjiga, Beograd, 1980.(In Serbian)
9. S.Đorđević, M.Maksimović, M.Pavlović i K.Popov, Galvanizacija, Tehnička knjiga, Beograd, 1998. (In Serbian)
10. D.Stanojević, M.B.Rajković i M.Jakšić, Poboljšanja u industrijskoj proizvodnji cinka, II jugoslovenski kongres za hemijsko inženjerstvo i procesnu tehniku sa međunarodnim učešćem, Dubrovnik, 10.–14.

maj1987.god., 10–III–5.(In Serbian)

11. D.J.MacKinnon and J.M.Brannen, Zinc Electrowinning from Chloride Electrolyte, *Mining Engineering*, (1982) 409-414.

12. D.J.De Biasio and C.J.Krauus, Electrolytic Production of Zinc, Canadian Patent, No. 978137, Nov. 4, 1971.

13. S.M.Rothman, Modernization Trends in Zinc Electrolysis Parameters for Zinc Electrolysis, Inter.Sym.Ind.Electrochem., Indian Inst.Technol., Madras, India (SAEST, Karaikudi), 1976, Dec. 14-17, Book of Abstracts, pp. 55-63.

14. M.L.Connoly, R.N.Honey and C.J.Krauss, High – Productivity Zinc Electrowinning Plant, 6th Annual Hydrometallurgical Meeting, *CIM Bulletin*, (1977) 144-151.

15. R.H.Farmer, Anode Pre – Conditioning and Other Changes in Cominco's Electrolytic Zinc Operations, Electrometallurgy, Proc.Extractive Metallurgy Division Symposium on Electrometallurgy, Clevland, Ohio, Dec. 2-3, 1968, Book of Abstracts, pp. 242-250.

16. C.J.Krauss, R.C.Kerby, R.D.H.Willans and D.Ybema, Cominco Zinc Electrowinning Anode Technology. Anodes for Electrowinning, Proceeding of the sessions sponsored by The Electrolytic Processes Committee of the Metallurgical Society of AIME held at the AIME Annual Meeting in Los Angeles, California, February, 28, 1984.

17. V.Montagne, Method of Purifying Zinc Sulphate Solutions, Patent spec. 139606, May 16, 1972.

18. M.B.Rajković, D.Stanojević and M.Jakšić, A Preconditioning Process for Extended Passivation of Alloyed Anodes in Zinc Electrowinning, The 11th International Congress of Chemical Engineering, Chemical Equipment Desing and Automation, CHISA '93, August 29 – September 3 1993, Praha, Czech Republic Republic, C: Technology and Engineering New Process Development, Ref.No.41.

19. M.B.Rajković, D.Stanojević, N.Krstajić i M.Jakšić, Pasivirajući efekat prekondicioniranja olovnih anoda na elektrolitičku proizvodnju cinka, IX jugoslovenski simpozijum o elektrohemiji, Dubrovnik, 03.-07. juni 1985.god., Knjiga radova, s. 242-244. (In Serbian)

20. M.B.Rajković, G.T.Vladisavljević, N.M.Ristić and M.M.Jakšić, A Preconditioning Process for Extended Passivation of Alloyed Lead

Anodes in Zinc Electrowinning, Bulletin of Electrochemistry, 14(3) March 1998, pp. 107–114.

21. M.B.Rajković, S.Štrbac and M.M.Jakšić, Improvements in Silver Alloyed Lead Anodes for Zinc Electrowinning, 8th International Conress CHISA '84, Praha, Czeckoslovakia, September 3–7, 1984, Poster V8.16, In Session: Electrochemical Engineering, No. 1106.