

## ION TRANSPORT VIA ELECTROSORPTION

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The aim of this study was the metal ion removal of the gas scrubber effluents of an olefins plant by Electro Swing Adsorption. This electrochemical method has an advantage it does not use hazardous chemicals and it does not produce pollution. This paper is a report about preparation of nickel electrodes with high specific surface area, estimating the electrochemically accessible surface area, and experimentally demonstrating the existence of the double-layer, determination of the capacity of the electric double-layer, demonstrating the ion transport by electrosorption. Moreover an attempt is made at the determination of the relative role of the physical adsorption and the electrosorption in the ion transport. Measurements were carried out on an automated electro swing adsorption apparatus. Finally optimal operating parameters were determined by maximizing the removal efficiency.

**Keywords:** electrosorption, physical adsorption, “nickelized” nickel electrode, porous nickel electrode, mass transfer

### Introduction

Environmental pollution is one of the most challenging problem of the continuously developing, industrialized world. Recycling of the effluents containing large amount of impurities can only be realized by appropriate treatment. Effluents from caustic scrubbers of pyrolysis gases are heavily loaded with metal ions of which the removal is not yet solved. We aimed to develop a process for reducing the metal ion content in spent caustic effluents to minimize the environmental effect.

The basis of the proposed process was ion transport via electrosorption. The electrosorption is a kind of adsorption, which takes place on the surface of charged electrodes [1]. The electric polarization can be carried out galvanostatic or potentiostatic ways [2]. In practise the galvanostatic method is preferred [2-4]. The electrosorption of cations takes place on the cathodic polarized (negative) electrode. This electrosorption is superimposed on the physical adsorption (on non-charged electrode). In case of reversed electric polarization the cations desorb. When the ionadsorption is carried out in a given solution and the desorption in another solution, then ions can be transported from one solution to another [5-8]. This is called ion transport via electrosorption.

In the electrosorption an electric double-layer comes into being at the electrode-solution interface. The electric double-layer consists of two parts: the Helmholtz-layer and the diffuse layer. If the electrode moves the diffuse layer can break and a zeta-potential appears between the fixed and the moving parts.

The electrosorption, as it is an electrochemical method, has an absolute advantage: it does not use hazardous chemicals, but only inert electrodes. In addition it does not produce pollution, and the electrochemical parameters can be measured and controlled easily.

The electrosorption is a surface phenomenon. Its efficiency grows with the electrode surface area. The applied electrodes are mostly porous carbon-electrodes with high specific surface area [1, 3, 9-14]. Electrode with high specific surface area also can be prepared from metals, several methods of this procedure are known. Macroporous Ni, Co and Fe can be prepared via reduction of NiO, Co<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> by hydrogen [15]. Heating of metal-oxalates in nitrogen also can result in high specific surface area metals [15]. Porous Ni, Cu, Ag, Pt and Au can be prepared via precipitation of metal on colloidal silica, and after calcinations the silica is removed with HF [16]. Among the electrochemical methods the preparation of platinum is well known. Accordingly “black” or “grey” nickel electrode also can be prepared with high specific surface area [17-19]. The high surface in itself area is not sure enough, because in case of insufficient pore-size distribution not the whole surface will be accessible electrochemically.

Inorganic ions can be removed from aqueous solution by means of electrosorption [20]. Numerous examples are known of removing of organic compounds from dilute aqueous solution, e.g. phenols and derivatives [10], pyridine [2], aniline and bipyridines [3], tiocianate [1] or even colloidal particles [21]. The electrosorption is applied at industrial level in wastewater treatment [2, 3, 10, 19] and water desalination [22-29].

### Preparation of nickel electrodes of high specific surface area

The preparation was carried out by two different techniques: by electrochemical and powder metallurgic methods. The nickel coated nickel was prepared by electrolysis, and the porous disc electrode was made by powder metallurgic technique.

