

## Study of the Electrolytic Regeneration of Spent Pickling Solutions under Conditions of Separated Electrode Spaces

S.I. Pinchuk, A.M. Greshchik, Ye.V. Belaya, A.N. Kovzik

*NMetAU*

The effect of current density, the cathode material and the duration of electrolysis on the process parameters (current output of the metal, the degree of extraction and the extent of acid regeneration) of the electrolytic regeneration of spent pickling solutions in the separated electrode spaces was investigated.

Keywords: ELECTROLYTIC REGENERATION, CATHODIC REDUCTION, PICKLING SOLUTION, IRON POWDER, CURRENT EFFICIENCY

### Introduction

The study of the regularities of the cathodic iron reduction from acid sulfate solutions have allowed to establish the fundamental possibility of recycling waste sulfuric acid electrolytic pickling solutions [1, 2]. With such processing, along with the problem of disposal of environmentally harmful waste of pickling plants [3, 4] it is possible to regenerate original pickling solution, and get valuable product in the form of iron powder.

It is established [2] that the traditional pattern of electrolysis with combined electrode spaces the power of extraction of dispersed iron increases with the duration of electrolysis. When the amount of electricity passed through the electrolytic cell is about  $120 \text{ A} \cdot \text{h/l}$  the level of iron extraction reaches its maximum - 70%. Further increase in the number of missed electricity causes a sharp decrease of the current efficiency of the iron deposit that is connected with a significant acidification of the electrolyte anode reaction products.

Improving the efficiency of the extraction process in the electrolytic iron refining of pickling solution can be achieved by the division of the cell electrode spaces to avoid mixing of solutions of the cathode and anode spaces. For the separation the electrochemical membrane selectively reflecting or not reflecting the electrolyte ions are used [5]. Proper selection of membranes ensures accumulation of hydrogen ions in the anode and cathode of iron in the cell spaces. Industrial production of electrochemical membranes is carried out in Russia (MF - 4 UK) and the USA

("Nafion").

The conditions of formation of cathodic reduction of iron powder in the cell with separated electrode spaces are studied. As a model of the electrochemical membrane porous glass partition with a relatively low electrical resistance was used, which significantly hinders mixing electrolyte.

### Results and Discussion

The results of studies of the effect of cathodic current density on the current efficiency of the iron sediment from the solution composition  $200 \text{ g/l FeSO}_4 + 20 \text{ g/l H}_2\text{SO}_4$ , as the most suitable composition of spent pickling solutions, are shown in **Figure 1**.

Dependence of the yield of current efficiency on the density is extreme. Maximum yield of current is about 65% at a current density of  $60 \text{ A/dm}^2$ . The structure of the deposit is essentially dependent on the magnitude of the current density. For small values of ( $5-10 \text{ A/dm}^2$ ) dense sediment with good adhesion to the substrate is formed. At current densities in the range of  $10-60 \text{ A/dm}^2$  predominantly powdery residue in separate easily destroyed by mechanical action dendrites are formed and at  $60-70 \text{ A/dm}^2$  the number of dendrites is about 80% of the total mass of sediment. All the sediment is relatively easily removed from the surface of the cathode.

The increase in current density up to  $90-100 \text{ A/dm}^2$  is accompanied by decrease in the proportion of dendrites in the sediment; one part of the sediment is difficult to remove from the surface

