Obtain of sulfuric acid at the electrochemical processing of eluates

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Abstract – It is shown that by the electrolysis of eluates it is possible to obtain sulfuric acid solutions. It was found that in process of electrolysis sulfuric acid concentration can be increased up to 44% at very satisfactory values for the current output. It was found that with increasing current density the rate of electrochemical concentration of sulfuric acid significantly increases at the anode with decreasing acid current efficiency.

Key words – sulfuric acid, anion exchange membrane, electrodialysis; electrolysis; reverse osmosis; ion exchange; concentration; desalting; processing of eluates.

I. Introduction

The problem of rational water consumption is under the high interests in world in general, same in Ukraine particularly. The main reason of this situation is that the most difficult problems of water supply and water treatment are not solved. The local and industrial installations of baromembrane and ion exchange desalinization of water are widely spread and common. Unfortunately, the problem of regeneration of solutions after ion exchange still has no it's solution, even due the fact, of its construction and automatization of process. Discharge of these solutions down the city sewer system or into the natural water bodies leads to a significant water salinity. It is well illustrated by a sharp increase of water salinity in the densely populated industrial regions. Actually, this is the main reason for interest of researchers in issues of softening, desalination of water and saline eluates processing. It is well-known, reagent methods of concentrates and eluates processing requires the supply of expensive reagents, such as high-basic aluminum coagulants and their usage has some limitations. More universal are the methods of electrolysis and electrodialysis. Different sources describe the results of experiments to obtain solutions of acids and alkalis in the salt solutions processing in the electrolyzers with ion-exchange membranes [1-2]. In [1] was studied in the details the sulfuric acid and alkali processes in trilocular electrolyzer with cation and anion exchange membranes. However, some studies [2] have shown that after electrochemical process the acids and alkalis were obtained which had certain restrictions on concentrations of reagents. Satisfactory results for current output where obtained when a concentration of acids and alkalis were 5÷10%. Further increase in the reagents concentration is accompanied by a sharp decline in output of acids and alkalis. Such low concentrations of acids and alkalis can be used directly in the field of production, but transportation such dilute solutions is impractical.

The aim of this work was to study the repeated electrolysis processes of diluted sulfuric acid solutions for their concentration to 30÷40%, which significantly expand the possibility of using sulfuric acids, which is obtained by electrolysis process.

During the electrolysis of solutions, which contains sulphates in trilocular electrolyzer [2] sulfuric acid is formed with concentration up to 5÷10%. So as model solutions in the cathode region was used sulfuric acid with concentration of 0,1÷2,0 g-eq/dm^3. In the anode region solutions with acidity of 1÷8 g-eq/dm^3 were used.

For electrolysis where used two-chamber electrolyzer (volume of chamber is 100 cm^3) with anionic membrane MA-41. As cathode we used the stainless steel plate 12X18H10T, and as anode – lead plate. The electrodes area was $S_K = S_A = 0.11$ dm^2. Electrolysis was carried out at a current of 0,2÷3,0 A, and voltage of 2÷20V.

While carrying the electrolysis, in the equal intervals of time the acidity and the volume of solutions weres controlled the cathode and anode areas.

Current output is calculated as the ratio of the actual amount to the theoretically of substance transferred during electrolysis, which is calculated by Faraday's law.

The experimental data are processed by the method of least-squares. These regression models that are based on Fisher's F-test generally are adequate and all regression coefficients are significant, because of the actual value of the criterion was bigger than the tabular $F_{act} > F_{theor}$.

In this experiment, dilute solutions of sulfuric acid were placed in the cathode area. Concentrating of acid in the anode area occurred due to diffusion of sulfate anions from cathode to anode area through anion exchange membrane MA-41. In this case, in both chambers of the electrolyzer was kept acidic environment, so the hydroxide anions (which could compete with sulfates in diffusion through the anionic membrane) were absent in the catholyte. The main cathodic process was the restoring of protons to the free hydrogen. The water oxidation took place at the anode with oxygen release and the formation of protons.

In the first phase of research in the cathode and anode chamber solutions of 1N sulfuric acid were placed. In the cathode region the acidity was maintained in the range of 0,65÷1,00 g-eq/dm^3. Electrolysis was carried out for 28 hours. The results are shown in Fig. 1. During the anolyte electrolysis the pH level increased to g-eq/dm^3 (36.75%). Despite the absence of hydroxide anions in the catholyte, the current output reached about 50% at the beginning of the process, and at the last stage dropped to 6÷22%. Obviously, this is due to increasing resistance in the total of the system with increasing of anolyte acidity. This leads to a significant loss of energy for the heating of fluids.

