

Development of a two-stage electro dialysis set-up for economical desalination of sea-type artesian and surface waters

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Abstract

A two-stage desalination process is proposed for mineralized water with a salt content of $>8 \text{ kg/m}^3$ in order to improve economical efficiency of the electro dialysis (ED) technique. The first stage involves ED desalination of the initial water in the galvanostatic regime at increased current density; the liquor is obtained with the salt content which is limiting for this method, and the dialyzate with the residual salt content allowing to avoid membrane polarization. The second stage involves profound desalination of the dialyzate in the potentiostatic regime resulting in desalinated water and the concentrate that is mixed with the initial water. For the mineralized water from the Tyumen' region, two-stage ED desalination and water preparation were investigated. A two-stage desalinating installation was developed and tested under industrial conditions; a model technological scheme of the industrial installation was developed for the complex processing of mineralized water from the oil and gas industry of western Siberia.

Keywords: Mineralized water; Two-stage electro dialysis desalination; Galvanostatic and potentiostatic regimes; Liquor; Dialyzate; Concentrate; Desalinated water

The lack of drinking water all over the world makes it urgent to use natural waters of various composition in the production of drinking water.

The most promising solution for this problem is the use of ocean water and underground brackish water. Oceans account for about 97% of the total water resources of the earth. Therefore, the preparation of drinking water from sea-type

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waters is one of the best ways to replenish drinking water resources. An urgent problem is to obtain desalinated water from natural salty waters.

The electro-osmotic technique is a rather widespread method of seawater desalination. However, the installations based on this technique are very expensive and require special high headwater pumps which puts substantial limitations on their application. Desalinating installations based on electrodialysis (ED) are much cheaper, but till recently they have been believed [1] to be economical (taking into account maintenance costs) only for desalination of water with a salt content up to 8 kg/m³.

However, in our opinion, this limitation is caused not by the features of the ED desalination technique itself but by non-optimal conditions of its performance when processing water with high salt content. Under such conditions, ED desalinating units operate in the regime of membrane underloading with respect to the transport of salts, i.e., at low current densities, which causes the decrease of the productivity and, as a consequence, to an unreasonable increase in investment and maintenance cost. The reason is the impossibility to obtain, simultaneously in one and the same apparatus, highly purified water (with a residual salt content of 0.5 kg/m³) and the concentrate (liquor) with salt content which would be maximum for this technique.

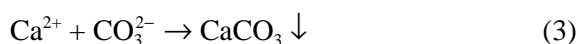
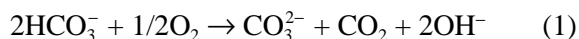
In order to improve the economical efficiency of the ED technique, we propose to perform ED desalination in two stages [2]. The first stage involves ED desalination of the initial mineralized water in the galvanostatic regime at increased current density in order to obtain the flow of liquor with a salt content that would be maximum for this technique, and the flow of dialyzate with residual salt content avoiding the polarization of membranes. The second stage is profound ED desalination of the dialyzate in a potentiostatic regime (classical desalinating ED),

resulting in desalinated water (with a residual salt content of 0.5 kg/m³ and below) and the flow of concentrate to be mixed with the initial mineralized water. A classical desalination scheme (a) and the scheme proposed by us (b) are shown in Fig. 1.

For the water from the Tyumen' district (underground water of the Senoman stage, and water accompanying oil mining, mineralized up to 20 kg/m³), we studied the process of their two-stage ED desalination. Quantitative ion composition of the mineralized waters under investigation is shown in Table 1.

Definite limitations on ED desalination are made by the presence of impurities in the mineralized water, including insoluble disperse phase, iron(II), alkaline earths, carbonate and bicarbonate ions, as well as an organic phase in the water accompanying oil production. In order to cope with this problem, we studied and mastered water preparation procedures that would allow the preparation of fresh water and liquors by means of ED desalination of sea-type mineralized natural waters. In the case when Senoman water, containing no oil or other organic phases, is used as the initial raw, in order to provide profound purification from iron and disperse phase, it is reasonable to remove gases (methane, hydrogen sulfide, and other reducing gases) before ED concentrating by dispersing the initial water followed by aeration with air, settling and infusive filtration with specific load of 2.2–2.5 m³/m² h through four layers of needle-punching Dornite-type Dacron material.