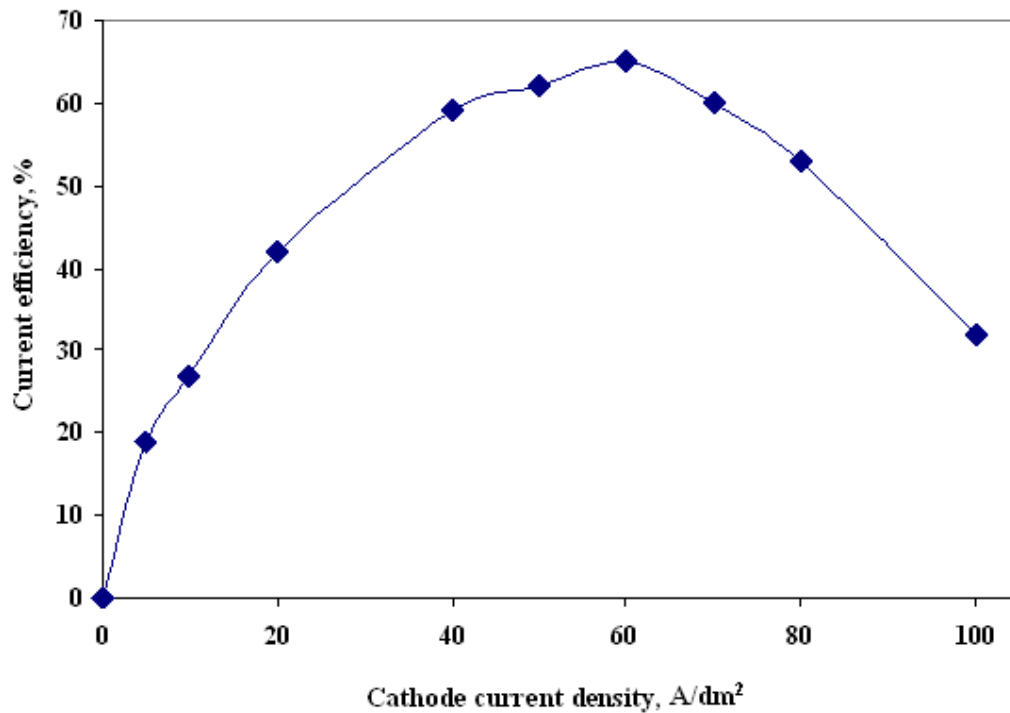


Figure 1. Effect of cathode current density on the current efficiency of metal

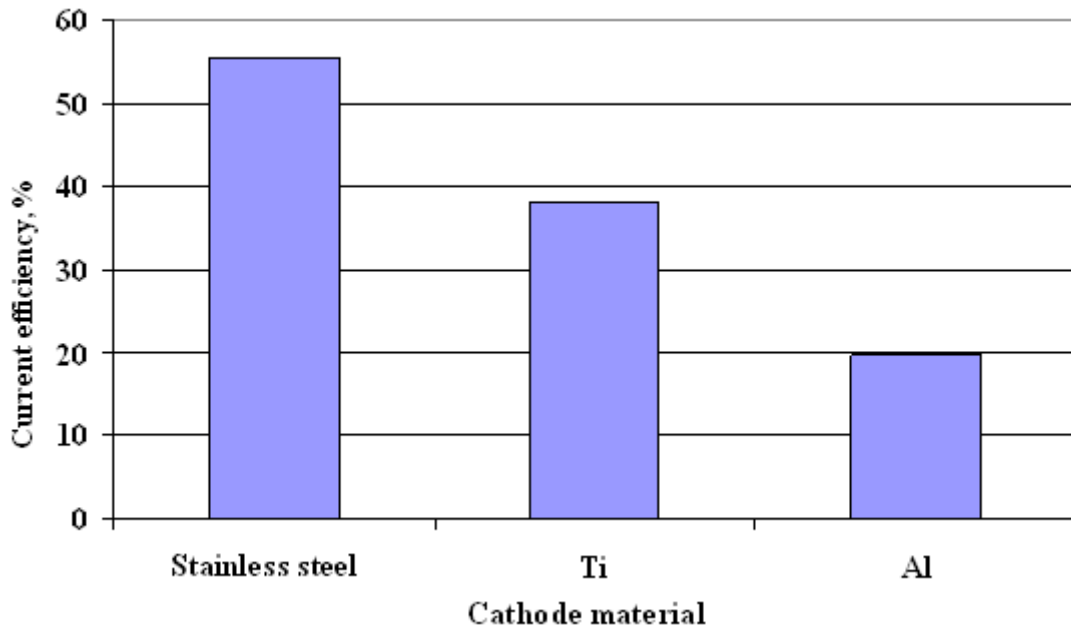


Figure 2. Effect of cathode material on the current efficiency of iron powder

of the cathode. The iron output of current efficiency decreases.

Thus, we can recommend the reduction of iron powder from spent sulfuric acid of pickling solutions under conditions of separated electrode spaces at a current density of about 60 A/dm<sup>2</sup>.

