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TEST OF SALINE WATER SOFTENING BY DONNAN DIALYSIS

A concept of saline water softening by Donnan dialysis is proposed. The concept involves exchange of magnesium and calcium ions in saline water for sodium ions according to the mechanism of counter-ion interdiffusion. The tests were run in a large laboratory system with membrane of effective surface area of 432 cm^2 .

There were investigated model solutions of calcium chloride and magnesium chloride as well as saline water of salt concentration amounting to 0.2 kmol/m^3 . The solutions were passed co-currently through the dialyzer at two velocities: $5 \text{ dm}^3/\text{h}$ and $10 \text{ dm}^3/\text{h}$. Despite an efficient removal of calcium and magnesium ions, there was observed a concomitant escape of sodium chloride.

1. SOFTENING CONCEPT

In the past few years, the increasing salinity of surface and ground waters has become a problem of serious concern in Poland. Of the many contributing factors, the development of mining industry is primarily responsible for this rise. To abate this kind of pollution it is necessary to implement such treatment methods as distillation or membrane processes. Unfortunately, membrane techniques have not been in use so far, because domestic membranes are lacking. The recent start-up of cation- and anion-exchange membrane manufacture gives good prospects for the future. Now, it is time to intensify research on electro-dialytic desalination of water.

It is a well-established fact that the costs of electro-dialytic desalination increase proportionally to the initial salinity of the water to be treated. During electro-dialysis of saline waters, the soluble salts, which precipitate simultaneously in the concentrate tank, bring about a scaling of the membrane surface, thus reducing noticeably the efficiency of the process. It is worth keeping in mind that electro-dialysis is economic only when the

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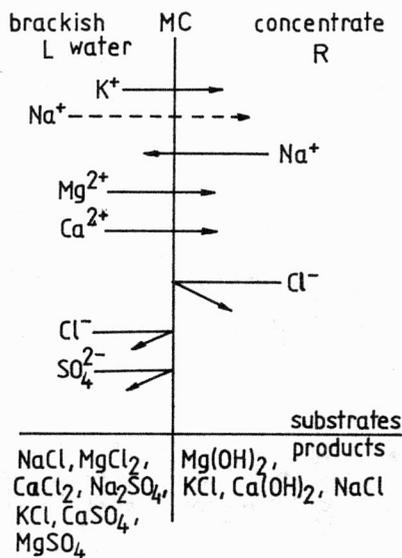


Fig. 1. Scheme of saline water softening

calcium and magnesium ions has become a prerequisite, the more so as the elimination of magnesium ions reduces the persistence of troublesome magnesium hydroxides in the cathode compartment. As a matter of fact, removal of magnesium and calcium ions should be a preliminary step in electrodialytic desalination of saline water.

The method of softening the saline water presented here makes use of Donnan dialysis as an energy-saving process. In figure 1 the method of removing Mg^{2+} and Ca^{2+} ions from saline water is presented. A cation-exchange membrane (MC) separates two solutions. The solution on the left-hand side (L) of the membrane contains ions which are commonly found in seawater, so it is regarded as the dialysate. The right-hand side (R) solution includes concentrated sodium chloride, so it is regarded as the concentrate. We assume that there is neither co-ion (anion) transport nor water transport in the system. Hence, sodium ions are transported from the concentrate solution to the dialysate solution on the opposite side of the membrane, thus initiating a joint transport of Mg^{2+} and Ca^{2+} ions in the opposite direction. The transport of the latter cations would be infeasible if there were no possibility to couple it with the transport of Na^+ ions from the concentrate. Coupling of the two oppositely directed flows should be attributed to the condition of zero-electric current (which is fulfilled in the system) and to the Donnan effect (which excludes ions from the ion-active membrane phase). The zero-electric current condition is described by the following relation:

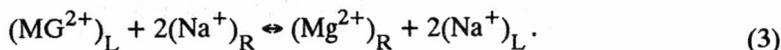
$$\sum_j z_j J_j = \frac{i}{F} = 0 \quad (1)$$

where J_j is flux of component j (mol/m²s), i denotes current density (A/m²), z_j indicates ionic valence, F is Faraday constant (96 500 C/gram-equivalent). Summation is performed for positive and negative ions.

