

# **ELECTROCHEMICAL PROCESSING OF REGENERATION SOLUTIONS FROM ION- EXCHANGE TREATMENT OF WATER WITH PRODUCTION OF ACIDS AND ALKALIS**

**T. Shabliy, E. Goltvianyskaya, N. Gomelya**

Department of Ecology and Plant Polymers Technology, National Technical University of Ukraine "KPI", Pobedy av. 37; 03056 Kyiv, Ukraine (e-mail: tania1@voliacable.com, milleniya@mail.ru, eco-paper@kpi.ua)

## **ABSTRACT**

This paper studies processes of purification of acid, neutral and alkaline solutions containing sulfate or sodium chloride.

The composition of used solutions was close to solutions that were formed during the regeneration of cation exchangers in the sodium form by sulfuric or hydrochloric acid, as well as the regeneration of anion exchangers in the salt form by alkali.

Our study determined the conditions for the production of sulfuric acid and alkali in the processing of sulfate-containing solutions in three-chambered electrolysis cells with using cation exchange and anion exchange membranes. We also determined the concentrations of chemicals produced in high efficiency of the electro dialysis.

It is shown that by using a four-chambered electrolyser in the electrolysis of solutions containing sodium chloride, along with an alkali solution, the solution of hydrochloric acid can be obtained. It is also established that with the usage of electro dialysis of cation exchange and anion exchange membranes, the effectiveness of the process largely depends on the initial concentration of sodium chloride. In the concentration of sodium chloride exceeding 40 g/dm<sup>3</sup> the efficiency of electrolysis is greatly reduced due to the diffusion transport of chloride anions to the cathodic area.

Current efficiency of acids and alkali decreases with increasing concentrations respectively in the cathodic and the anodic areas.

When the concentration of alkali and acid exceeds 3000 mg-eq/dm<sup>3</sup>, a significant reduction of the current efficiency of electrolysis products was observed with a significant increase the time of process for all used voltages and current densities.

**KEYWORDS:** electro dialysis; processing of regeneration solutions; current efficiency

## **INTRODUCTION**

Nowadays the problem of softening and demineralization of natural and mine water in Ukraine is very serious. First of all, it concerns industrial areas - Donbass, Azov Sea and Black Sea regions, some areas of central and northeastern regions, the Crimea, and certain areas of western Ukraine. In these areas. As a result of development of mineral deposits (coal mining, iron ore and uranium ore mining, mineral raw materials, oil, gas, etc.), surface water bodies have significant amounts of mineralization and are often polluted with mine waters. Usually, these water reservoirs are small and significantly polluted by industrial and municipal waste. In addition, industrial regions have many slime-storing sites that contain high concentrations of mineral and organic compounds. These

factors lead to a significant degradation of soil and groundwater. Industrial use of poor-quality water increases water intake and increases volumes of sewage.

A promising direction to solve this problem is to widely utilize highly mineralized natural and mine waters. The most promising methods of demineralization of water are ion exchange, reverse osmosis and nanofiltration. However, these methods have disadvantages such as formation of processed regeneration solutions and concentrates. According to the existing environmental regulations, discharge of these solutions and concentrates into drains or reservoirs is prohibited, and yet there are no economically feasible methods to recycle these solutions and concentrates.

Concentrates and regeneration solutions formed in the process of demineralizing water contain ions of hardness, sodium, chlorides and sulfates. Removing hardness ions from neutral solutions is extensively studied and is not a big problem. For example, published work developed removal of sulfate from water (Salnikov *et al.*, 1992) with some approaches using electrolysis (Pisarska *et al.*, 2005).

However, the processes of electrolysis of acid and alkaline solutions of sodium sulfate, which are formed during regeneration of ion exchangers by ion-exchange desalting water, are not sufficiently studied.

