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Applications of electrodialysis for acid pickling wastewater treatment

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Abstract

In acid pickling before electroplating, the effective acid concentration deteriorates while the dissolved metal concentration increases continuously. By introducing electrodialysis (ED) between this operation and the following rinsing baths, these disadvantages are largely rectified. Recovered acid is continuously returned to the pickling bath and the amount of waste is drastically reduced. Depleted solution is reused in rinsing baths. Moreover, ED can avoid metallic impurity build-up in the acid pickling bath. First manipulations conducted on our laboratory equipment failed. So, ion-exchange membranes (IEMs) were characterized by conductivity measurements and polarization curves. Afterwards, a new selection of IEMs was performed. Faradic yields were calculated for various commercial anion- and cation-exchange membranes (AEMs and CEMs) in a Hittorf cell and ED conditions were refined. The relation between the hydrodynamics of ED and the limiting current density was checked by new measurements based on a tracer method successfully applied to electrochemical cells by our laboratory. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electrodialysis; Acid pickling; Wastewater treatment

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1. Introduction

In acid pickling before electroplating, the effective acid concentration deteriorates while the dissolved metal concentration increases continuously. This results in a decrease in efficiency of the pickling and in replacement of the solution. The spent solution would then normally be neutralized and disposed of. This practice is not economic, causes waste disposal problems and compromises quality control during the pickling operation.

If a recycling process, such as electrodialysis (ED), is introduced within this operation, these disadvantages are largely rectified. Recovered acid is continuously returned to the pickling bath and the amount of waste is drastically reduced. During this time, deacidified wastewater is reused in rinsing steps. Furthermore, the recycling process regulates pickling metallic impurity concentrations.

Many publications [1–9] on ED agree that this recycling process is particularly well suited to this kind of effluent and application. This technique has many advantages compared with other classical recycling processes. ED is a complete, flexible and effective process. No chemicals have to be used. Usually, specific consumption is comparable or inferior to equivalent techniques.

In [1–9], ED was studied on a laboratory scale. This study has adapted ED from this scale to real industrial effluents. Experimentation was conducted with solutions from an S.M.E. specialized in surface plating treatments. Manipulations were achieved following conditions corresponding to future industrial working. The pickling solution contained hydrochloric and/or sulfuric acids polluted by ferric and zinc ions. Organic compounds were also present in the solution as surfactants and inhibitors. The static rinsing concentration was fixed at 10% of the pickling bath.

Most of the electroplating lines and so any added operation integrated in the line, such as a recycling process, work continuously [10]. This consideration is crucial from the point of view of ED adaptation to industrial situations. Indeed, most of the existing studies do not take into account continuous and stationary conditions. Several stages of ED were used to obtain a solution which is reconcentrated enough to be returned directly to the pickling bath, taking into account all ingoing and outgoing flows passing through

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these baths. Two different stages of ED were necessary to treat our industrial effluents.

This study highlights the selection of ion-exchange membranes (IEMs) and the difficulties of ED adaptation to real industrial solutions. This adaptation is based on a mathematical model of the plating line. Hydrodynamic considerations are proposed and a new method is developed to control the effect of the modifications.

2. Experimental details

2.1. Experimental solutions

Our study was firstly concerned with hydrochloric acid solutions. The dilute and concentrated compositions in the two ED stages were conditioned by the pickling and static rinsing compositions. The metal concentration was 1.5 g l^{-1} and the acid concentrations were maintained, respectively, in the dilute and the concentrated streams at 0.5 and 2 M for the first stage and 1 and 4 M for the second stage.

The organic additives were added to every solution in the same proportion as in industrial solutions. These organic compounds have formulations generally used for surface plating treatments. It is difficult to know the composition of these additives, but the product supplier kindly offered important information. These characteristics concern the ionic state of the compounds. They were very useful for the determination of all ionic transfers into IEMs.

2.2. Systematic study of the IEM couple

Initially, an IEM couple produced by Solvay® was used in the laboratory electrodialyzer with complete solutions simulating industrial ones.

Conductivity was measured on every IEM, before and after use. Polarization curves were more especially performed on cation-exchange membranes (CEMs) using equipment composed of two supplying and two measuring electrodes connected across the membrane. The IEM placed between the catholyte and anolyte has an active surface of 1 cm^2. Polarization curves were drawn from different acid concentrations without any concentration gradient between compartments and with stirring.

2.3. Selection of IEM in the Hittorf cell

An IEM selection was performed from a large range of commercial membranes. These membranes were CS92 and CS94 supplied by Solvay®, CMS, CMX-S and CMX-Sb supplied by Tokuyama Soda® and CHV and CMV supplied by Asahi Glass® (CEMs); AW08, AW09 and ADP supplied by Solvay®, ACM supplied by Tokuyama Soda® and AAV, AMV and ASV supplied by Asahi Glass® anion-exchange membranes (AEMs). These membranes were kindly placed at our disposal to realize this study.

