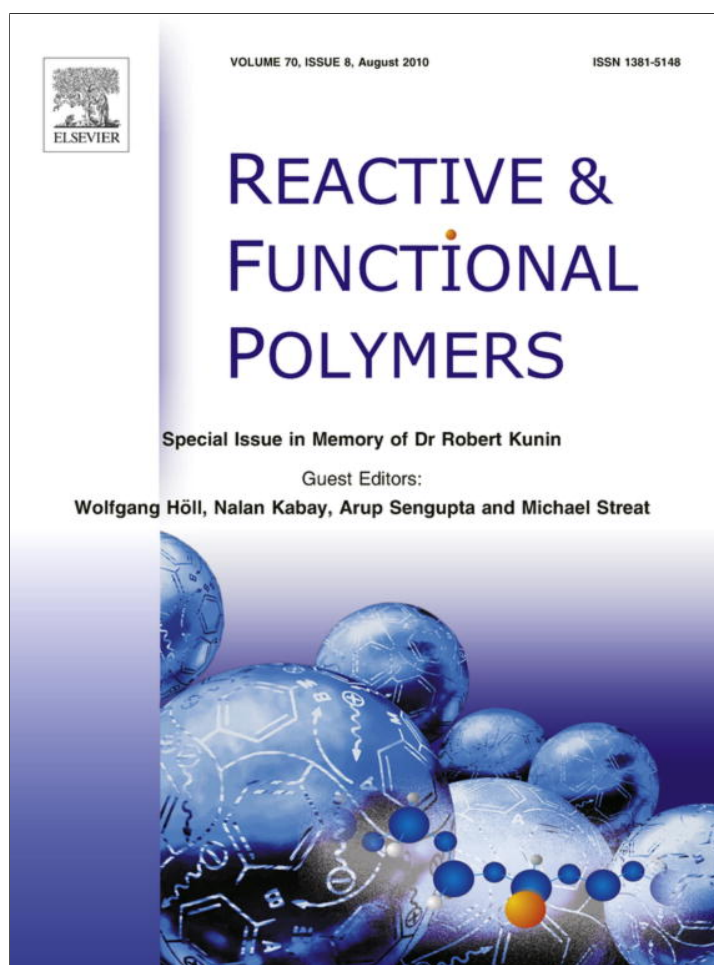


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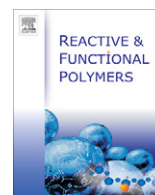
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Dual-temperature ion exchange: A review

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ABSTRACT

The article represents a review for special class of reactant-less ion-exchange processes regulated by temperature. Analysis of experimental results published before and new data, as well as thermodynamic characteristics of different ion-exchange reactions and short theoretical descriptions of equilibrium and dynamics are given. Along with the demonstration of experimental data, authors try to give an exact classification of temperature-driven methods based on fundamental physical and chemical regularities of temperature influence on ion exchange in columns.

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1. Introduction

Ion exchanging resins and inorganic polymers like zeolites play an important role in water treatment, hydrometallurgy and other areas. At the same time, we see the contemporary tendency that some advanced technologies like membrane separation replace gradually traditional ion exchange in columns. It takes place due to main restrictions of conventional ion-exchange processes consisting in the use of auxiliary reagents and appearance of “secondary” wastes related to sorbent regeneration. To overpass these problems, temperature-driven separation technique can be used. Researches on sorption and ion-exchange dual-temperature methods [1–31] are continued during past four decades since the pioneering works of Andreev et al. [9,10] with the idea of cyclic columns, Wilhelm et al. with parametric pumping [11] and Bolto et al. with Sirotherm processes [12]. In spite of it, these methods remain not so popular yet in the treatment of liquid solutions, and the necessity of thermal energy is one of their limitation [3]. A number of reviews on dual-temperature processes can be found in the literature [1–7]. Nevertheless, there are some reasons to consider this field again: 1) last 20 years, new results making dual-temperature ion exchange more applicable for real practice were got; 2) in the nearest future, reagent-free methods will take the priority in industrial technologies due to hardening the ecological requirements. We expect particular significance of temperature-driven ion-exchange and sorption methods for environment friendly processing of seawater and other natural waters with the aim of extraction of valuable components [16–24] and for purification

of natural and industrial waste waters [25–30]. Other prospective application of such methods is the high-grade purification of substances [4–6], as well as the concentration of trace quantities of isotopes of wide-spread elements [8].