Obviously, that the process of acid concentration in the anolyte followed by reduction in the acid concentration in the cathode region. With usage of the electrolyzer of continuous action the solution in the cathode and anode area could be discharged as a countercurrent and parallel

flows. At the same time the variants of exposure concentrated (diluted) catholyte in accordance with the diluted (concentrated) anolyte in parallel flows are possible. When the solutions are running of by countercurrent, concentrated catholyte (in the range $1 \div 2$ g-eq/dm^3) contacts through the membrane with concentrated anolyte ($5 \div 8$ g-eq/dm^3) and diluted catholyte ($0,01 \div 0,1$ g-eq/dm^3) contacts with low concentrated anolyte ($\sim 1 \div 2$ g-eq/dm^3). Therefore, further studies are addressed to the electrolysis process using diluted and concentrated catholyte at the different acidity of anolyte.
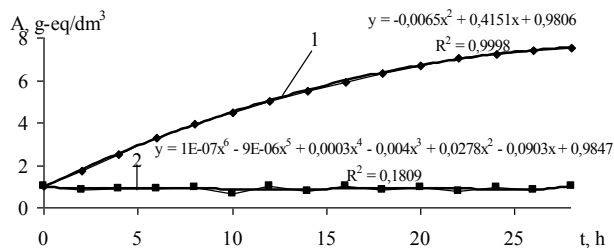

Fig. 1. The dependence of sulfuric acid concentration on the electrolysis time using two-chamber electrolyzer (membrane MA-41) with anode current density of 9.09 A/dm^2, with concentration of sulfuric acid of 1.0 g-eq/dm^3 in the cathode region

Note: 1 – acidity in the anode zone; 2 – acidity in the cathode zone

In Fig. 2 we can see the results, which were obtained with usage of 0.1 N sulfuric acid in the cathode region and 1.00, 2.00, 5.77 N acids in the anode region are shown. In this case, the anode region shows the increase in the concentration of acidity within 0,05-0,10 g-eq/dm^3 for a 150 min, with the initial values of $1 \div 6$ g-eq/dm^3. Current output reached 45-80% in the first minutes of the experiments. With the decrease in the concentration of acid in the cathode region, current output decreases rapidly. In general, results show that in the catholyte acidity > 0.02 g-eq/dm^3 concentration process of sulfuric acid in the anode region is quite slow.
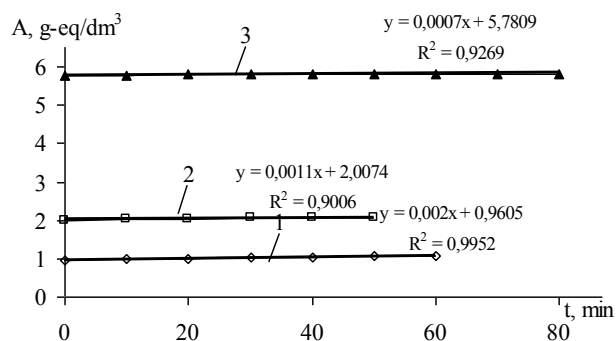

Fig. 2. The dependence of sulfuric acid concentration in the cathode and anode region on the electrolysis time at the initial acidity in the anode region of 1,000 g-eq/dm^3 (I); 2,000 g-eq/dm^3 (II) and 5.770 g-eq/dm^3 (III) at the anode current density of 4.54 A/dm^2

Best results were received with 1N sulfuric acid in the cathode region and 2N acid in the anode region used. In this case rising of process efficiency with an increase in anodic current density from 4.84 to 9.09 A/dm^2 is observed. At that current output of acid increased from $23,2 \div 65,8\%$ to $51,6 \div 98,06\%$. Perhaps in the anode current density of 9.09 A/dm^2 for selected concentrations of acid, sulfate diffusion runs fast enough and the loss of energy in heating of solutions decreases.

With an increase in acidity level in anode region grew to 5.8 and 6.0 g-eq/dm^3, a significant decrease in acid current output at all current densities in the range from 9.09 to 27.27 A/dm^2 is observed.

Obviously that with increasing of acid concentration in the anode region, the electrical resistance of the system increases, that leads to an increasing of energy loss for the heating of the system. At the same time, with an increase in acidity in the anode zone from 6.0 to 6.9 g-eq/dm^3 current output of acid reached $34 \div 48\%$ reached.

With an increase of acidity in anode region from 8.130 to 9.274 g-eq/dm^3 current output is $30 \div 31\%$. It should be noted that at high concentrations of acid in the anolyte with acidity in cathode region within $0,6 \div 2,0$ g-eq/dm^3, current output of acid has been slowly changed during electrolysis. Conductivity of the solution is quite considerable and the process is limited mostly by the increasing of the resistance of the system due to significant differences in the concentrations of acid in the anode and cathode region. However, as mentioned above, in the electrolysis the increasing of acid concentration up to 9,0 g-eq/dm^3 ($\sim 44\%$) at very satisfactory values for the current output was achieved.

Conclusion

It is shown that using of two-chamber electrolyzer with anion exchange membrane MA-41 in the process of electrolysis makes it possible to increase the concentration of sulfuric acid from $0,1 \div 2,0$ g-eq/dm^3 to $7,5 \div 9,2$ to g-eq/dm^3. The influence of catholyte acidity on the efficiency of acid concentration process in the anode zone was determined. It is shown that with increasing of current density and with decreasing the catholyte acidity, current output of acid in the anolyte is reduced. Found that in the catholyte acidity of $0,6 \div 2,0$ g-eq/dm^3 and at the output anolyte acidity of $6 \div 8$ g-eq/dm^3 current output of acid is practically independent of the catholyte acidity during the time of electrolysis at current density from 9, 09 to 27.27 A/dm^2.

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