#### *Preparation of nickel coated nickel electrodes by electrolysis*

Nickel was precipitated on the surface of nickel sheet. Before the electrolysis the nickel sheet was prepared: mechanical polishing, degreasing by sodium hydroxide solution (10 M), washing by water, drying, soaking in chloroform or carbon tetrachloride, and finally acidic etching in boiling hydrochloric acid (30 wt%).

The electrolytes applied in the former papers contain  $\text{NiSO}_4$  ( $33 \text{ g dm}^{-3}$ ),  $(\text{NH}_4)_2\text{SO}_4$  ( $33 \text{ g dm}^{-3}$ ) and K-Na-tartarate ( $14 \text{ g dm}^{-3}$ ) with pH 5.1. In accordance with our experience by this solution it can not be prepared smooth, stable coating. It was found that the properties of the nickel layer precipitated via electrolysis strongly depend on the pH. At pH 7.0 a bright, gleaming grey surface forms, while at pH 8.0 a black and cracking surface evolves.  $\text{NH}_4\text{OH}$  was used to increase the pH. At pH 7.5 some opalescence was observed due to the formation of  $\text{Ni}(\text{OH})_2$  precipitation, that can be taken into complex by EDTA. In the pH range of 9.5–10.0 the solution is dark blue, and from this solution smooth, black, stable coating can be precipitated. The current density of the electrolysis has to be less than  $0.1 \text{ A cm}^{-2}$ . The pH of the solution can change during the electrolysis that results in deterioration of the surface. The pH can be kept constant with application of sufficient solution volume or  $\text{NH}_4\text{OH}$  feeding.

#### *Preparation of porous nickel electrodes by powder metallurgic technique*

Porous electrodes were made by this method, the porosity guarantees higher surface area. The initial powder contains Raney-nickel (90–93 wt%, glowed at  $60 \text{ }^\circ\text{C}$ ), silver chloride (2–5 wt% referred to the silver) and paraffin (5 wt%). The paraffin needed to prepare to get the required homogeneity and porosity. It was melted in warm water ( $70 \text{ }^\circ\text{C}$ ) and surfactant (dish-washing agent) was added with strong mixing. The emulsion was cooled quickly pouring onto ice, then the paraffin particles were dried at room-temperature.

After then the powder was pressed (6–8 ton) in a steel ring by means of a hydraulic pressing machine and pastille was formed. The pastilles were treated by heat and reduction.

The heat treating had two stages. First the whole organic substance was fired out in oxidative atmosphere. The heating rate was approximately  $200 \text{ }^\circ\text{C h}^{-1}$ . The

pastilles were kept between  $400\text{--}450 \text{ }^\circ\text{C}$  for 30 minutes. This way the solid paraffin melted then turned into cracking gas. In case of higher heating rate the forming gases can break the pastille. In the second stage the pastilles were kept between  $960\text{--}1100 \text{ }^\circ\text{C}$  for 30 minutes in inert atmosphere (nitrogen). Under these conditions the silver and the nickel form an alloy, that has increased electric conductivity and provides enhanced disc electrode with better mechanical properties. If the first stage misses, the porous electrode will be useless because of the surface cracks.

The reduction was carried out in hydrogen atmosphere at  $550 \text{ }^\circ\text{C}$ . At the end of the reduction process the output gas of the reactor does not contain water.

### Nickel electrodes tested

#### *The electrochemically accessible surface area*

An electrolytic double-layer forms at the electrode-solution interface, that consists of a Helmholtz-layer and a diffuse layer. The Helmholtz-layer is independent of the ion concentration (contrasted) in contradiction with the diffuse layer. The double-layer regards as a capacitor.

When electric current flows in an ideally polarisable electrode, the current changes only the charge of the capacitor and there is no charge transition.

$$\frac{dQ}{d\varepsilon} = \frac{I dt}{d\varepsilon} = C_t \quad (1)$$

Where:

- Q – charge,
- $\varepsilon$  – potential,
- I – current intensity,
- t – time,
- $C_t$  – polarisation capacity at a given t.