At high current densities, a significant impact on the structure of the sediment and nature of its crystallization as well as the output current of the metal is caused by the nature of the cathode

material [6, 7]. The character of expansion of powdered cathode deposit depends on the ratio of the velocity of the nucleation and growth of crystallization center on the surface of the cathode. If the surface of the cathode is covered with thick oxide films then the structure of deposited metal is finely crystalline, since there is a significant number of crystallization centers. On the primary layers of sediment in the future many small branched of crystals are created i.e. in general

## Anticorrosive Protection of Metals

finely loose sediment is obtained.

The substrate has an effect on the crystallization of loose cathodic reduction of iron sediments due to different ratios of active and passive parts of the surface of cathodes and macro- and micro-relief. That is, the nature and surface conditions of cathodes are determined by laws of the initial stage of formation and distribution of nuclei on the surface that causes the formation and the subsequent character of the deposit.

Dependence of the yield of iron current efficiency during electrolysis on the nature of the cathode material is related to the hydrogen overvoltage at the cathode. This impact, however, occurs mainly in the initial stages of electrolysis. More significant impact on the current efficiency is provided by structure and nature of the subsequent expansion of loose sediments. Particularly significant it is manifested in the use of different metals as cathodes. The use of alien to the material sediment of cathodes, i.e. iron, leads to a different nature of redistribution between the co-flowing current during the discharge of metal ions and hydrogen.

**Figure 2** shows the effect of the nature of cathode metal on the current efficiency of iron powder at current density of  $60 \text{ A/dm}^2$ .

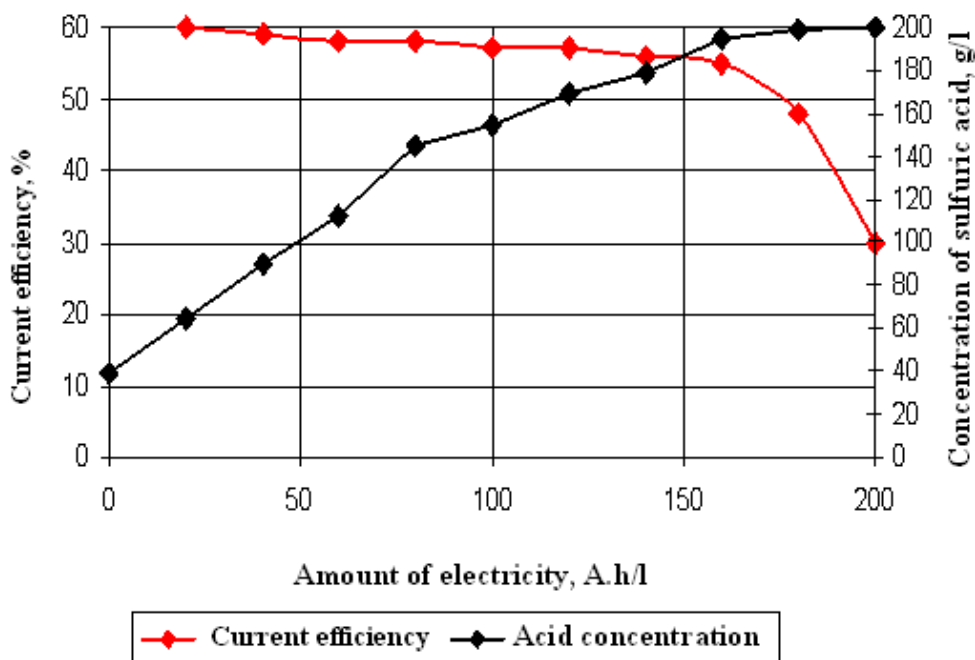
The highest current efficiency occurs at the cathodes of stainless steel that gives the basis to recommend this material in the organization of industrial processing of spent pickling solutions

under conditions of separating electrode spaces in electrolytes. This mode allows obtaining the iron powder with current efficiency of at least 60%, the powder is highly dispersed, contains powdery dendrites and is easily separated from the cathode surface.