In this paper, we tried to demonstrate new experimental results on dual-temperature separation. Using physical and chemical regularities of the equilibrium and dynamics of ion exchange, we also tried to give more exact classification of temperature-driven processes.

2. Physical and chemical regularities of temperature influence on ion exchange

2.1. Equilibrium of ion-exchange

The exchange reaction:

$$\frac{1}{Z_B} B^{Z_B} + \frac{1}{Z_A} \bar{A}^{Z_A} = \frac{1}{Z_B} \bar{B}^{Z_B} + \frac{1}{Z_A} A^{Z_A} \quad (1)$$

in which the equivalents of ions *A* and *B* with corresponding charges Z_A and Z_B participate, is described with the following equilibrium parameters [32]: separation factor and selectivity coefficient, respectively:

$$\alpha = \frac{\bar{X}_B \cdot X_A}{X_A \cdot \bar{X}_B} \quad \text{and} \quad k = \frac{\bar{X}_B^{1/Z_B} \cdot X_A^{1/Z_A}}{X_A^{1/Z_A} \cdot \bar{X}_B^{1/Z_B}} \quad (2,3)$$

thermodynamic constant, equilibrium coefficient and corrected equilibrium coefficient:

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Nomenclature

\bar{a}_i and a_i thermodynamic activities of ion i in exchanger and solution phases, respectively
 \bar{c}_i and c_i concentrations of ion in phases in molarity, molality or mole fractions
 \bar{c}_Σ and c_Σ total concentrations of all the ions in phases
 \bar{f}_i and f_i activity coefficients of ion in phases
 t time

\bar{X}_i and X_i equivalent fractions of ion i in phases
 x distance along the column from the solution inlet point
 u speed of frontier points along the column
 v linear speed of liquid motion in column
 $\bar{\mu}_i$ and μ_i chemical potentials of ion in phases
 ε porosity of sorption bed (inter-space fraction) in column

$$K = \frac{\bar{a}_B^{1/z_B} \cdot a_A^{1/z_A}}{\bar{a}_A^{1/z_A} \cdot a_B^{1/z_B}} = \tilde{K} \frac{\bar{f}_B^{1/z_B} \cdot f_A^{1/z_A}}{\bar{f}_A^{1/z_A} \cdot f_B^{1/z_B}} \text{ and } \tilde{\tilde{K}} = \frac{\bar{c}_B^{1/z_B} \cdot c_A^{1/z_A}}{\bar{c}_A^{1/z_A} \cdot c_B^{1/z_B}} \quad (4, 5)$$

The constant K relates to the standard Gibbs energy and standard enthalpy, as follows:

$$\Delta G^0 = \bar{\mu}_B^0 - \bar{\mu}_A^0 + \mu_A^0 - \mu_B^0 = -RT \ln K \quad (6)$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^0}{RT^2} \quad (7)$$

ΔG^0 and ΔH^0 are referred to the exchange of ions in standard states. Mostly, mono-ionic forms of exchangers are chosen as the standard states for ions in sorbent phase [33,34].

Studies of temperature effects in ion exchange on strong-acid cationic were started since their introduction into a practice, and following main principals were found [35–37]: a) temperature slightly influences on selectivity of ion exchange on resins, excluding the exchange between metal and hydrogen ions; b) increase of degree of “cross-linking” in resins brings to enhancement of the influence of temperature on ion exchange equilibrium; c) at the exchange of ions with equal charges, elevation of temperature brings down the selectivity of sorbents, opposite case takes place for ions with different charges.