In case of partially polarisable electrode  $C_t$  is the electrode capacity of the double-layer at  $t=0$ . Under constant current intensity the potential of the electrode was measured compared to a saturated calomel electrode ( $\Delta\varepsilon = \varepsilon - \varepsilon_{\text{calomel}}$ ) in the function of time. The counter electrode was graphite. The slope of the curve  $\Delta\varepsilon$  vs. t:

$$\text{tg}\alpha = \frac{d(\Delta\varepsilon)}{dt} = \frac{d\varepsilon}{dt} \quad (2)$$

The polarisation capacity from the equations (1) and (2):

$$C_t = \frac{dI dt}{d(\Delta\varepsilon)} = \frac{dI}{\text{tg}\alpha} \quad (3)$$

Supposing flat condenser (4):

$$C_t = \frac{\varepsilon_0 A}{d} \quad (4)$$

Where:

- $\varepsilon_0$  – the permittivity of the vacuum,
- A – the area,

$d$  – the distance between the condenser plates.  
Considering the equation (4):

$$\frac{\varepsilon_0 A}{d} = \frac{I}{\operatorname{tg} \alpha} \quad (5)$$

Comparing the electrochemically active surface area of two electrodes under the same conditions where index 1 and 2 refer to the electrodes:

$$\frac{A_1}{A_2} = \frac{\operatorname{tg} \alpha_2}{\operatorname{tg} \alpha_1} \quad (6)$$

On the basis of the above-mentioned consideration the high surface area of the electrodes were compared to the nickel electrode's flat surface (polished). The constant current intensity was 10 mA. The solution contained NaOH (0.2 wt%). The electrode distance was 10 mm. Referring to the flat nickel surface area, the electrochemically accessible surface area for nickel coated nickel (nickel-soot coated nickel) and for the porous nickel electrode are 50 and 214, respectively. These values are in accordance with the data measured by others with different methods in case of copper coated copper [4, 30] or nickel coated nickel [18].

BET surface area analysis was carried out by nitrogen adsorption in a Micromeritics ASAP 2000 instrument. The ratio of the BET surface area and the geometric surface area for the nickel coated nickel and for the porous nickel were 31370 and 38680, respectively. It means that only a part of the BET surface area is accessible electrochemically: this value is 0.16% for the nickel coated nickel, and 0.52% for the porous nickel.

#### Diffuse part of the electric double-layer

The electrode has to be moved to transport ions with electrosorption from a solution to another. Moving the electrode (compared to the "stationary" solution) the diffuse part of the double-layer breaks and zeta-potential evolves. The zeta-potential depends on the rate of the relative moving. On the other hand the place of the breaking has effect on the efficiency of the ion transport. The higher part of the double-layer gets from one solution to another, the more efficient the ion transport is. It seems reasonable to examine how the zeta-potential (and this way the place of the double-layer breaking) changes with the relative rate. The applied instrument for the zeta-potential measurements can be seen in the Fig. 1. The solution containing NaOH (0.2 wt%) flowed in a plastic tube ( $R = 15$  mm) in the direction as the arrow shows.

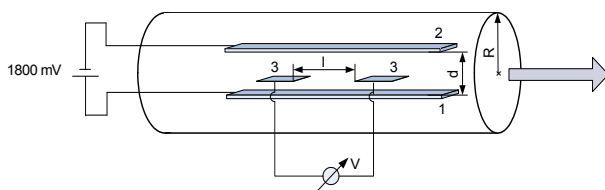


Figure 1: Measurement of the zeta-potential

1800 mV potential-difference was switched on the cathode (1) and on the anode (2). The electrode distance,  $d$  was 15 mm. The potential-difference was measured between the reference electrodes (3) by a voltmeter (V). The reference electrode distance,  $l$  was 40 mm.

A series of measurement can be seen in the Fig. 2. The reference electrode distance is plotted in the function of the laminar rate of flow. The zeta-potential,  $\zeta$  does not change significantly over flow rate of  $25 \text{ cm s}^{-1}$ . This way it is not reasonable to apply higher relative rate.

