V.I. Vernadskii Institute
of General and Inorganic Chemistry
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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE

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EDITORS: Yu.S. Dzyazko

T.V. Plisko

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V.G. Myronchuk

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CHAPTER 14

ION EXCHANGE MEMBRANES FOR REGENERATION OF HYDROCHLORIC ACID FROM ETCHING SOLUTIONS

S. Bolshanina, V. Serdiuk, L. Ponomarova, A. Yanovska, A. Ableev
Sumy State University, 2, Rymsky-Korsakov Str., Sumy 40007, Ukraine
email svet.bolshansna@gmail.com

Abstract. *The process of regeneration of utilized hydrochloric acid etching solutions using electrochemical equipment with ion exchange membranes was examined. The products of cathode reactions were studied. It was proved that the waste solution was not only purified from contaminate ions, but the acid content increased during the electrolyzer operation.*

Keywords: *membrane, ion exchange membrane, electrodialysis, chloride acid, regeneration.*

Introduction. One of main stages of production of metallic devices before the deposition of galvanic coating is cleaning of their surface from corrosion products and other contaminants. For this goal the etching with solutions of various acids (mainly HCl or H_2SO_4) is used. Rust and shruff are dissolved during the etching and metal surface is purified. At the same time the etching solution is polluted, the acid concentration is reduced the solution cannot be used further. After the etching the acid solution is neutralized with calcium hydroxide before dropping in the sump. Soluble metal chlorides obtained by neutralization are dissolved in ground waters polluting the environment. Thus, hydrochloric acid is lost.

Known methods for acid regeneration are energy consuming processes and require additional expensive equipment. For instance, the waste acid is thermally treated in the air stream in a reactor under the temperature of 600–800 °C [1].

Electrodialysis is the economically efficient technique for regeneration of acidic etching solutions. Two- or three-compartment electrolyzers and various alternation of cation exchange and anion exchange membranes are used for such purpose.

However, these methods are used for sulfuric acid baths [2]. It is caused by the fact that the anodic process is provided by water molecules during sulfuric acid electrodialysis, which is accompanied by oxygen evolution. In the case of electrolysis of hydrochloric acid, gaseous chlorine is generated on anode, its evolution is undesirable. The trapping released gas seems to be a very difficult process, which requires special equipment. The ways of regenerations using bipolar membranes for saline solutions are also proposed [3-5]. However, there is no information about their application for regeneration of etching solutions. Furthermore, bipolar membranes are not economically effective for this process.

Experimental. In this work, we discussed the possibility of regeneration of the utilized etching solutions of hydrochloric acid by means of electrochemical equipment with ion exchange membranes. For regeneration of the solutions, we used an electrolyser consisting two modules (cathode chamber and anode chamber) that were divided from the etching solution with a RALEX®CM-PES 11-66 cation exchange membranes. A 1 wt.% solution of sulfuric acid filled each chamber, where cathode and anode were placed. The anode was made of lead (grade C2), the cathode was manufactored from titanium (BT1-0). Electrolysis was carried out at current density of 5-10 A/dm^2.

The scheme of experimental setup is presented in the Figure 14.1

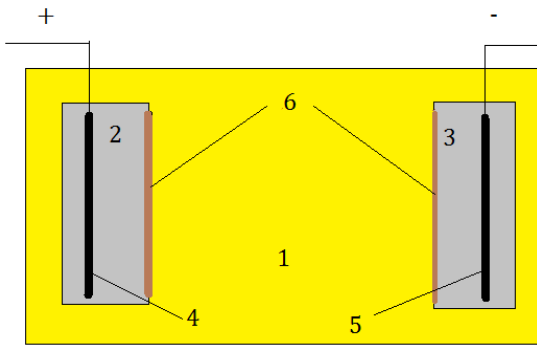
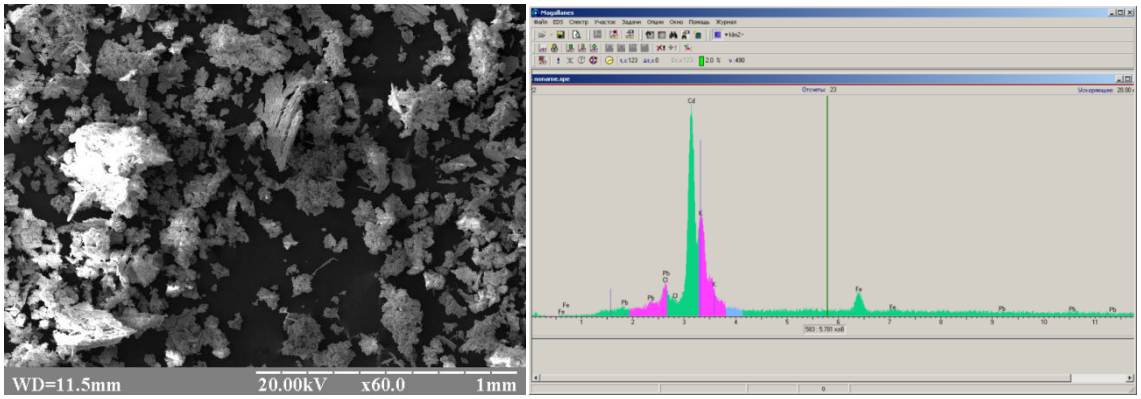