If anions are effectively removed from the membrane phase, the co-ion flux equals zero, and eq. (1) will be reduced to the form

$$J_{\text{Na}^+} + 2J_{\text{Ca}^{2+}} + 2J_{\text{Mg}^{2+}} = 0. \quad (2)$$

Ion transport occurs until the equilibrium between the two solutions is achieved. The dynamics of the process can be described in terms of the thermodynamics of irreversible processes as an exchange reaction between two solutions. Na^+ and Mg^{2+} ions exemplify this exchange. Hence, we have



The driving force A (J/mol) of the reaction takes the form

$$A = - \sum_j \frac{1}{z_j} \mu_j. \quad (4)$$

where

$$\mu_j = \mu_j^0 + RT \ln a_j, \quad (5)$$

μ_j denotes the chemical potential of component j (J/mol), μ_j^0 is the standard chemical potential of component j (J/mol), R stands for gas constant ($R = 8.314 \text{ J/mol} \cdot \text{K}$), T indicates absolute temperature (K) and a_j is activity of component j .

Hence, for Na^+ and Mg^{2+} ions we can write

$$A = RT \ln \left[\frac{(\text{Mg}^{2+})_{\text{L}}^{1/2}}{(\text{Mg}^{2+})_{\text{R}}^{1/2}} \right] \left[\frac{(\text{Na}^+)_{\text{R}}}{(\text{Mg}^{2+})_{\text{R}}^{1/2}} \right]. \quad (6)$$

The reaction proceeds from the left-hand side to the right-hand side of the membrane until an equilibrium between the ion concentrations is achieved. Thus, we have

$$\left[\frac{(\text{Na}^+)_{\text{R}}}{(\text{Na}^+)_{\text{L}}} \right] = \left[\frac{(\text{Mg}^{2+})_{\text{L}}^{1/2}}{(\text{Mg}^{2+})_{\text{R}}^{1/2}} \right]. \quad (7)$$

From this relation it is obvious that – at the sodium concentration ratio from 100 to 1 – the bivalent magnesium will be transported oppositely to the concentration gradient, viz. to a solution whose concentration is 10 thousand times as high as that of the solution on the left-hand side of the membrane.

By virtue of eq. (7) it might be expected that the concentrations of Mg^{2+} and Ca^{2+} ions on the right-hand side of the membrane, i.e. in the concentrate, are high. Such concentrations are not achieved in engineering practice. Limiting concentrations will be restricted by salt dissolubility. In the system presented in this paper, the ion exchange rate

depends on the following factors: concentrations of Mg^{2+} and Ca^{2+} ions in the water, concentrate concentration, membrane properties (ion-exchange capacity, thickness, conductivity, etc.) and hydrodynamic conditions.

2. CHARACTERISTICS OF THE MEMBRANES

The preparation of domestic KESD-2 membranes [1]–[3] involves a polyethylene matrix modified by means of styrene and divinylbenzene copolymers and thereafter sulfonated (to obtain sulfone groups). The parameters of the membrane are listed in table 1.

Table 1
Characteristics of KESD-2 membranes

Parameter	Value
Type	cation-exchange
Resistivity ($\Omega \times cm^2$)	1.5–3.0
Ion exchange-capacity (mmol/g)	1.9–2.6
Transport number	0.98
Water content (%)	50–60
Tensile strength(MPa)	7–10
Thickness (mm)	0.25

3. EXPERIMENTAL SYSTEM

The experimental system enabling removal of Ca^{2+} and Mg^{2+} ions from saline water is shown in fig. 2. The two-compartment plate dialyzer (9) forms the body of the system.

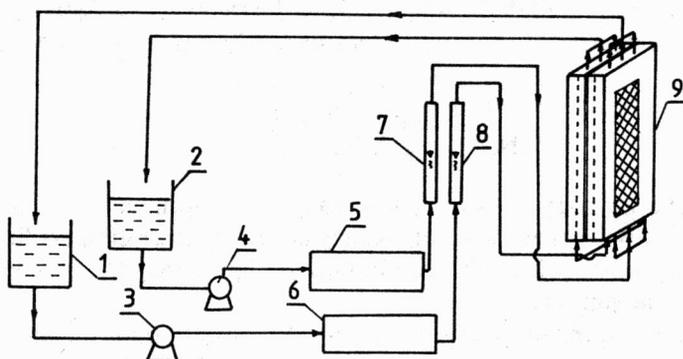


Fig. 2. Experimental system: 1, 2 – feeding tanks; 3, 4 – plunger pumps NDA-8RS; 5, 6 – gas accumulators; 7, 8 – rotameters; 9 – dialyzer

The compartments include a polyethylene network to protect the membrane against mechanical damage. In addition, the pathway of fluid flow in the compartments is extended. The dialysate tank and the concentrate tank are equipped with inlet and outlet stub pipes. The effective surface area of the membrane and the volume of the compartments amount to 432 cm² and 130 cm², respectively. Plunger pumps of NDA-8RS type (3, 4) move the solutions from the feeding tanks (1, 2) to the system. Gas batteries (5, 6) have been applied to prevent pulsation. The rotameters (7, 8) placed in front of the dialyzer enable control of the flow rate.