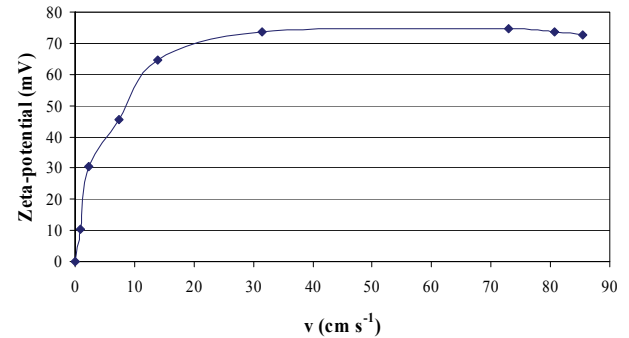


Figure 2: Zeta-potential vs. flow rate of the solution

#### The capacity of the double-layer and the electrosorption of the sodium ions

F. Béguin et al. [11] investigated the electrosorption of lithium on activated carbons using the flowing model cell (Fig. 3).

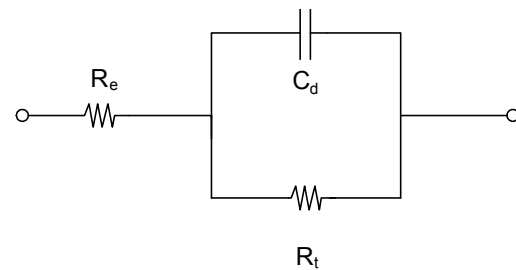


Figure 3: The model cell

Where:

- $R_e$  – the resistance of the electrolyte solution,
- $R_t$  – the charge transport resistance
- $C_d$  – is the capacitance of the double-layer.

It was found that under constant current intensity the potential difference,  $U$  changes in time as follows:

$$U = R_e I + R_t I - R_t I e^{-\frac{t}{R_t C_d}} \quad (7)$$

If  $t = 0$ , then considering equation (7):

$$U(t = 0) = R_e I \quad (8)$$

$R_e$  is coming from (8). If  $t \rightarrow \infty$ , then

$$U(t = \infty) = (R_e + R_t) I, \quad (9)$$

$R_t$  is coming from (9). The derivative of potential with respect to time under constant current intensity,  $I$ :

$$\left. \frac{dU}{dt} \right|_{t=0} = \frac{1}{C_d} I e^{-\frac{t}{R_t C_d}} \quad (10)$$

If  $t = 0$ , then

$$\left. \frac{dU}{dt} \right|_{t=0} = \frac{I}{C_d} \quad (11)$$

i.e. the capacitance of the double-layer,  $C_d$  can be calculated from the initial slope of the  $U$  vs.  $t$  curve.

The potential-difference in time can be seen in the *Fig. 4* for the nickel coated nickel under current intensity  $I = 0.01$  A. The solution contained NaOH (0.2 wt%), the counter electrode was graphite. The parameters of the electrochemical cell:  $R_e = 122 \Omega$ ,  $R_t = 225 \Omega$ ,  $C_d = 1.84$  F.

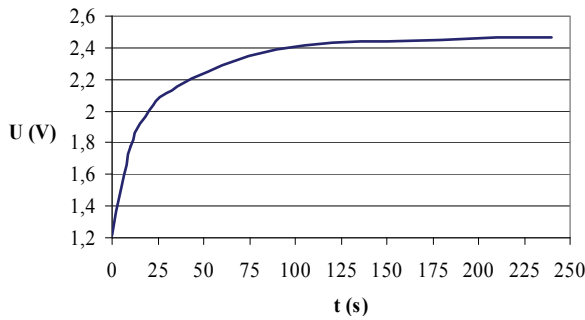


Figure 4:  $U$  vs.  $t$  curve for the nickel coated nickel

The  $U$  vs.  $t$  curve for porous nickel electrode can be seen in the *Fig. 5*. The parameters of the electrochemical cell:

