Electrodialysis concentration of highly mineralized wastes of water treatment plants modeling

A A Chichirov, N D Chichirova, A A Filimonova, A I Minibaev, L I Tolmachev
Kazan state power engineering university, Russia, 420066 Kazan, Krasnoselskaya, 51
minibaev-a@list.ru

Abstract. Studies on electrodialysis concentration/desalination of concentrated salt solutions (NaCl) as a model of soft highly mineralized liquid waste have been carried out. The apparatus of the EMA line manufactured by JSC «Membranines Technologijos LT» were used as electro-membrane devices. Apparatus are distinguished by reliable operation in concentrated mineral solutions under high currents. IONSEP-HC/MC ion-selective cation- and anion-exchange membranes intended for work with highly mineralized sewage was used. Studies have shown the possibility of utilization of concentrated electrolyte solutions, as models of highly mineralized VPU waste with high efficiency. To a residual electrolyte concentration in dialysate at a level of 0.2-0.25 g/l, the unit cost of electricity for salt transfer is approximately 1 kWh/kg, the desalination ratio is 100-150. When the concentration of electrolyte in dialysate is less than 0.1 g/l, the process practically stops due to the increasing influence of the reverse diffusional salt transfer. The calculated maximum salt (NaCl) concentration in the concentrate is 15-16 mass. %

In the production of pure and deionized water from a natural water by ion exchange, electrodialysis or reverse osmosis methods a bulk amount of highly mineralized wastewaters (regenerates and brine) forms, that generates secondary pollution problems.

Thermal power plants (TPP) are one of the main sources of highly mineralized effluent [1]. The main source of highly drains on TPP are water treatment plants (WTP), mainly ion-exchange baromembrane desalting plants. At present, at most TPP acidic highly mineralized effluents from cationite filters and alkaline highly mineralized effluents from anionite filters are mutually neutralized, and the final highly mineralized discharge is dumped. In some countries, the method of utilization of highly mineralized effluent by evaporation with the disposal of solid salts is used, which cannot be called successful. In this case all valuable chemical components of the effluent are irretrievably lost.

In solving the problem, it is of interest to use electrodialysis concentration of liquid wastes prior to neutralization to a level suitable for reuse in the cycle of TPP. In this soft liquid wastes containing mainly sodium salts and alkaline liquidwastes of ion exchange WTP are of great interest, since they do not contain hardness ions, and sodium salts and alkalis are valuable reagents themselves. There is experience, mainly foreign, of using electrodialysis for concentrating reverse osmosis concentrates with obtaining a salt masterbatch suitable for evaporation with obtaining dry salts [2, 3].

The tasks of the work included testing the operability of the electrodialysis method using promising industrial electro-membrane devices and membranes.
Methods and objects

Investigations were carried out on EMA-400/2 electromembrane apparatus in the version of two – channel assembly with flushing (near-electrode) chambers. The main characteristics of the apparatus are shown in Table 1.

| Characteristics                                      | Value          |
|------------------------------------------------------|----------------|
| The number of cameras on 1 path                      | 200            |
| Bandwidth per path                                   |                |
| - working range                                      | 3.5-5.0 m³/h   |
| - maximum flow                                       | 6.0 m³/h       |
| Maximum voltage on the device (U<sub>max</sub>)      | 494 V          |
| Maximum current per device (I<sub>max</sub>)         | 28.7 A         |
| Chamber thickness (distance between membranes)       | 1 mm           |
| Working area of membranes                            | 24 dm²         |
| Path length in the active zone                       | 7.9 dm         |

The apparatus were installed heterogeneous membrane produced by IONTECH (table 2).

| Model             | IONSEP-HC-C | IONSEP-HC-A |
|-------------------|-------------|-------------|
| Thickness, mm     | 0.42        | 0.42        |
| Water content, %  | 40          | 40          |
| Ion exchange capacity, mol/kg | 2.2        | 2           |
| Burst strength, MPa | 0.6        | 0.6         |
| Water permeation time, min | 45         | 90          |
| Solution diffusion index x10³ mmol, NaCl/(cm²·h·mol/L) | 3.2        | 3.7         |
| Selective ratio, % | 92          | 92          |
| Surface electric resistance, Ω·cm²                   | 10-12        | 10-13        |

The experimental plant included two EMA-400/2 units connected sequentially with a parallel flow of dialysate and concentrate, intermediate recirculation tanks with a volume of 500 l and pumps with variable frequency drive ohm. Power supply apparatus – independent from two DC power sources.