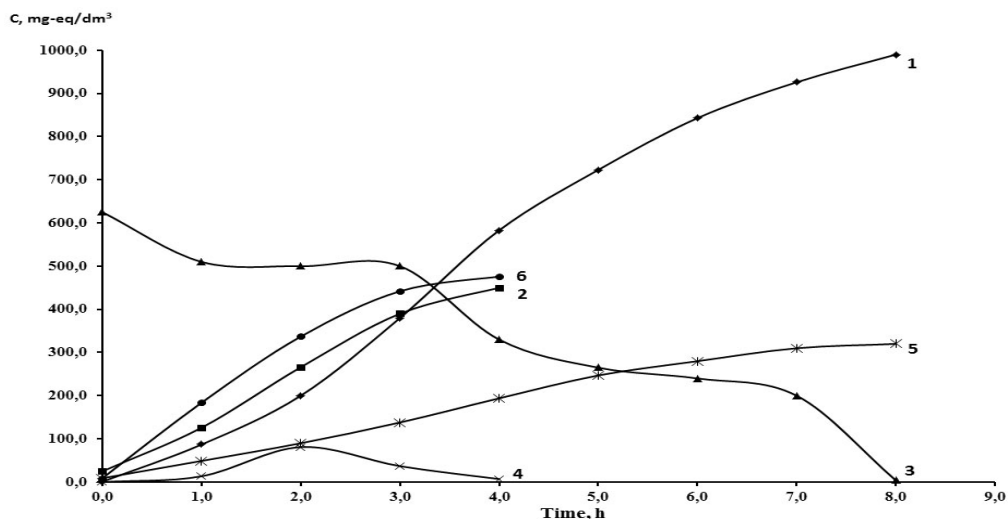
In addition, mixtures of salts containing chlorides together with sulfates, as well as hardness cations and sodium ions, are usually present in concentrates and in regeneration solutions. Therefore it is important to develop practical methods of their separation. Ions of hardness salts are separated in the form of insoluble sediments and thus can be easily separated from other ions. The method described in (Salnikov *et al.*, 1992) separates chloride from sulfate by sedimentation of sulfates. Sodium chloride can be treated by electrolysis process to obtain alkali and active chlorine (Nosachova *et al.*, 2010). However, in most cases, water treatment plants do not recycle or utilize active chlorine. Therefore, one needs to develop a recycling method of sodium chloride to obtain alkali solutions and hydrochloric acid.

The objectives of this work were: 1) to study the processes of electro dialysis of acidic, alkalic and neutral solutions of sodium sulfate to obtain sulfuric acid and alkali, 2) to determine the effects of acid concentrations in cathodic area and alkali's in anodic area on the efficiency of electrolysis and 3) to study the electrolysis of sodium chloride solution and to determine conditions to obtain solutions of hydrochloric acid and alkali as a function of the initial concentration of catholyte and anolyte solution and hydrochloric acid.

## **METHODS AND RESULTS**

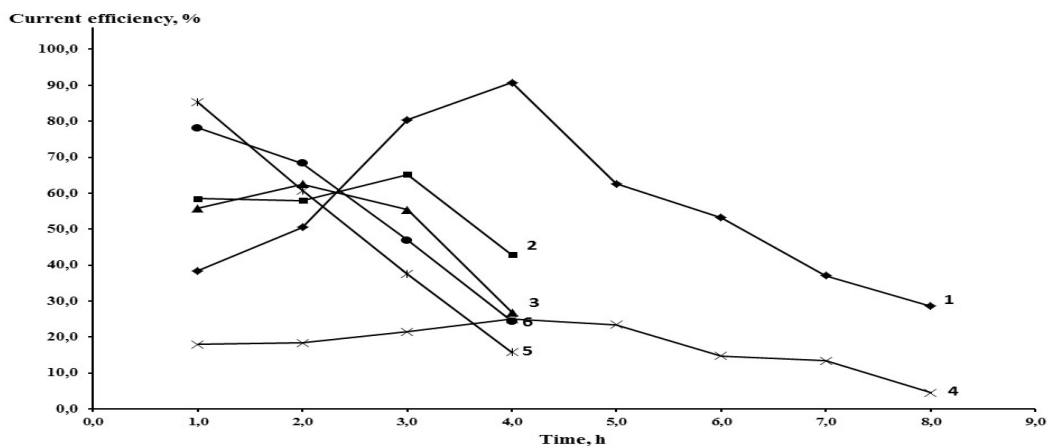
The results of electrolysis of acidic and alkalic solutions of sodium sulfate are shown in Figure 1.