$$R_e = 63 \Omega, R_t = 109 \Omega, C_d = 5.08 \text{ F.}$$

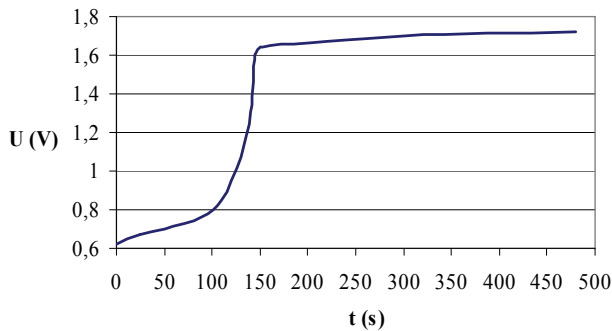


Figure 5:  $U$  vs.  $t$  curve for porous nickel electrode

Knowing the capacitance,  $C_d$  and the potential-difference between the two electrodes,  $U$  the charge can be determined on the electrodes:

$$Q = C_d U \quad (12)$$

The charge,  $Q$  was calculated from the  $U$  at 25 s. Knowing the charge,  $Q$  considering the Faraday's law the amount of the sorbed sodium ions can be determined, that was 298 mg  $\text{Na}^+$  for nickel coated nickel and 127 mg  $\text{Na}^+$  for the porous nickel electrode.

### Electrosorption and physical sorption

In electrosorption assisted ion transport the ion adsorption takes place in a solution and the desorption is carried out in another solution. This way the physical adsorption is superimposed on the electrosorption, and in addition the hydrodynamic adhesive layer also takes part in the ion transport. The relative extent of three effects was estimated. The electrode was immersed in a solution containing NaOH 0.2 wt%. The physical adsorption of the sodium ions took place. The desorption was carried out in distilled water. The extent of the sodium ion transported with physical adsorption was 320 mg  $\text{m}^{-2}$  for the nickel coated nickel, and 120 mg  $\text{m}^{-2}$  for the porous nickel. After this the desorption was carried out by switching 1800 mV potential-difference between the studied electrode and the counter electrode. The desorption took place in also distilled water, but the polarity of the electrodes was reversed. It is supposed that under this conditions the electrosorption and the physical adsorption take place simultaneously. In this later case the quantity of the transported sodium ions was 500 mg  $\text{m}^{-2}$  for the nickel coated nickel, and 160 mg  $\text{m}^{-2}$  for the porous nickel. The extent of the sodium ions transported by electrosorption could be calculated from the difference of the two solutions (measured with and without potential-difference). This value was 180 mg  $\text{m}^{-2}$  for the nickel coated nickel, and 40 mg  $\text{m}^{-2}$  for the porous nickel. These values are less than the calculated ones from the capacity of the double-layer, but considering the roughness of the measurement it can be said that they are comparable with each other.

It is necessary to explain the effect of the hydrodynamic adhesive layer, as well. The hydrodynamic adhesive layer moving with the electrode could carry some ions with itself even without any ion adsorption. In this case the sodium ion concentration is the same in the hydrodynamic adhesive layer as in the bulk. The effect of the hydrodynamic adhesive layer was determined by distilled water. Using the bulk concentration the quantity of the sodium ion transported by the adhesive layer was calculated. This value was 90 mg  $\text{m}^{-2}$  for the nickel coated nickel, and 45 mg  $\text{m}^{-2}$  for the porous nickel. Thus the effect of the hydrodynamic adhesive layer is much less than the effect of the adsorption, but it is still not negligible.

### Mass transfer by electrosorption apparatus

A fully automated electrosorption apparatus was designed and built. Measurements were carried out on this apparatus. The used parameters are summarised in *Table 1*.

Table 1: Parameters of the measurements

Parameters	
Polarization potential	1000–2400 mV
Distance between the electrodes	2.5–40 mm
Time	25–600 s

Parameters can be changed fast and in wide range due to the structure of apparatus. Experimental setup can be controlled easily and it works reliable.

Purification of used model solutions was carried out by cyclic procedure. This purification is based on Electro Swing Adsorption. 4 wt% NaOH solution was used instead of the effluent and porous nickel electrode was used in the experiments. The latter was prepared by powder metallurgic techniques.