For every IEM, polarization curves were measured in hydrochloric acid at 0.5/2 M with the same equipment as previously. Faradic yields were measured for CEM and AEM in the Hittorf cell. This cell is composed of two asymmetrical compartments with the membrane placed between them. Current is supplied by two platinum-plated titanium electrodes.

IEMs were tested in two different cases. The first was a gradient of about 0.5 M (for acid)/2 M with a current density of about 50 mA cm^{-2}, and the second was a gradient of 1 M/4 M with a current density of about 70 mA cm^{-2}. Industrial solutions were approached in three steps. First, faradic yields were measured in ‘simple’ hydrochloric acid solutions. Then iron and zinc were added at 1.5 g l^{-1} for both, for every acid solution. Lastly, organic compounds were added to the system. Settings were chosen to avoid electrode reaction perturbations with the mass balance calculations.

2.4. Middle term ED with the most interesting IEM couple selected

Faradic yields were calculated for different gradient conditions under 50 mA cm^{-2} with solutions containing acid and metals on laboratory scale equipment composed of five ED compartments between two electrode compartments. Every compartment concentration was studied during ED.

3. Results

3.1. Systematic study of the IEM couple

The polarization curves drawn for different acid concentrations are presented in Fig. 1. They show the second-order relationship between acid concentration and limiting current density.

This pattern can be explained by theory. In a first approximation, the membrane counter-ion concentration is proportional to the square of the bulk counter-ion concentration. The observed limiting current densities are not linearly proportional to the acid bulk concentration, but proportional to the square of this concentration. From these observations, our interpretation of this phenomenon is that the limiting diffusion control does not take place in the diffusion layer of the solution in front of the CEM, but directly in the modified surface layer of the membrane giving it its selectivity. This interpretation is confirmed by the fact that stirring does not influence the results obtained. So, this unusual CEM behavior is not appropriate and the membrane will not be used for our kind of application.

In the case of the AEM, the conductivity measurements revealed a large membrane surface heterogeneity. Furthermore, a slight organic fouling effect was detected.

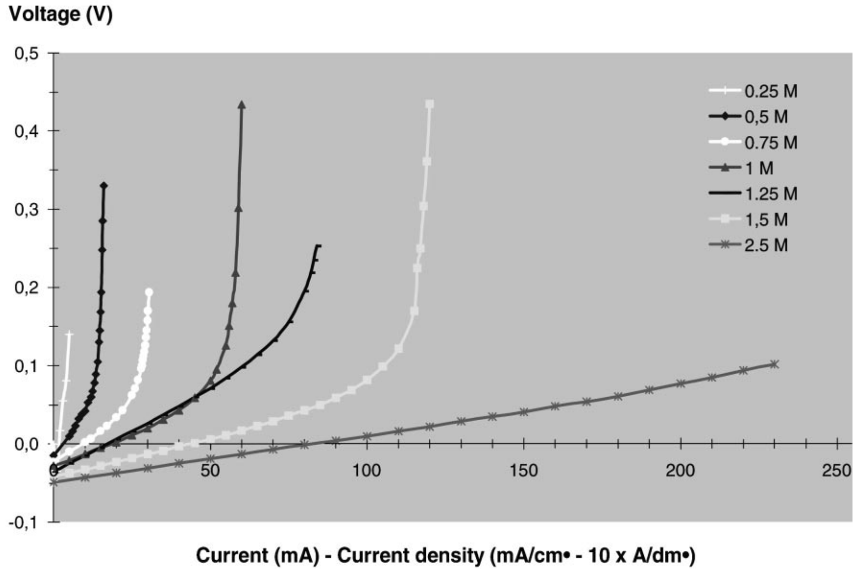

Fig. 1. Polarization curves for different acid concentrations.

3.2. Selection of IEM in the Hittorf cell

The faradic yields were calculated for each membrane, according to the two different cases, and for each of the three kinds of solution (Table 1). They were correlated with the polarization curves that gave the IEM conductivity measurements. The results allowed the selection of AEMs and CEMs adapted to the recycling of the solutions. These membranes were CMS and CMX-S from Tokuyama Soda® and CHV from Asahi Glass® (cationic membranes) and AW08 and AW09 from Solvay® and AAV from Asahi Glass® (anionic membranes).

The large difference between the faradic yields with or without additives can be explained by the complex formation capacity of ions in solution in the presence of organic compounds. This can improve or deplete the mass transfer of ionic species across the IEM.

The polarization curves (Fig. 2) were drawn for each tested membrane to avoid the special effect confirmed for the first CEM studied (CS94).