The following processes take place:



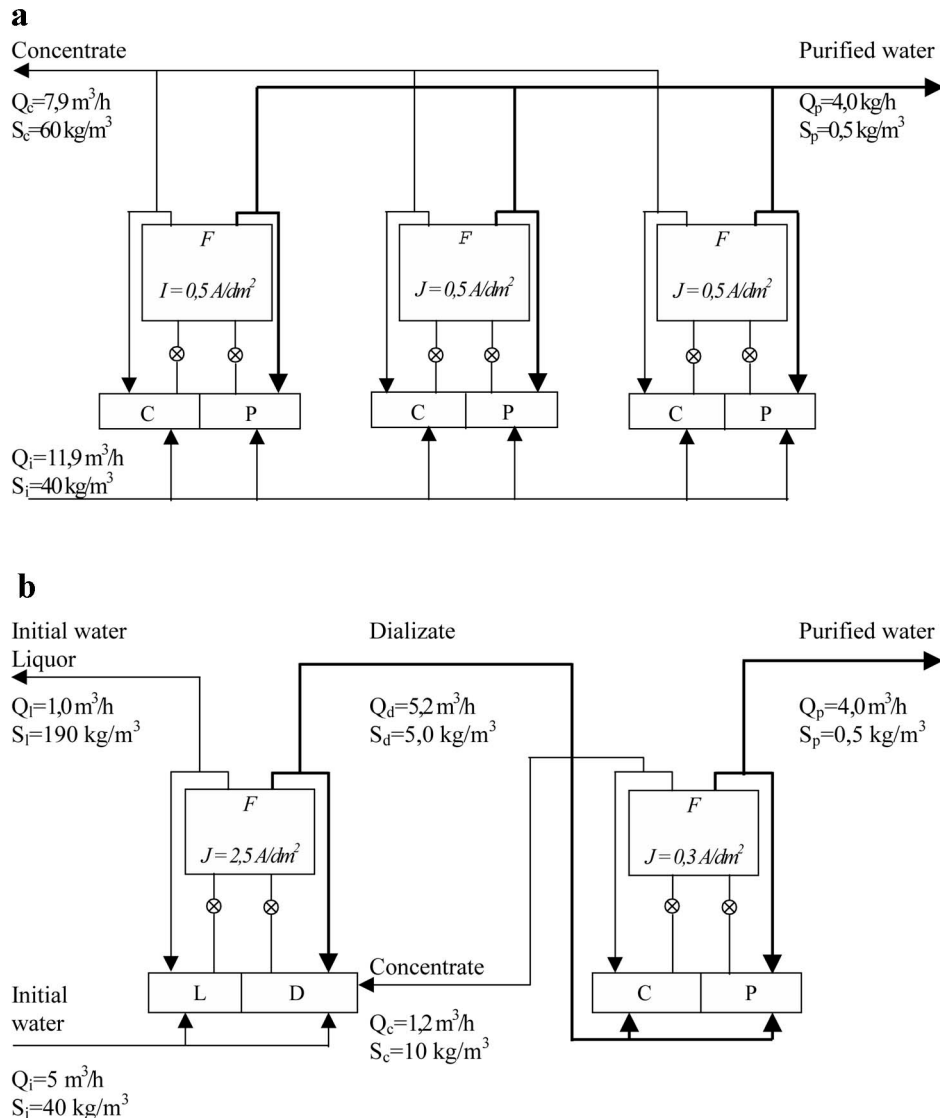


Fig. 1. Desalination of mineralized water. a: traditional scheme of the process; b: scheme proposed in the present study. F, membrane surface area; J, current density; S, salt content, Q, flow rate; \otimes , pumps. Subscripts: i, initial water; l, liquor; d, dialyzate; c, concentrate; p, purified water.

It follows from Table 2 that there is an optimal time of aerated water settling (40–80 min), as well as an optimal gas-to-liquid ratio for aeration (5–6 volume units of gas per 1 volume unit of aerated water).

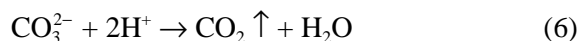
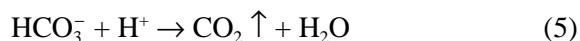
In order to diminish the risk of CaCO_3

deposition on the membranes of the concentrator, the residual carbonate and bicarbonate ions are decomposed by acidifying the filtered water to pH 5.5–6.0 before ED concentrating (Table 3). The decomposition is accompanied by the processes:

Table 1
Quantitative ion composition of mineralized waters

Content of components, kg/m ³	Water type	
	Senoman	Accompanying ^a
Organic phase	—	0.02
Insoluble disperse phase	Up to 0.05	Up to 0.10
Na ⁺	6.55	6.00
K ⁺	0.02	0.07
Ca ²⁺	0.80	0.74
Mg ²⁺	0.18	0.03
S ₂ ²⁺	0.06	0.22
Li ⁺	0.4×10 ⁻³	4.0×10 ⁻³
Cl ⁻	12.43	11.37
HCO ₃ ⁻	0.20	0.35
J ⁻	0.02	0.10
Br ⁻	0.04	0.02
Fe ²⁺	1.55	0.10
SO ₄ ²⁻	<0.01	<0.01
Total	21.86	18.92

^aContains oxidized iron.