We could say about real practical prospects of dual-temperature methods when it has been shown 20 years ago [38] and confirmed in many subsequent works [39–44] that temperature influenced on ion exchange on weak-acid cationic resins and polyampholytes much more strongly than it has been known for sul-

Table 1
Some experimental coefficients of equilibrium of ion-exchange of bi- and monovalent ions on weak-acid cation-exchange resins and polyampholytes at different temperatures*.

Sorbent	Exchanging ions		Solution composition		$\tilde{\tilde{K}}_A^B$	Reference
	$B^{z_B} - A^{z_A}$	$T, ^\circ\text{C}$	C_Σ (equiv./l)	C_A/C_Σ (equiv. part)		
KB-4	Ca ²⁺ -Na ⁺	10	2.58	3×10^{-2}	5.0	[38–40]
	Ca ²⁺ -Na ⁺	90	2.58	3×10^{-2}	11.5	[38–40]
	Zn ²⁺ -Na ⁺	20	2.51	4×10^{-3}	14.2	[4,41,42]
	Zn ²⁺ -Na ⁺	90	2.51	4×10^{-3}	19.2	[4,41,42]
	Ni ²⁺ -Na ⁺	20	2.51	4×10^{-3}	9.5	[4,41,42]
	Ni ²⁺ -Na ⁺	90	2.51	4×10^{-3}	20.9	[4,41,42]
	Co ²⁺ -Na ⁺	20	2.51	4×10^{-3}	9.0	[4,41,42]
	Co ²⁺ -Na ⁺	90	2.51	4×10^{-3}	23.8	[4,41,42]
	Ca ²⁺ -Mg ²⁺	13–16	0.1	3.3×10^{-1}	1.4	[39,40]
Ca ²⁺ -Mg ²⁺	77–80	0.1	3.3×10^{-1}	1.9	[39,40]	
KB-4P2	Ca ²⁺ -Na ⁺	4–6	2.58	3×10^{-2}	3.5	[38–40]
	Ca ²⁺ -Na ⁺	90	2.58	3×10^{-2}	10.3	[38–40]
ANKB-50	Ca ²⁺ -Na ⁺	6–8	2.58	3×10^{-2}	14.5	[38–40]
	Ca ²⁺ -Na ⁺	76–78	2.58	3×10^{-2}	16.5	[38–40]
	Zn ²⁺ -Na ⁺	20	2.51	4×10^{-3}	30.0	[4,41,42]
	Zn ²⁺ -Na ⁺	90	2.51	4×10^{-3}	26.5	[4,41,42]
	Ni ²⁺ -Na ⁺	20	2.51	4×10^{-3}	27.8	[4,41,42]
	Ni ²⁺ -Na ⁺	90	2.51	4×10^{-3}	23.3	[4,41,42]
	Co ²⁺ -Na ⁺	20	2.51	4×10^{-3}	27.2	[4,41,42]
	Co ²⁺ -Na ⁺	90	2.51	4×10^{-3}	26.2	[4,41,42]
	Ca ²⁺ -Mg ²⁺	18–19	0.1	3.3×10^{-1}	2.2	[39,40]
Ca ²⁺ -Mg ²⁺	76–79	0.1	3.3×10^{-1}	1.5	[39,40]	
Lewatit R249-K	Ca ²⁺ -Na ⁺	20	0.93	9×10^{-2}	7.1	[4,25,46]
	Ca ²⁺ -Na ⁺	80	0.93	9×10^{-2}	13.8	[4,25,46]
	Mg ²⁺ -Na ⁺	20	0.93	5×10^{-1}	3.9	[4,25,46]
	Mg ²⁺ -Na ⁺	80	0.93	5×10^{-1}	7.5	[4,25,46]
Lewatit R250-K	Ca ²⁺ -Na ⁺	20	0.93	9×10^{-2}	3.4	[4,25,46]
	Ca ²⁺ -Na ⁺	80	0.93	9×10^{-2}	7.8	[4,25,46]
	Mg ²⁺ -Na ⁺	20	0.93	5×10^{-1}	1.9	[4,25,46]
	Mg ²⁺ -Na ⁺	80	0.93	5×10^{-1}	4.4	[4,25,46]
Lewatit R252-K	Cu ²⁺ -Zn ²⁺	10	0.3	1.2×10^{-1}	1.3	[27]
	Cu ²⁺ -Zn ²⁺	80	0.3	1.2×10^{-1}	1.2	[27]
Lewatit TP207	Cu ²⁺ -Zn ²⁺	20	0.3	1.2×10^{-1}	9.2	[27]
	Cu ²⁺ -Zn ²⁺	80	0.3	1.2×10^{-1}	7.5	[27]