Table 1
Faradic yields (%)

	HCl		HCl+Me+additives	
	0.5/2 M	1/4 M	0.5/2 M	1/4 M
CMS	92	47	89	44
CMX-S	94	46	84	43
CHV	97	68	85	51
AW08	75	55	66	37
AW09	78	48	60	42
AAV	62	55	61	67

From the faradic yield results and the polarization curves, some of the selected IEMs can be considered as similar, e.g. CMS and CMX-S and AW08 and AW09.

3.3. Middle term ED with the most interesting IEM couple selected

Middle term tests were performed to observe the faradic yield stability with CHV as CEM and AW08 as AEM. Faradic yields were measured with concentration gradients from 0.5/0.5 to 0.5/3.5 M during more than 50 h.

The faradic yields and the reconcentration rates are very satisfactory. Longer term ED should be performed to investigate the membrane resistance to fouling and thermal and mechanical effects.

4. Future prospects

Contacts with industry, in the field of surface treatments and in the field of recycling equipment, have convinced us that, for the moment, existing electrodialyzer design is not economically suitable for some ‘common’ industrial applications, such as surface treatment effluent recycling. For these effluent treatments, new electrodialyzers should be more flexible and cheaper than existing equipment. Moreover, this new equipment should be easier to use and should reduce maintenance costs.

These objectives can be reached by design modifications leading to high flow rate hydrodynamic conditions in the ED equipment. These modifications are based on our previous laboratory work on electrochemical cells. They mainly consist of an enlargement of the compartment width and

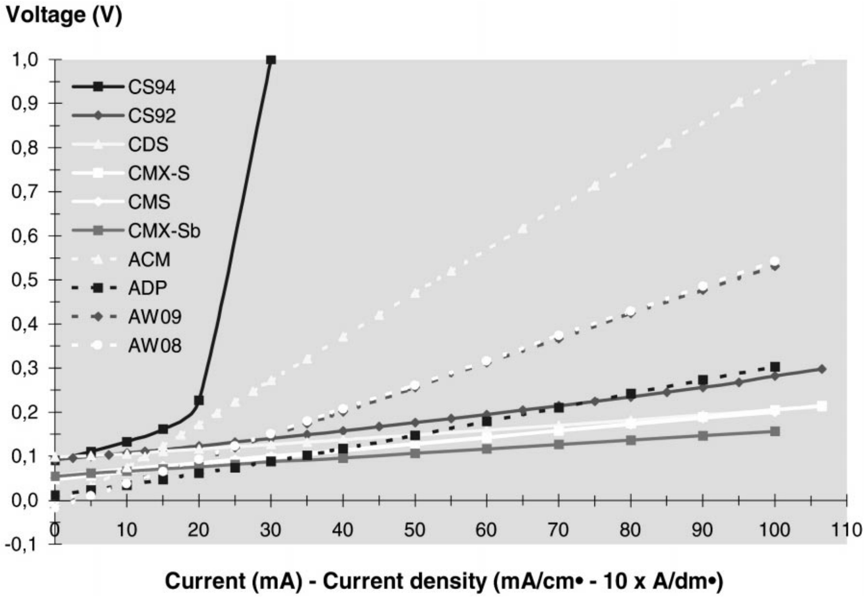

Fig. 2. Polarization curves of tested IEMs.

a hydraulic circulation adaptation in these compartments. These modifications have been suggested to improve ED hydrodynamic control which directly influences mass transfer and the limiting current density [11–14].

Relations between ED hydrodynamics and limiting current density are important. They can be checked by a tracer method. The tracer method for mass transfer measurements has been successfully applied to electrochemical cells. It is described in the literature [15].

For greater facility, the transfer of the cation ($C^{z_\mathrm{C}+}$) towards the CEM is observed. As in cathodic metal deposition, the cation limiting current density ($J_{\mathrm{dl/C}}$) along the membrane is determined by the following relationship:

$$J_{\mathrm{dl/C}} = z_\mathrm{C} F \frac{D_\mathrm{C}}{\delta} C_{\mathrm{b/C}} \tag{1}$$

where z_C is the cation charge, D_C the cation diffusion coefficient, δ the diffusion layer related to the hydrodynamic conditions and $C_{\mathrm{b/C}}$ is the cation concentration in the bulk of the solution.

Usually, mass transfer can be characterized by diffusion overvoltage. In electrodeposition, this overvoltage is easy to measure with synthetic solutions, but is very difficult to observe with real solutions. The same behavior is found in ED. Perturbative phenomena appear which modify the limiting current density and hide the diffusion overvoltage. So, a new method has been developed.