When accompanying water is used as the mineralized sample, in order to purify it from admixtures, it is reasonable to apply ascending floatation using atmospheric air (Table 4) and taking an air to water volume ratio of 25–30:1 and a settling time of 40–50 min.

Dynamic tests of ED desalination in the galvanostatic regime (current density, 200 A/m²) using mineralized waters preliminarily purified from admixtures and acidified to 6.0 (for results, see Fig. 2) showed that for the galvanostatic ED of pre-treated Senoman water (a), salt transfer remains constant for a fixed concentrating-desalinating level. As far as the accompanying

Table 2
The effect of the settling and aeration regimes on the degree of water purification from iron and disperse phase

Experiment no.	Process parameters		Impurities in the filtrate	
	Settling time, min	Air volume per water volume, m ³ /m ³	Iron, mg/l	Disperse phase, mg/l
1	20	7	0.15	0.02
2	30	7	0.08	0.01
3	40	7	0.05	<0.01
4	50	7	0.03	<0.01
5	60	7	0.03	<0.01
6	20	6	0.30	<0.01
7	30	6	0.12	<0.01
8	40	6	0.05	<0.01
9	50	6	0.03	<0.01
10	60	6	0.03	<0.01
11	20	5	0.60	<0.01
12	30	5	0.25	<0.01
13	40	5	0.05	<0.01
14	50	5	0.05	<0.01
15	60	5	0.03	<0.01
16	20	4	0.90	<0.01
17	30	4	0.45	<0.01
18	40	4	0.15	<0.01
19	50	4	0.08	<0.01
20	60	4	0.06	<0.01

water is concerned (b), for the increased content of the organic phase (CAO>40), salt transfer somewhat decreases with time, perhaps due to the poisoning of the membranes by organic impurities.

The tests of the proposed ED technique were carried out with the pilot installation incorporating the unit of Senoman water purification from the iron and disperse phase, acidifying to pH 6.0, ED of pre-treated water in the galvanostatic

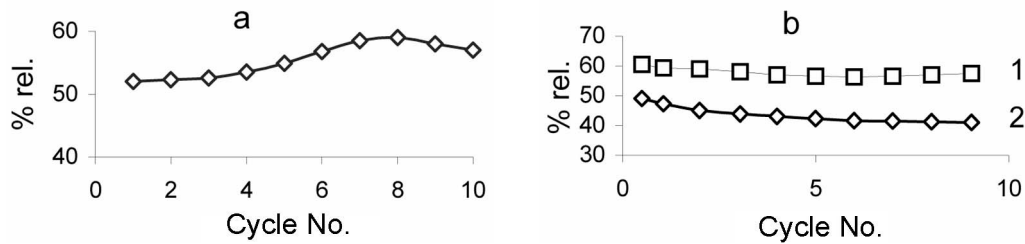


Fig. 2. The plot of salt concentrating degree vs. the number of cycles in dynamic tests: a: with Senoman water; b: with accompanying water, 1, CAO = 40; 2, CAO = 70.

Table 3

The effect of pH of Senoman water on the formation of precipitate on membranes^a

Experiment no.	pH of water before dialysis	Time till voltage grows by 20%, h	Results of visual exploration of membranes
1	7.2	4.5	White crystalline precipitate, uniform
2	6.5	12.5	White crystalline precipitate, partly
3	6.0	—	Small separate grains
4	5.5	—	No precipitate

^aMaximum testing time was 58 h.

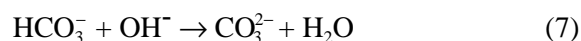
Table 4

The effect of ascending floatation regimes and the settling of accompanying water on the degree of water purification from impurities

Experiment no.	Process parameters		Impurities in the filtrate		
	Air to water volume ratio, m ³ /m ³	Settling time, min	Iron, mg/l	Dispersed oil products, mg/l	Dissolved organics, CAO ^a
1	0	60	0.6	0.1	230
2	20	50	<0.05	<0.1	90
3	24	50	<0.05	<0.1	75
4	25	50	<0.05	<0.1	40
5	25	40	<0.05	<0.1	60
6	28	40	<0.05	<0.1	40
7	30	40	<0.05	<0.1	35
8	31	40	<0.05	<0.1	35
9	31	50	<0.05	<0.1	30