4. METHODS

The following five solutions were investigated:

1. Model solution of magnesium chloride with three initial concentrations, ≈ 0.0045 kmol/m³, ≈ 0.009 kmol/m³ and ≈ 0.013 kmol/m³.
2. Model solution of calcium chloride with three initial concentrations, ≈ 0.004 kmol/m³, ≈ 0.008 kmol/m³ and ≈ 0.012 kmol/m³.
3. Model solution of the magnesium chloride and calcium chloride mixture with initial concentration of 0.0044 kmol/m³ (MgCl₂) and 0.0039 kmol/m³ (CaCl₂).
4. Saline water with salt concentration of 0.02 kmol/m³.
5. Concentrate solution, viz. sodium chloride, with initial concentration of 0.2 kmol/m³.

The solution flows through the dialyzer at a rate of 5 or 10 dm³/h. 10 dm³ volume samples of dialysate and concentrate were dialyzed. Samples were collected every two hours to determine the concentrations of Mg²⁺, Ca²⁺, Cl⁻ and SO₄²⁻ ions. Cations, chloride ions and sulphate ions were determined photometrically, by the Mohr method and by precipitation, respectively.

On the basis of analytical results, the elimination coefficient α of Mg²⁺ and Ca²⁺ ions in the dialysate was calculated:

$$\alpha = \frac{C_i - C_f}{C_i} 100\% \quad (8)$$

where C_i is initial ion concentration in dialysate (kmol/m³), C_f is final ion concentration in dialysate (kmol/m³).

The experiments were conducted at room temperature and were repeated three times. The results are averages from three measurements.

5. DISCUSSION OF RESULTS

The saline water, which is to be softened by Donnan dialysis, consists of a seawater and drinking water mixture. The softening concept proposed in this paper involves exchange of Mg²⁺ and Ca²⁺ ions in saline water for Na⁺ ions according to the mechanism of counterion interdiffusion.

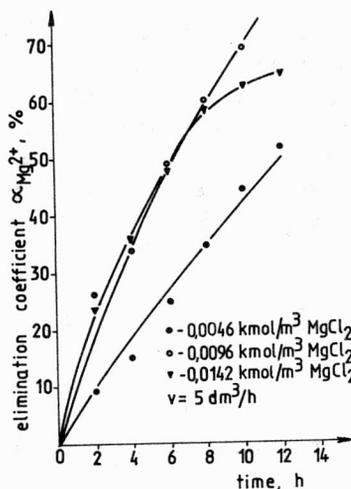


Fig. 3. Elimination coefficient of Mg²⁺ ions versus time for various initial concentrations of MgCl₂

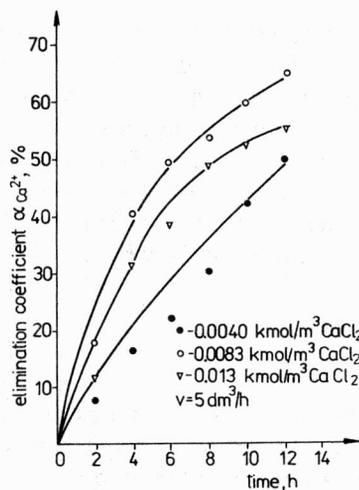


Fig. 4. Elimination coefficient of Ca²⁺ ions versus time for various initial concentrations of CaCl₂

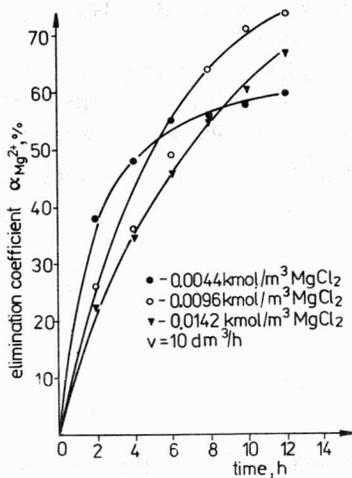


Fig. 5. Elimination coefficient of Mg²⁺ ions versus time for various initial concentrations of MgCl₂