This method is based on the presence of a small amount of another cation, the tracer ($T^{z_\mathrm{T}+}$), that is transported across the CEM at the same time as the major cation. Moreover, the tiny concentration of tracer in the bulk ($C_{\mathrm{b/T}}$) compared to the major cation ensures that this cation is transported to its limiting current density. Tracer addition cannot change the initial properties of the solution and cannot alter the major cation transfer.

The transfer of the tracer across the CEM, controlled by chemical analysis, corresponds to a current amount dedicated to this transfer. A proportional relationship exists between the tracer limiting current density ($J_{\mathrm{dl/T}}$) and that of the cation ($J_{\mathrm{dl/C}}$):

$$J_{\mathrm{dl/C}} = \frac{z_\mathrm{c}}{z_\mathrm{T}} J_{\mathrm{dl/T}} \frac{C_{\mathrm{b/C}}}{C_{\mathrm{b/T}}} \left(\frac{D_\mathrm{C}}{D_\mathrm{T}}\right)^{2/3} \tag{2}$$

This relationship is established for a fully developed forced turbulent flow in a channel cell according to the Chilton–Colburn equation

$$Sh \propto Re^{0.8}\, Sc^{1/3} \tag{3}$$

where Sh is the Sherwood number characterizing the mass transfer, Re the Reynolds number characterizing the hydrodynamic conditions and Sc is the Schmidt number defined as the ratio of the kinematic viscosity to the diffusion coefficient.

Relationship (2) is also available in the case of fully developed forced laminar flow in a channel cell according to the formula proposed by Pickett and Stanmore [16] and Rousar et al. [17]

$$Sh \propto Re^{1/3}\, Sc^{1/3} \tag{4}$$

By this new method, hydrodynamic change effects in the electrodialyzer can be directly considered as connected to the tracer transfer across the CEM. These hydrodynamic change effects can be quantified if tracer and major cation diffusion coefficients are known and if the hydrodynamics are established. Similar arguments can be applied for AEM.

5. Conclusions

The study has taken two complementary paths. On the one hand, IEMs have been studied and selected for acid pickling ED. The high faradic yields of selected IEMs allow reconcentration of static rinsing bath effluent to the pickling bath. On the other hand, ED adaptation has been undertaken. Consequently, some existing electrodialyser design modifications have been considered that have an influence on the electrodialyser hydrodynamics. These are based on our experimental observations and on the correlation between the electrochemical cells and the electrodialyzers. A new method to quantify hydrodynamic conditions in the electrodialyser, based on a tracer technique developed for electrochemical cells, has been proposed.

Research must continue with adjustments of an industrial prototype.

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References

[1] M. Boudet-Dumy, A. Lindheimer, Cl. Gavach, J. Membr. Sci. 57 (1991) 57–68.
[2] I. Tugas, G. Pourcelly, Cl. Gavach, J. Membr. Sci. 85 (1993) 183–194.
[3] G. Pourcelly, I. Tugas, Gavach Cl., J. Membr. Sci. 85 (1993) 195–204.
[4] A. Lindheimer, M. Boudet-Dumy, Cl. Gavach, Desalination 94 (1993) 151–165.
[5] G. Pourcelly, I. Tugas, Cl. Gavach, J. Membr. Sci. 97 (1994) 99–107.
[6] A. Chapotot, V. Lopez, A. Lindheimer, N. Aouad, Cl. Gavach, Desalination 101 (1995) 141–153.
[7] F. Aouad, A. Lindheimer, Cl. Gavach, J. Membr. Sci. 123 (1997) 207–223.
[8] J. Wisniewski, G. Wisniewska, Desalination 109 (1997) 187–193.
[9] V. Baltazar, G.B. Harris, C.W. White, Hydrometallurgy 30 (1992) 463–481.
[10] L. Schuster, M. Degrez, Oberflächen Werkstoffe — Surfaces Matériaux 1/2 (1997) 6–12.
[11] V. Mavrov, W. Pusch, O. Kominek, S. Wheelwright, Desalination 91 (1993) 225–252.
[12] F. Lapicque, in: Proceedings of the European School on Electrochemical Engineering, Toulouse, France, 25–29 September 1995.
[13] A. Storck, D. Hutin, Electrochim. Acta 26 (1981) 117–125.
[14] A. Storck, D. Hutin, Electrochim. Acta 26 (1981) 127–137.
[15] H.M. Wang, S.F. Chen, T.J. O'Keefe, M. Degrez, R. Winand, J. Appl. Electrochem. 19 (1989) 174–182.
[16] D.J. Pickett, B.R. Stanmore, J. Appl. Electrochem. 2 (1972) 151.
[17] I. Rousar, J. Hostomsky, V. Cesner, B. Stverak, J. Electrochem. Soc. 118 (1971).