Fig. 14.1. *The scheme of experimental setup for regeneration of etching solution. 1 – bath with utilized etching solution; 2 – anode chamber; 3 – cathode chamber; 4 – anode; 5 – cathode; 6 – cation exchange membrane.*

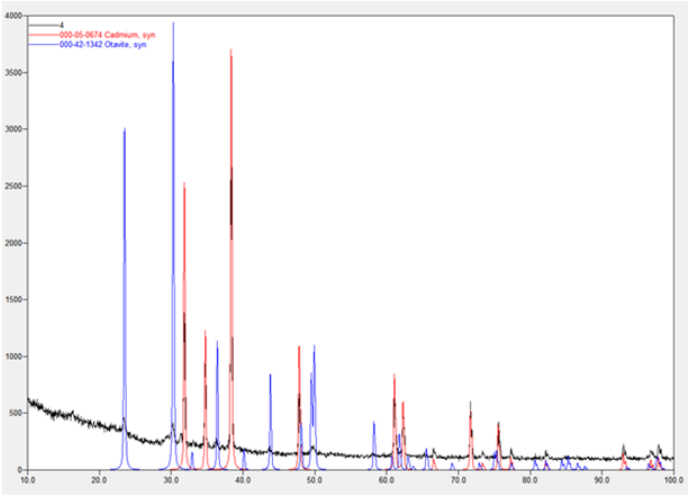
Results and discussion. When a cation exchange membrane is placed both near cathode and anode, such system is able to remove metal ions from the solution of hydrochloric at the side of cathode, furthermore migration of chloride anions towards anode and chlorine generation are suppressed. This excludes the transfer of H^+ and Cl^- ions from the cathode solution to the anolyte, and provides accumulation of these species in the solution of technological bath. As seen from the results of obtained experimental data, the acidity of a cathode solution has a great impact on this process. During the process, metal cations from the etching solution migrate to the cathode solution, which is neutralized by OH^- ions (they are generated on the cathode during electrochemical reaction of oxygen evolution). As a result the cathode medium is transformed from acidic to alkaline. Precipitation of insoluble compounds of metals as well as pure metals is observed in cathode solution (Figure 14.2). In this case, the cathode is coated with a thick layer of deposit.

Due to decrease of membrane conductivity, the resistance of the system increases followed by reducing current density. As found, the highest conductivity value is related to the solution pH of 1-2.

The cation exchange membrane performs isolation function and preventing the transfer of chloride ions to the anode space.



a



b

Fig. 14.2. *a) SEM – Morphology of the cathode deposit and average EDX analysis of the sample; b) XRD analysis of cathode slime (main fraction is cadmium and its compounds (cadmium carbonate).*

Instead of chloride ions, water molecules are discharged on anode according to the following scheme:

$$2H_2O - 4\,\bar{e} \rightarrow O_2 + 4H^+ \qquad (14.1)$$

Nevertheless, oxygen releases and acidification of the anode solution occurs. This process keeps the necessary level of the pH in the anode chamber to maintain the inertness of lead as anode material. Otherwise it will be dissolved very fast.

During operation of the electrolyzer, the etching solution was not only purified from ion impurities but the concentration of acid was also increased. The concentration of hydrochloric acid was estimated by potentiometric titration using a 0.1 M NaOH solution up to pH 3.7. During operation of the membrane system, the concentration of acid increases from 0.9 g/L to 1.4 g/L. This means the effectiveness of the membrane devise in the process of acid regeneration.

Conclusions. Hence, the proposed experimental setup provides not only extraction of metal cations from the utilized etching solution, but promotes the increase of acid concentration in this medium. Since no chlorine evolution at the anode occurs, the proposed method is related to ecologically safe.

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ІОНООБМІННІ МЕМБРАНИ В РЕГЕНЕРАЦІЇ ХЛОРИДНОЇ КИСЛОТИ З ТРАВИЛЬНИХ РОЗЧИНІВ

С. Большаніна, В. Сердюк, Л. Пономарьова, А. Яновська, О. Аблєєв
Сумський державний університет, вул. Римського-Корсакова 2, 40007, Суми, Україна, email svet.bolshansna@gmail.com

Резюме. *Розглядається процес регенерації відпрацьованих травильних розчинів на основі хлоридної кислоти з використанням електрохімічних пристроїв з іонообмінними мембранами. Вивчено продукти реакцій на катоді. Доведено, що при роботі електролізера відпрацьований травильний розчин не тільки очищується від забруднюючих його іонів, але і збільшується вміст кислоти.*

Ключові слова*: мембрани, іонообмінні мембрани, електродіаліз, хлоридна кислота, регенерація.*