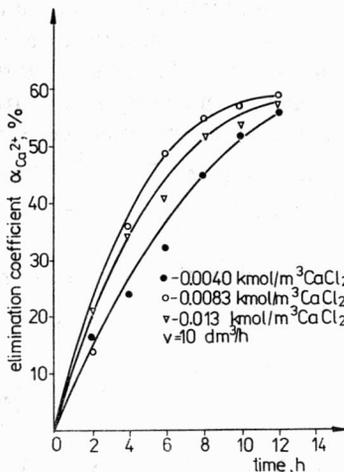


Fig. 6. Elimination coefficient of Ca²⁺ ions versus time for various initial concentrations of CaCl₂

To have more information, at first model solutions of salts containing Mg²⁺ and Ca²⁺ ions, viz. MgCl₂ and CaCl₂, and also a mixture of those salts were dialysed. Initial concentrations were two or three times as high as the concentrations of Ca²⁺ and Mg²⁺ ions in saline water amounting to 0.0039 kmol/m³ and 0.0044 kmol/m³, respectively. The total concentration of all ions, which are found in seawater, is 0.02 kmol/m³. Taking into account the concentration of saline water, the concentration of 0.2 kmol of NaCl₂/m³ has been adopted as the lowest value recommended for Donnan dialysis. Suggesting a co-current process of dialysis with recirculation of concentrate and dialysate, we aimed at continuing

faster than during a single flow through the dialyzer, because during recirculation the time of solution-membrane contact is extended.

The process was investigated in two variants. In variant I, model solutions of calcium chloride and magnesium chloride were applied. The dialysate and the concentrate were recirculated at the same rates in the following systems: NaCl-MgCl₂, NaCl-CaCl₂ and NaCl-CaCl₂ + MgCl₂.

In variant II, the concentrate was recirculated at a constant rate ($v_c = 5 \text{ dm}^3/\text{h}$), and two dialysate rates ($v_d = 5 \text{ dm}^3/\text{h}$ and $v_d = 10 \text{ dm}^3/\text{h}$) were applied. There was investigated the following system: saline water-NaCl.

Figures 3-6 show the elimination coefficient vs. time for Mg²⁺ and Ca²⁺ ions. As shown by these plots, the removal of Mg²⁺ ions is considerably higher than that of Ca²⁺ ions at both the rates - 5 dm³/h and 10 dm³/h. After 12 hours of dialysis, the removal of

Table 2
Results of parallel flow dialysis: concentrate - 0.2 kmol/m³, dialysate - Baltic Sea water mixed with distilled water (1:1)

Time (h)	Final concentration of ions in concentrate (kmol/m ³)				
	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻
0	0.00	0.00	0.176	0.183	-
1.5	0.000210	0.000314	0.177	0.182	0.00152
3	0.000320	0.000472	0.176	0.182	0.00173
5	0.000417	0.000830	0.174	0.182	0.00184
7	0.000468	0.000860	0.174	0.182	0.00193

Mg²⁺ ions and Ca²⁺ ions amounted to 80% and 60%, respectively. The process was discontinued because of the considerable leakage of sodium chloride (chloride ion concentration in the dialysate was substantially higher than the initial concentration of chloride ions in the concentrate). The rate of removal of Mg²⁺ and Ca²⁺ ions was found to increase with the increasing initial dialysate concentration and flow rate of solution.

The increase of chloride and sodium ions in the dialysate proves that the escape of salts dominates the mechanism of Mg²⁺, Ca²⁺ and Na⁺ ion interdiffusion governing the Donnan dialysis process. In this particular case, the Donnan effect, which eliminates cations from the membrane phase, was very poor.

During dialysis of the model solution consisting of the MgCl₂-CaCl₂ mixture in the 0.2 kmol of NaCl/m³ of system, the removal of Mg²⁺ ions proceeds similarly to that during dialysis of single salts. Removal of Ca²⁺ ions was by 20% lower than that of Mg²⁺ ions (figs. 7 and 8).

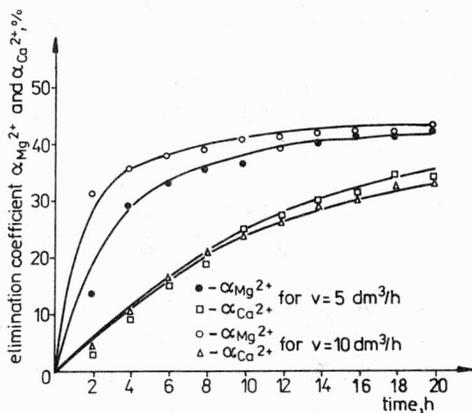


Fig. 7. Elimination coefficient of Ca^{2+} and Mg^{2+} ions versus time for the mixture of model solutions: CaCl_2 (0.0039 kmol/m^3) and MgCl_2 (0.0044 kmol/m^3)