Optimal operating parameters were determined by maximizing the removal efficiency. The amount of ions removed in one cycle was determined as a function of the number of cycles, concentration of sodium ions, polarization potential and desorption time.

Fig. 6 illustrates the influence of polarization potential on the mass transfer. The polarization potentials have been varied from 1000 mV to 2400 mV. At first high polarization potential was used however in this case a huge energy consumption appeared because of hydrolysis. It was proved that a good mass transfer can be reached with lower polarization potentials when the energy consumption is lower.

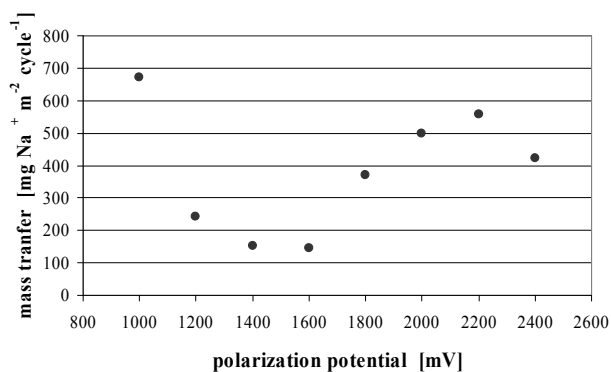


Figure 6: Mass transfer for porous nickel electrode 25 s adsorption time, and 120 s desorption time

Previously we have demonstrated that adsorption process is faster than desorption process. If porous nickel electrodes are used pore diffusion inhibition will occur.

In Fig. 7 it can be seen that desorption time have to be more than 300 s, in this way a more efficient mass transfer can be reached.

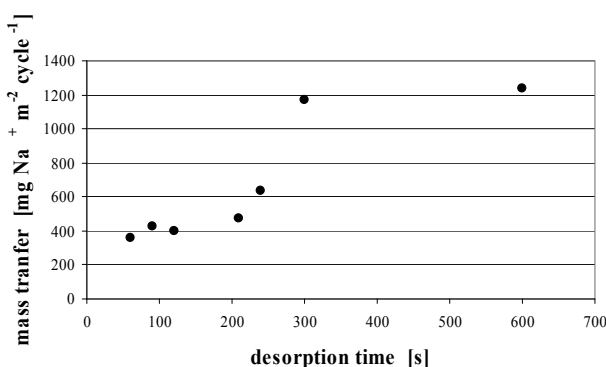


Figure 7: Mass transfer for porous nickel electrode 1200 mV adsorption and desorption polarization potential

In the early part of the investigations electrical efficiency was 30–35% but after the optimization of the parameters it has improved to 60%.

## Summary

Nickel electrodes were prepared with high specific surface area to produce ion transport by electrosorption. Nickel coated nickel electrode was prepared by electrolysis and porous nickel electrode was made by powder metallurgic method. It was found that the electrochemically accessible surface area of the electrodes is much less than their BET surface area. Measuring the zeta-potential it was shown that it is not worth-while to apply higher relative moving rate than 25 cm s<sup>-1</sup> between the solution and the electrode. Using graphite counters electrode the parameters of the electrochemical cell were determined. Knowing Faraday's law and the capacitance of the electrolytic double layer the extent of the adsorbed sodium ions (by electrosorption) was calculated. This value was 298 mg m<sup>-2</sup> for the nickel coated nickel, and 127 mg m<sup>-2</sup> for the porous nickel. The role of the electrosorption, the physical adsorption and the hydrodynamic adhesive layer was estimated via independent measurements. It was found that all of the three effects take part in the ion transport. Under the experimentally determined optimal conditions electric efficiencies up to 60% were achieved.

Removed sodium ion was 1200 mg m<sup>-2</sup> cycle<sup>-1</sup> from a 4 wt% NaOH solution, using a polarization potential of 1200 mV and a distance of 2,5 mm between the electrodes with an adsorption and desorption time set to 25 and 300 s, respectively. We can conclude that our laboratory scale electrosorption apparatus fulfilled the requirements and measurements were reproducible. On the basis of the lab-scale results the scale-up of the process to pilot scale seems to be possible.

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