Figure 1 shows that presence of acid or alkali in the working solution has little effect on the efficiency of the process. In general, if we compare this pattern with neutral solutions (Figures 2, 3), we can say that the electrolysis of acidic solutions decreases current efficiency of alkali, and the electrolysis of alkalic solution decreases current efficiency of acid. In general, during the electrolysis of acidic solutions, the acidity in the anodic area reached 1000 mg-eq/dm<sup>3</sup>, and in the work area decreased to 4mg-eq/dm<sup>3</sup>. The output of sulfuric acid by sulfates (or degree of removal of sulfate) reached 96 %. With this approach, the output of alkali was about 98 % although the current efficiency of acid and alkali was relatively low (Figure 2).



**Figure 1.** Dependence of pH in the cathodic area (1, 2), in the work area (3, 4) and alkalinity in the anodic area (5, 6) on the acidic electrolysis ( $C(\text{H}_2\text{SO}_4) = 625 \text{ mg-eq/dm}^3$ ,  $C(\text{Na}_2\text{SO}_4) = 324 \text{ mg-eq/dm}^3$ ) (1, 3, 5) and alkalic electrolysis ( $C(\text{NaOH}) = 53 \text{ mg-eq/dm}^3$ ,  $C(\text{Na}_2\text{SO}_4) = 423 \text{ mg-eq/dm}^3$ ) (2, 4, 6) solutions of sodium sulfate at current density in  $5 \text{ A/dm}^2$  in the three-chambered electrolyzer with cation exchange membrane MK-40 and the anion exchange membrane MA-40.

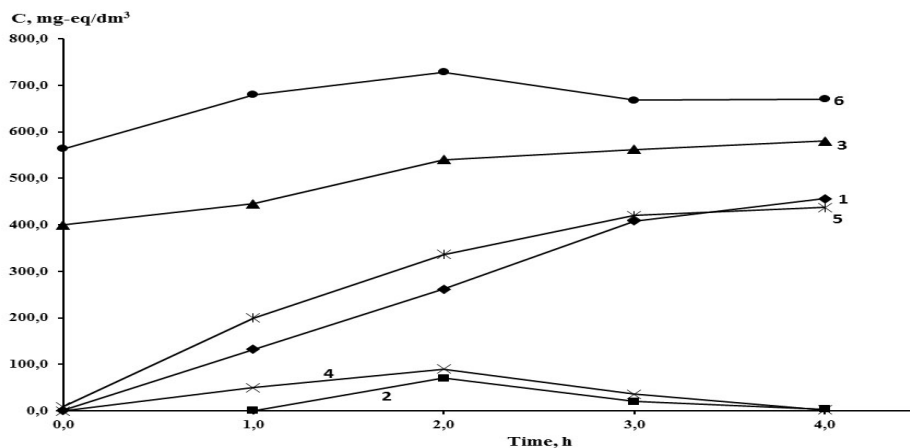
Note that during this process the cation exchange membrane is more selective on sodium cation in comparison with protons as the anion exchange membrane is more selective on sulfate anion in comparison with the hydroxide anions. This produced an increase of acidity in the work area when neutral working solutions were used. Even when alkalic solution with alkalinity about  $50 \text{ mg-eq/dm}^3$  was used, after an hour of electrolysis the media at the work area were acidic. This finding is consistent with the results reported in (Shabliy *et al.*, 2010). In all cases, as concentrations of sodium ions in the work chamber decreased, acidity fell due to the transfer of protons into the cathodic area.