Concentrated NaCl solutions as models of soft highly mineralized liquid waste were used. Studies were performed in the recirculation mode until the complete development of the initial solutions. In the experiments, the feed rates of the concentrate and dialysate were varied. Conducted constant monitoring of current (I), voltage (U), temperature and salt content of the solutions. Then, using known methods, the process efficiency was calculated – current efficiency (η), specific consumption of electrical energy for salt transfer (w<sub>s</sub>). In addition, parasitic side processes were calculated: reverse diffusion, salt transfer and osmotic water transfer. The salt flow through a membrane pair (j<sub>s</sub>, mol-eq/m²·s) was determined by the change in salt concentration in circulation storage tanks and by the change in salt concentration in the concentrate and dialysate at the inlet/outlet of the apparatus.

Results and discussion

The experimental results were processed in the framework of the limit electrodialysis concentration model [4]. According to the model, the flows salt and water through the membranes include diffusion and osmotic ones:

\[ j_s = -P_s(c_k - c_A) + \eta \frac{i}{P} \]

\[ j_w = P_w(c_k - c_A) + \tau_w \frac{i}{P} \]
where \( j_s \) and \( j_w \) – respectively, flows of salt and water into the concentration chambers; 
\( P_s = P_s^a + P_s^k \), \( P_w = P_w^a + P_w^k \) – diffusion and osmotic permeability of the membrane pair, respectively; 
\( t_w = t_w^a + t_w^k \) – the transfer number of water through a membrane pair; 
\( \eta = 1 - t_w^a + t_w^k \) – current output for the transfer of cations (c) and anions (a); 
\( c_c \) and \( c_A \) – salt concentration in the concentration and desalting chambers of, respectively 
\( i \) – current density, 
\( F \) – Faraday number.

In the model, it was assumed that in concentrated solutions the electroosmotic transfer of free water is negligible (water is transferred predominantly as part of hydration shells of ions). Therefore, the number of water transfer was represented as 
\( t_w = t_w^a + t_w^k = h\eta \), where \( h \) – the number of salt hydration.

Figure. 1. Dynamics of salt concentration in concentrate and dialysate lines at a circulation rate om EMP 5000 l/h

![Figure 1](image1.png)

Figure. 2. The change in the volume of concentrate and dialysate at the rate of circulation of each solution 5000 l/h

![Figure 2](image2.png)
All four phenomenological parameters of the model: \( P_s \), \( P_w \), \( \eta \) and \( h \) can be determined by linearizing equations 1 and 2, dividing their right and left parts by \( \Delta c \):

\[
\begin{align*}
\frac{j_s}{\Delta c} &= -P_s + \frac{\eta i}{F \Delta c} \\
\frac{j_w}{\Delta c} &= P_w + \frac{h \eta i}{F \Delta c}.
\end{align*}
\]

(3)

(4)

The experimental data were processed in coordinates \( \frac{j}{\Delta c} - \frac{i}{\Delta c} \) and \( \frac{j}{\Delta c} - \frac{i}{\Delta c} \) using the method of least squares to determine the transport characteristics of the membrane pair.

![Figure 3. The salt flow of through the membrane pair, depending on the current density at a circulation rate of 1000 l/h.](image)

Characteristics of mass transfer processes in the concentration of model solutions on a cascade of two EMAs with a sweep in the circulation rate of dialysate and concentrate are presented in table 3.