^aError of CAO (chemical absorbing of oxygen) determination is ± 5.0 .

regime (the first stage) resulting in the flows of liquor and dialyzate, the electrolysis of this dialyzate in the potentiostatic regime (the second stage) resulting in the flow of concentrate (which is returned to the first-stage ED), and the flow of purified water. Hydrodynamic productivity of the ED installation at the first stage over the dialysis channel was $40 \text{ m}^3/\text{h}$, active membrane area was 1 m^2 , and the total number of chambers was 800. Hydrodynamic productivity of the ED installation at the second stage (a serial ED unit EDU) was $5 \text{ m}^3/\text{h}$, active membrane area was 0.30 m^2 , and total number of chambers was 400. The acid for the decomposition of carbonate and bicarbonate ions was obtained in a three-channel electrochemical convector with MB-1 bipolar membranes using the dialyzate of the first stage of ED. The alkaline flow, which was a by-product of acid preparation, was mixed with the initial Senoman water at the stage of its purification, thus providing, on one hand, the most favorable conditions for iron oxidation by creating alkaline conditions (reaction 2), and on the other hand, the conditions for preliminary deposition of calcium carbonate due to the transformation of a part of bicarbonate ions into carbonate ions:



The results of the tests are shown in Figs. 3–7. The dependencies (Fig. 3) suggest that the current density in the galvanostatic dialysis should be maintained within the range of $180\text{--}200 \text{ A/m}^2$ in order to provide maximum yield as a function of current. The residual salt content of the dialyzate should not be less than 4 kg/m^3 because otherwise the flow of ions through the membranes would exceed the overall flow of salts entering the apparatus, which would result in the decomposition of water, polarization of membranes, increase of energy consumption, and increase of the risk of the deposition of insoluble salts on the membranes because of changed pH of the dialyzate and liquor. At the same time, it is

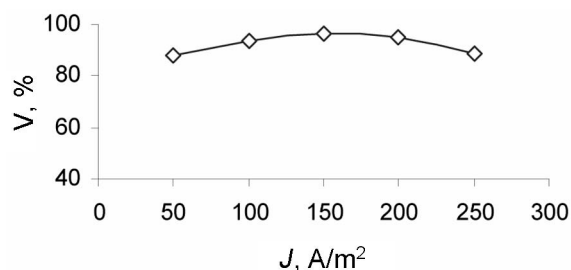


Fig. 3. Dependence of the yield as a function of current on the current density during desalination of Senoman water using electro dialysis in the galvanostatic regime.

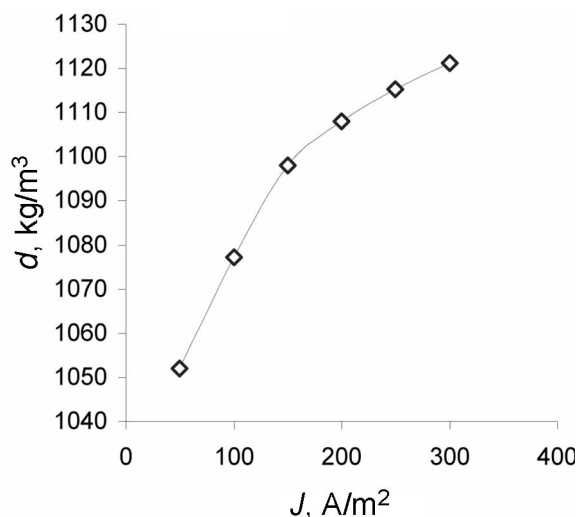


Fig. 4. Dependence of the density of liquor, obtained in the galvanostatic regime of electro dialysis on the current density.

not reasonable to maintain the residual salt content of the dialyzate above 4.5 kg/m^3 in order to minimize the consumption of water to be desalinated. An optimal density of the liquor (under the conditions providing maximal yield as a function of current) is $1100\text{--}1110 \text{ kg/m}^3$ (Fig. 4). Maximum productivity of the apparatus with respect to the liquor is $0.55\text{--}0.65 \text{ m}^3/\text{h}$

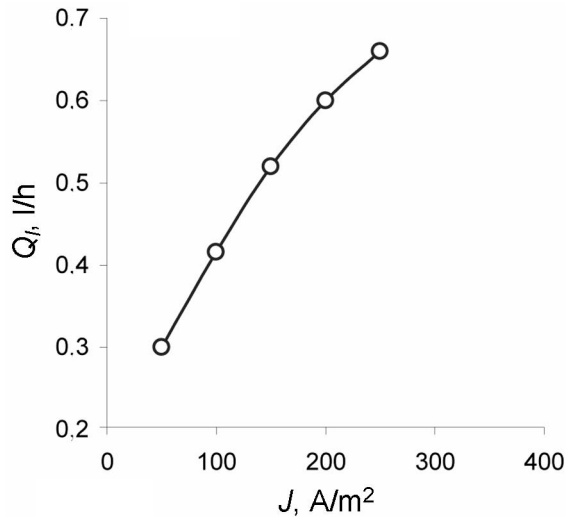


Fig. 5. Dependence of volume productivity (with respect to the liquor) of the electrodesalination apparatus operating in the galvanostatic regime on the current density.