**Figure 2.** Dependence of current efficiency of acid (1, 2, 3) and alkali (4, 5, 6) on the time of electrolysis of sodium sulfate solutions in three-chambered electrolyzer at current density  $5 \text{ A/dm}^2$ : acid solution ( $C(\text{H}_2\text{SO}_4) = 625 \text{ mg-eq/dm}^3$ ,  $C(\text{Na}_2\text{SO}_4) = 324 \text{ mg-eq/dm}^3$ ) (1, 4); neutral solution ( $C(\text{Na}_2\text{SO}_4) = 450 \text{ mg-eq/dm}^3$ ) (2, 5) and alkalic solution ( $C(\text{NaOH}) = 53 \text{ mg-eq/dm}^3$ ,  $C(\text{Na}_2\text{SO}_4) = 423 \text{ mg-eq/dm}^3$ ) (3, 6).

Overall, the efficiency of electrochemical methods of recycling of regeneration solutions is determined by acid and alkali concentrations obtained as a result of these processes. The scope of used obtained reagents considerably expands when concentrations are high (20 % and above). At low concentrations of acid and alkali their reuse is very limited.

In contrast to encouraging results in (Shabliy *et al.*, 2010), this study—which is aimed to determine the effect of concentrations of acid in the anodic area and alkali in the cathodic area to the removal efficiency of sodium sulfate from water by electrodialysis—showed that the concentrations of acid in the anodic area and alkali in the cathodic area are quite limited.



**Figure 3.** Influence of initial pH in the anodic area, alkalinity in the cathodic area to the concentrations of acid in the anodic (1, 3) and work areas (2, 4), alkali in the cathodic area (5, 6) during electrolysis of solution of sodium sulfate in concentration  $450 \text{ mg-eq/dm}^3$  in the trilocular electrolyzer at a current density  $5 \text{ A/dm}^2$ .

Figure 3 shows that the efficiency of electrolysis decreases as the initial concentrations of acid and alkali in the anodic and cathodic areas increase respectively to  $400$  and  $564 \text{ mg-eq/dm}^3$ .

Acidity reached  $586 \text{ mg-eq/dm}^3$  in the work chamber. However, with increasing acidity in the anodic area and alkalinity in the cathodic area, current efficiency of both acid and alkali decreased.

We used four-chambered electrolyzer for the electrolysis of sodium chloride to obtain hydrochloric acid and alkali. The cathode is a stainless steel plate 12X18H10T, the anode is a titanium plate which is covered with ruthenium oxide. We used cation exchange membrane MK-40 and anion exchange membrane MA-40. The order of the membranes was as follows: cathod, cation exchange membrane, anion exchange membrane, cation exchange membrane, anode.

The results of electrolysis of sodium chloride are given in Table 1.

**Table 1.** The effect of initial concentrations of alkali and acid on the water treatment efficiency of sodium chloride in four-chambered electrolyzer at a voltage of 30 V and the concentration of acid in the anodic area 50 mg-eq/dm<sup>3</sup>.

I - in the cathodic area (C1)  
 II - in the model solution (C2)  
 III - in a solution of hydrochloric acid (C3).