Table 3. The transport characteristics of the IONSEP-HC-C/IONSEP-HC-A membrane pair in EMA-400/2 apparatus, depending on the circulation rate.

| № | \( \theta_A \), L/h | \( \theta_K \), L/h | \( P_s \cdot 10^7 \), m/s | \( \eta \) | \( P_w \cdot 10^5 \), m/s | \( t_w \), mol/F | \( h \cdot \frac{\text{mol H}_2\text{O}}{\text{mol salt}} \) |
|---|------------------|------------------|----------------|---|----------------|--------------|----------------|
| 1 | 2000             | 2000             | 1.96           | 0.682 | -             | -            | -              |
| 2 | 6000             | 6000             | -              | 0.75  | -             | 9.65         | 12.9           |
| 3 | 4000             | 4000             | 1.86           | 0.715 | 0.5           | 10.62        | 14.85          |
| 4 | 3000             | 3000             | 2.24           | 0.71  | 0.56          | 9.17         | 12.9           |
| 5 | 5000             | 5000             | 4.33           | 0.9245| 0.41          | 11.1         | 12.0           |
| 6 | 1000             | 1000             | 4.034          | 1.023 | 1.46          | 20.7         | 20.2           |
| 7 | 2000             | 1000             | 4.85           | 0.982 | 1.54          | 14.57        | 14.8           |
| 8 | 1000             | 600              | 3.9            | 0.907 | 0.7           | 8.44         | 9.31           |
Figure. 4. Dependence of the specific electric power consumption on salt transfer through the membranes on the output salt concentration in dialysate. The circulation rate of the concentrate – 1000 l/h, dialysate – 2000 l/h

From the obtained dependences, we can draw a conclusion on the characteristics of the process.

In the range of salt concentrations in transferred dialysate 12-1 g/l (i.e. more than 1 g/l) specific energy consumption of about 1 to Wh∙h/kg t salt. When the salt concentration in the dialysate is less than 1 g/l efficiency does not decrease (up to 2 Wh∙h/kg). When the output salt concentration in dialysate ≈ 0.1 g/l the process practically stops (figure. 4). You can roughly set the minimum output concentration of salt in dialysate at 0.2-0.25 g/l in which the high efficiency is maintained. By ratnost desalting \( \frac{C_c}{C_d} \) it will be 100-150.

From the transport characteristics, the calculated maximum concentration of salt in the concentrate will be 15.4±1 mass. % or 2.9 M.

The linear flow rate of solutions in the chambers of the apparatus varies from the minimum in the middle part of the chamber, where the gap width is 40 cm to the maximum at the entrance and exit of the chamber, where the gap width is 2. Calculated average speed data are presented in Table 4.

| Volumetric circulation rate (υ), l/h | Minimum linear velocity in chambers, cm/s | Maximum linear velocity in chambers, cm/s |
|-------------------------------------|------------------------------------------|------------------------------------------|
| 1000                               | 0.85                                     | 14.0                                     |
| 6000                               | 5.0                                      | 82.5                                     |

The obtained data indicate that water speeds on average exceed critical values [5] even at low space velocities. circulation (costs) up to 1000 l/h in the streams saved turbulent mode.

From the obtained conclusion it follows that it is possible to obtain finished products – partially desalinated water and concentrate in one pass at a low flow rate of solutions (2000-1000 l/h), which is confirmed experimentally. At the same time, significant heating of the solutions (more than 5 °C ) is not checked.
Conclusion

Studies conducted on promising industrial electro-membrane devices equipped with cation-and anion-exchange membranes resistant to high current loads have shown the possibility of utilization of concentrated electrolyte solutions, as models of highly mineralized VPU waste with high efficiency.

To a residual electrolyte concentration in dialysate at a level of 0.2-0.25 g/l, the unit cost of electricity for salt transfer is approximately 1 kWh/kg, the desalination ratio is 100-150. When the concentration of electrolyte in dialysate is less than 0.1 g/l, the process practically stops due to the increasing influence of the reverse diffusional salt transfer. The calculated maximum salt (NaCl) concentration in the concentrate is 15-16 mass. %

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