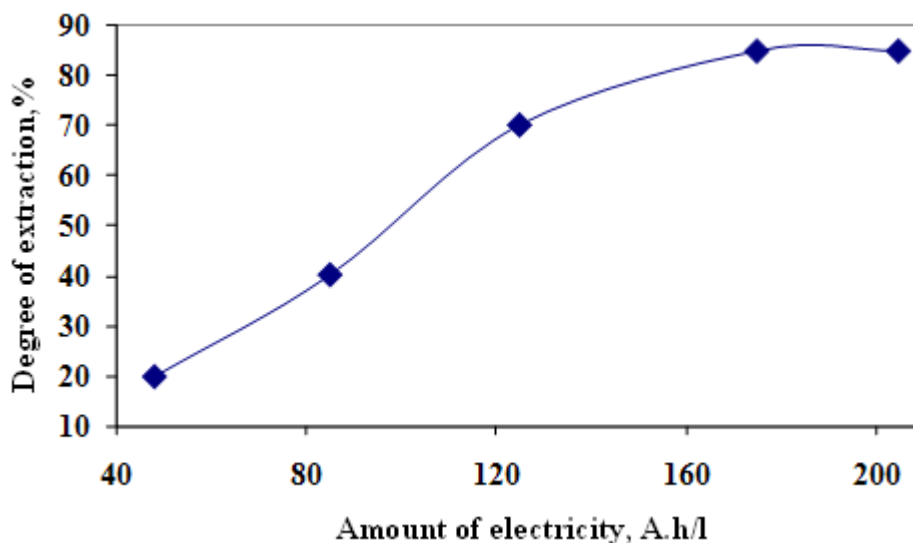
For development of technologies of the electrolytic regeneration of spent pickling solution the changes of the current efficiency of metal, the concentration of iron and sulfuric acid in the electrolyte are studied, i.e. as its production at increase in quantity of electricity passed through the electrolytic cell. The development of the electrolyte was carried out at a density of  $60 \text{ A/dm}^2$  cathode current, using a stainless steel cathode and the anode of lead. Periodically, at intervals of two hours, the electrolysis was stopped and the current concentration of sulfuric acid in the electrolyte was determined. By the mass of iron powder its current efficiency was calculated. The results are presented in **Figure 3**.

With increasing number of electricity passed through the electrolytic concentration of sulfuric acid in the anode space increased by about ten times (20 to  $200 \text{ g/l}$ ). Changes in the iron current efficiency, namely its sharp decline becomes noticeable after passing of electricity through the electrolyte of  $160 \text{ A} \cdot \text{h/l}$ .

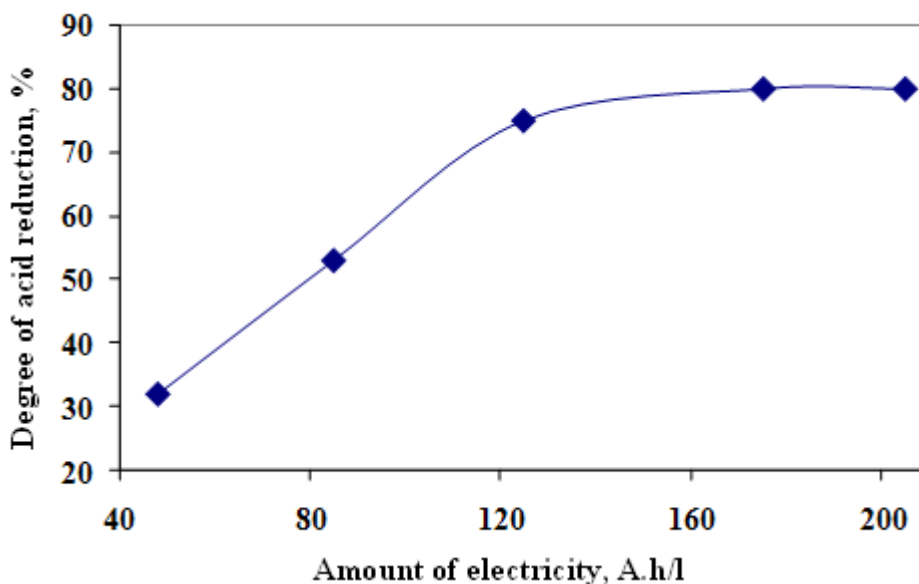
The calculated values of the degree of extraction of iron from the electrolyte to the extent of its production are shown in **Figure 4**.



**Figure 3.** Influence of the duration of electrolysis on the iron current efficiency and concentration of the acid in the electrolyte



**Figure 4.** Influence of the duration of electrolysis on the degree of extraction of iron



**Figure 5.** Influence of the duration of electrolysis on the level of acid reduction

As can be seen in **Figure 4**, the degree of extraction of iron with the number of the missed electricity increases with the amount of about 160 A • h / l and reaches its maximum - about 90%.