Time, h	I, A	Alcalinity, mg-eq/dm <sup>3</sup>		Acidity, mg-eq/dm <sup>3</sup>		C <sub>Cl<sup>-</sup></sub> , mg-eq/dm <sup>3</sup>	Current efficiency, %		Z, %
		I	II	III	II		NaOH	HCl	
0	--	10	10.0	50	--	500	--	--	--
1	1.25	250	13.0	280	--	270	77.3	74.0	46.0
2	0.60	400	--	430	8.0	120	100.0	100.0	76.0
3	0.26	465	0.0	495	0.0	55	100.0	100.0	89.0
4	0.09	487	5.0	518	--	32	97.1	100.0	93.6
0	--	970	2.0	890	--	502	--	--	--
1	1.80	1212	--	1120	20	272	54.1	51.4	45.6
2	1.80	1390	--	1330	14	62	39.8	47.0	87.6
3	0.30	1420	--	1360	15	26	40.2	40.2	94.8
4	0.18	1440	--	1380	5	2	44.7	44.7	99.6
5	0.12	1450	--	1380	5	0	33.5	0.0	100.0
0	--	1470	2.0	1500	--	454	--	--	--
1	1.50	1640	--	1730	60	224	45.5	61.6	50.7
2	1.00	1750	--	1850	22	108	44.2	48.3	76.2
3	0.80	1810	--	1920	17	44	30.2	44.8	90.3
4	0.60	1848	--	1950	12	14	25.4	19.2	96.9
5	0.34	1850	--	1950	7	6	1.8	0.0	98.7
0	--	1930	2.0	2120	--	500	--	--	--
1	2.80	2195	--	2405	111	272	39.8	41.1	45.6
2	2.20	2290	--	2500	150	196	17.4	17.3	60.8
3	1.80	2365	--	2580	168	126	16.8	17.9	74.8
4	0.42	2380	--	2590	50	72	14.0	9.4	85.6
5	0.18	2380	--	2560	18	30	0.0	0.0	94.0
0	--	2250	2.0	2160	--	586	--	--	--
1	3.30	2540	--	2550	90	296	38.8	52.2	50.5
2	1.00	2610	--	2670	50	70	25.6	43.9	88.1
3	0.50	2640	--	2725	35	38	20.5	37.5	93.5
4	0.28	2650	--	2575	20	20	13.4	0.0	96.6
0		2900	5.0	2870	--	586	--	--	--
1		3100	--	3000	90	386	24.4	15.8	34.1
2		3150	--	3110	50	331	20.1	44.2	43.5
3		3170	--	3080	40	311	15.8	0.0	46.9
4		3186	--	3060	35	295	9.0	0.0	49.7

In contrast to results obtained in (Pisarska *et al.*, 2005), where the concentration of acid and alkali did not affect to the efficiency of the process, we found a significant decrease of current efficiency of both acid and alkali. This difference is mainly due to increased electric conductivity of system which was achieved by increasing the concentration of electrolytes, which generally leads to an increase in current strength and current density. This current density can be higher than necessary, and is resulting to excess consumption of electricity. In addition, the resistance of the system increases when concentration of hydrochloric acid and alkali increases, which also leads to a decrease of current efficiency of acid and alkali.

In general, it should be noted that the electrolysis is quite effective with increased initial concentrations of alkali and acid to 2200 mg-eq/dm<sup>3</sup>. The concentration of acid reaches 2725 mg-eq/dm<sup>3</sup> (83 g/dm<sup>3</sup>, 8.3 %), alkali concentration reaches 2650 mg-eq/dm<sup>3</sup> (106 g/dm<sup>3</sup>, 10.6 %), which allows reusing solutions during the regeneration of ion exchange resins.

The current efficiency of acid was 37-52 %, the current efficiency of alkali was 13-38 % (in the first stage at low initial concentrations of acid and alkali the current efficiencies were respectively 74-100 % and 77-100 %).

When the initial concentration of alkali solution in the cathodic area was 2900 mg-eq/dm<sup>3</sup> and concentration of hydrochloric acid was 2870 mg-eq/dm<sup>3</sup>, the efficiency of electrolysis decreased in terms of both the current efficiency and the degree of removal of chlorides. In previous experiments, the degree of removal of chlorides from the model solution reached 93-100 %, while in the present case it did not exceed 49.7 %. This can be explained by increased resistance of system due to increased concentrations of acid and alkali that in the constant voltage led to decreased current density and deterioration of the membranes, which are designed for normal operation by the salt concentration till 100 mg/dm<sup>3</sup>, but not at 30 g/dm<sup>3</sup> of sodium chloride and 80 or 100 g/dm<sup>3</sup> of acid or alkali.