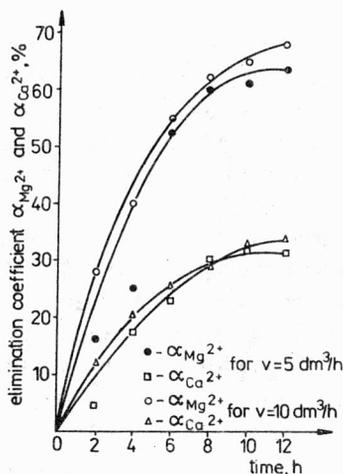


Fig. 8. Elimination coefficient of Ca^{2+} and Mg^{2+} ions versus time for the mixture of model solutions: CaCl_2 (0.0072 kmol/m^3) and MgCl_2 (0.008 kmol/m^3)

Cation transport through cation-exchange membranes depends on the degree of hydration. The hydration number of the cations investigated can be arranged in the following ascending order [4]: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$. It is worth remembering that during the transport of 1 F charge, the quantity of bivalent metals passing through the membrane is approximately half the quantity of monovalent metals. And that is why they produce lower flows despite the high degree of hydration.

The effective transport of the Mg^{2+} ion is additionally confirmed by its charge density which is very high as compared to its small volume. Despite a good removal of Mg^{2+} ions from the dialysate, the escape of sodium chloride to the dialysate was incomparably high.

Dialysis of saline water was also conducted in the 0.2 kmol/m^3 of the system (table 2). It is impossible to balance ion concentrations in the solutions because of incomplete analysis of saline water and concentrate. As it had been expected, removal of Mg^{2+} and Ca^{2+} ions was very high (almost 90% and over 90%, respectively), but there was observed escape of salts from the concentrate to saline water.

6. SUMMARY

Analysis of the data obtained shows that the domestic cation exchange membranes of KESD-2 type are inefficient when applied to the exchange of Mg^{2+} and Ca^{2+} ions in a system with concentrated sodium chloride solution. This is so, because the KESD-2 membrane displays a poor ion-exchange capacity and fails to be selective with regard to chloride ions.

[1] Patent PRL 110831, 1982.

[2] POŹNIAK G., TROCHIMCZUK W., *Angew. Macromol. Chem.*, 127(1984), 171.

[3] POŹNIAK G., TROCHIMCZUK W., *J. Appl. Polymer Sci.*, 27 (1982), 1833.

[4] ROBINSON A.R., STOKES H.R., *Electrolyte Solutions*, Butterworths, London 1959.

PRÓBY ZMIĘKCZANIA WÓD SŁONYCH METODĄ DIALIZY DONNANA

Представлено koncepcję zmiękczenia słonej wody metodą dializy donnanowskiej, zakładającą wymianę jonów magnezu i wapnia w wodzie słonej na jony sodowe zgodnie z mechanizmem interdyfuzji przeciwjonów. Badania przeprowadzono w instalacji wielkolaboratoryjnej o powierzchni czynnej membrany 432 cm^2 .

Dializie poddano modelowe roztwory chlorku wapnia i chlorku magnezu oraz wodę morską zmieszaną w stosunku 1:1 z wodą pitną w układzie z chlorkiem sodowym o stężeniu 0.2 kmol/m^3 . Roztwory recyrkułowały przez dializer współprądowo przy prędkościach 5 i $10 \text{ dm}^3/\text{h}$.

Pomimo dużych wartości współczynników odzysku jonów wapnia i magnezu obserwowano przeciek chlorku sodowego przez membranę kationowymienną.

ПРОБЫ УМЯГЧЕНИЯ СОЛЕННЫХ ВОД МЕТОДОМ ДОННАНОВСКОГО ДИАЛИЗА

Представлена концепция умягчения соленой воды методом доннановского диализа, предполагающая замену ионов магния и кальция в соленой воде ионами натрия согласно механизму интердифузии противоионов. Исследования были проведены в крупнолабораторной установке поверхности активной мембраны 432 м^2 .

Диализу подвергались модельные растворы хлоридов кальция и магния, а также морская вода, смешанная в отношении 1:1 с питьевой водой в системе с хлоридом натрия концентрации $0,2 \text{ кмоль/м}^3$. Растворы рециркулировали через диализатор прямоточно при скоростях 5 и $10 \text{ дм}^3/\text{ч}$.

Несмотря на большие значения коэффициентов регенерации ионов кальция и магния, наблюдалось протекание хлорида натрия через катионообменную мембрану.