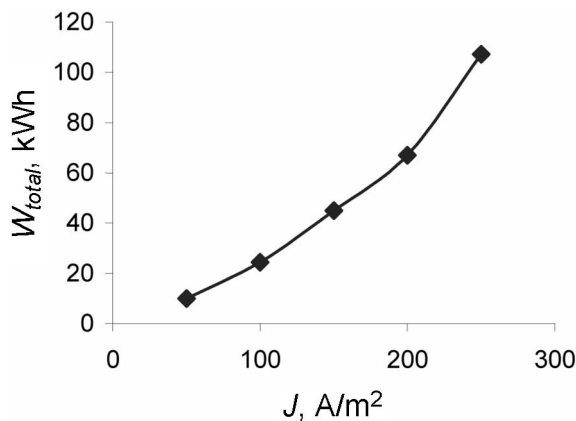


Fig. 6. Dependence of total energy consumption per 1 m³ of the liquor (obtained in the galvanostatic regime of electrodesalination) on the current density.

(Fig. 5), total energy consumption per 1 m³ of the liquor being 42–62 kWh (Fig. 6). Using the potentiostatic dialyzate for profound desalination

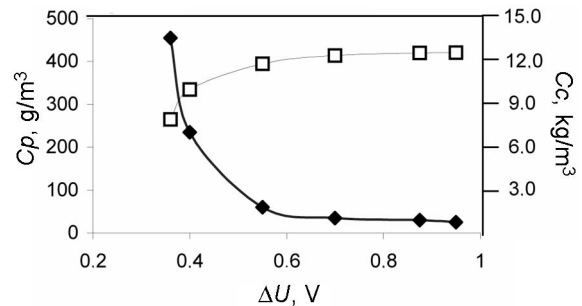


Fig. 7. Dependence of the salt content in purified water and concentrate on the quantity of the average value of voltage drop across the elementary chamber of the electrodesalination apparatus at desalting of the first stage dialyzate with a salt content of 4.3 kg/m³. \circ , purified water; \square , concentrate.

of the first-stage dialyzate (Fig. 7), it is not reasonable to maintain voltage providing more than 0.90 V mean voltage drop across the elementary chamber of the apparatus because further increase of this parameter practically does not lead to any improvement of desalination degree. At the same time, mean voltage drop should not be less than 0.55 V. As far as the preparation of drinking-quality water (residual salt content 500 g/m³) from dialyzate is concerned, it is sufficient for these purposes to maintain the voltage drop at the elementary chamber within the range 0.35–0.38 V.

Total energy consumption (taking account of energy consumed for purification and pumping) for the preparation of 1 m³ of drinking-quality water from Senoman mineralized water by means of two-stage ED was 9.5–12.5 kWh.

On the basis of the results of tests, a model apparatus-technological scheme has been developed for the industrial installation providing complex processing of mineralized water from oil and gas plants. The installation incorporates:

- the unit of water preparation for ED desalination, including purification from oil products;

- the unit producing acidic and alkaline solutions;
- the unit of ED desalination (the first stage) preparing the flow of liquor with a density of 1100t/m^3 and dialyzate with a residual salt content of $4.0\text{--}4.5\text{kg/m}^3$;
- dialyzate desalinating unit (the second stage) giving the flow of drinking-quality water, the flow of desalinated water for the needs of heat and power engineering, and salt concentrate with salt content $10\text{--}12\text{kg/m}^3$ entering the first stage of ED desalination;
- the unit of utilization of the accompanying gas, producing gaseous heat carrier;
- the unit providing vaporization of liquor from the density of 1100kg/m^3 to $1180\text{--}1200\text{t/m}^3$ with the help of gaseous heat carrier.

This technology will allow to exclude the transportation of large amounts of rock salt needed in oil-mining regions for the preparation of plugging solutions, avoid salinization of

depths, supply drinking water and desalinated water to the deposits, and to approach the realization of the technologies of the recovery of such valuable components as iodine, lithium, and bromine from the plugging solutions before they are consumed.

Acknowledgements

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