It is possible that at high acidity the cation exchange membrane loses its selectivity because at the high acidity the degree of dissociation of sulphonate groups is reduced, leading to a decrease in surface charge of the nanopores of membrane and facilitates the migration of chlorine anions into anodic chamber. This can be explained by decreased acidity in the chamber of hydrochloric acid in the final hours of electrolysis (Table 1) at the last three series of experiments. We could not explain this by the increased acidity in the model solution. Indeed, in almost all experiments, we observed the initial increase in acidity in the work solution then followed by loss in acidity. This pattern is explained by a better diffusion of sodium ions relative to protons and relatively high diffusion permeability of hydroxide anions relative to chlorides. Furthermore, we observed decreasing concentrations of hydrochloric acid in the final hours of electrolysis simultaneously with a decrease in acidity in the work solution. On the other hand, active chlorine and chlorides were recorded in the anodic area at the high concentrations of hydrochloric acid, which confirms the proposed explanation of the process.

## **CONCLUSIONS**

Our results can be summarized as follows.

1. We showed that the electro dialysis can be used for processing acidic, neutral and alkalic processed regeneration solution of sodium sulfate to obtain acid and alkali. We observed a decrease in the current efficiency of alkali (acid) in acidic (alkalic) solution because of the transfer of excess amounts of protons or hydroxide anions acidic and alkalic solutions respectively.
2. For all cases of electrolysis, we documented a significantly higher selectivity of cation exchange membrane MK-40 on sodium ions relative to protons when compared to the selectivity of anion exchange membrane MA-40 on sulfate ions relative to hydroxide anions. This higher selectivity caused acidification of work solutions in the early stages of the experiments.
3. When we used the cation exchange membrane MK-40 and anion exchange membrane MA-40, the acid concentration in anodic area was 1830 mg-eq/dm<sup>3</sup> and the alkali concentration in the cathodic area was 1450 mg-eq/dm<sup>3</sup>. With further increase in the concentrations of acid and alkali, the selectivity and electrical conductivity of anion exchange membrane are reduced which leads to less effective electro dialysis.

4. We showed that using four-chambered electrolyzer separated by two cation exchange membranes MK-40 and the anion exchange membrane MA-40, one can purify aqueous solutions of sodium chloride to obtain alkali and hydrochloric acid.
5. We established that the current efficiency of acid and alkali decreases in the course of electrolysis as well as from increased alkali concentration in the cathodic area and the concentration of hydrochloric acid to 3000 mg-eq/dm<sup>3</sup>. In addition, as concentrations of acid and alkali increase, the degree of purification of water from sodium chloride decreases.
6. We found that one can increase the current efficiency of hydrochloric acid and alkali by regulating current density at the minimum voltage at concentrations of acid and alkali at less than 3000mg-eq/dm<sup>3</sup>.

## REFERENCES

Salnikov E., Gofenberg I., Turanina E., etc (1992). Wastewater treatment of sulfate ions with lime and aluminum oxysulfate. *Chemistry and water technology*, 14(2), 152-157.

Pisarska B., Dylevski R. (2005). Analysis of the conditions to obtain H<sub>2</sub>SO<sub>4</sub> and NaOH from solutions of sodium sulfate by eletrodialysis. *J. Appl. Chemistry*, 78(8), 1311-1316.

Nosachova J., Zelenyuk O., Gomelya N. (2010). Wastewater treatment of sulfate ions with lime and aluminum containing coagulants. *Journal of the National technical university of Ukraine "KPI" Chemical engineering, ecology, resource saving*, 1, 48-50.

Shabliy T., Gomelya N., Panov E. (2010). Electrochemical treatment of spent solutions formed during regeneration of cation-exchanger. *Ecology and industry*, 2, 33-38.