If we assume that at etching a 20% sulfuric acid is used, ie acid with an initial concentration 230 g / L, then the regeneration rate (CP) of sulfuric acid can be calculated according to the equation

$$CP = C_{cur.} / C_{bas.} \cdot 100 \%,$$

where  $C_{cur.}$  – current concentration of acid in the anode zone, measured with increasing number of the missed electricity.

The degree of acid reduction in process of development electrolyte increases with the number of missed electricity 160 A • h / l and reaches its maximum - about 85% (**Figure 5**).

According to an analysis of the theoretical and experimental research for industrial use a cyclic scheme of electrolytic iron extraction from spent pickling solutions with the separation of the electrode spaces in cells is suggested. Each cycle of the process should be economically feasible to conduct the number of transmitted electricity not more than 150-160 A • h/l. The next cycles of the process include regeneration of the following portions of spent pickling solutions.

Calculation of the efficiency of the electrolysis

process of recycling waste of pickling solutions according to the method given in [2] showed that the performance of the electrolytic bath 1 m<sup>3</sup> is 2.5 kg / h, and the unit cost of electricity - 6.0 kW • h per kilogram of produced iron powder.

Thus, the rational mode of electrolytic refining of waste sulfuric acid pickling solutions under conditions of the electrode spaces separation in cyclical pattern of the process will provide the degree of extraction of iron from the spent pickling solution up to 90% at the degree of regeneration of sulfuric acid 85%.

### Conclusions

1. Under the conditions of the use of an insoluble anode and electrode spaces separation of electrochemical cell extraction of dispersed iron from spent pickling solutions is characterized by current efficiency of about 60% at a current density of 60 A/dm<sup>2</sup>.

2. Investigation of the effect of the cathode material on the efficiency of the iron extraction process allows recommending stainless steel X18H9 as the cathode material for electrolytic iron refining of pickling solutions.

3. It is established that according to the cyclic pattern the electrolysis refining process should be economically feasible conducted to the amount of missed electricity no more than 150-160 A • h / l. In this case, extraction of iron from spent pickling solutions will be about 90%, the degree of acid reduction - at least 85%, the unit cost of electricity will not exceed 6.0 kW • h per kilogram of cathode reduced iron powder.

### References

1. Issledovaniye protsessa vosstanovleniya zheleza iz kislykh sulfatnykh elektrolitov, S.I. Pinchuk, A.M.

Greshchik, Ye.V. Belaya, A.N. Kovzik, Metallurg. i gornorud. prom-st, 2008, № 4, P. 86-87.\*

2. Issledovaniye zakonornostey katodnogo vosstanovleniya zheleza iz otrabotannykh travilnykh rastvorov, S.I. Pinchuk, A.M. Greshchik, Ye.V. Belaya, A.N. Kovzik, Metallur. i gornorud. prom-st, 2010, № 6, P. 72-73.\*

3. Lipkin Ya.N., Devyatkina T.S., Goldshteyn Ya.I. Khimicheskaya obrabotka stalnogo prokata, K.: Tekhnika, 1980, 136 p.\*

4. Yampolskiy A.M. Travleniye metallov, M.: Metallurgiya, 1983, 168 p.\*

5. Koryta, Irzhi. Iony, elektrody, membrany. Per. s chesh., M.: Mir, 1983, 264 p.\*

6. Nichiporenko O.S., Pomosov A.V., Naboychenko S.S. Poroshki medi i ee splavov, M.: Metallurgiya, 1988, 206 p.\*

7. Kiparisov S.S., Libenson G.A. Poroshkovaya metallurgiya. M.: Metallurgiya, 1980, 495 p.\*

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### Исследование электролизной регенерации отработанных травильных растворов в условиях разделенных электродных пространств

Пинчук С.И., Грещик А.М., Белая Е.В.,  
Ковзик А.Н.

Исследовано влияние плотности тока, материала катода и продолжительности электролиза на параметры процесса (выход по току металла, степень его извлечения, степень регенерации кислоты) электролизной регенерации отработанных травильных растворов в условиях разделенных электродных пространств.