* In this table: KB-4P2, and KB-4 are the gel-type polymethacrylic cation-exchangers, correspondingly, with 2%, and 6.5% of linking agent – divinylbenzene (DVB); ANKB-50 is polyesterene type chelating resin with imino-diacetic groups; macro-porous ion-exchangers like Lewatit (Bayer company, Germany)⁴⁸: Lewatit R249-K is a polyacrylic cationic resin; Lewatit R252-K is a polyesterene type chelating resin with aminophosphonic groups Lewatit TP207 is a polyesterene type chelating resin with imino-diacetic groups.

Table 2
Coefficients of equilibrium of ion exchange on synthetic and natural zeolites at different temperatures.

Sorbent	Exchanging ions $B^{z_B} - A^{z_A}$	T, °C	Solution composition		\tilde{K}_A^B	Reference
			C_Σ (equiv./l)	C_A/C_Σ (equiv. part)		
Zeolite A	$Ca^{2+} - Na^+$	20	1.0	3×10^{-1}	0.9	[54,55]
	$Ca^{2+} - Na^+$	70	1.0	3×10^{-1}	1.2	[54,55]
Clinoptilolite	$K^+ - Na^+$	13	0.55*	2×10^{-2}	26.4	[54,56,57]
	$K^+ - Na^+$	70	0.55*	2×10^{-2}	12.5	[54,56,57]
	$Ca^{2+} - Na^+$	13	0.55*	4×10^{-2}	1.1	[54,56,57]
	$Ca^{2+} - Na^+$	70	0.55*	4×10^{-2}	1.7	[54,56]
	$Mg^{2+} - Na^+$	13	0.55*	2×10^{-1}	0.6	[54,56,57]
	$Mg^{2+} - Na^+$	70	0.55*	2×10^{-1}	0.9	[54,56,57]
Mordenite	$Cs^+ - Na^+$	25	0.1	5×10^{-1}	29.2	[58]
	$Cs^+ - Na^+$	70	0.1	5×10^{-1}	18.3	[58]

* Model solution of seawater.

ponic resins. Now, a lot of experimental data for weak-acid cationic resins and polyampholytes, inorganic exchangers and anionic resins can be found in the literature [4,7,16,22,24,27,31,38–84]. Some part of these data is presented in Tables 1–3. The listed principals for strong-acid materials still work for other ion-exchangers. Important difference is in more strong temperature effects (Table 1). Data in Tables 2 and 3 testify that zeolites and strong-base anion-exchangers are also promising for dual-temperature separation. Brief overview on the heat effects of reaction of anion-exchange is given in Table 4. The data illustrate that exothermic effects take place the selective exchange of equally charged inorganic ions on strong-base resins. Similar processes with the participation of hydrophobic ionizable organic compounds described by Li and SenGupta [60–63] show an exclusion from the common regularities. Equilibrium constants increase with temperature, and endothermic effects take place. Authors [62,63] explained such entropy-driven processes by direct interaction of non-polar moieties of organic ions and hydrophobic matrix of resin and de-hydration effects at the sorption of aromatic compounds.

From the data discussed, we see that temperature changes the equilibrium distribution of ions between solution and sorbent phases.

2.2. Dynamics of ion exchange

Temperature effects can be explained with the equilibrium approximation for the dynamics. With the premises that inter-phase mass transfer is infinitely quick and axial dispersion in column is neglected, the dynamics can be described by the balance equations:

Table 4
Standard and integral enthalpy of exchange reactions on different anion-exchangers.

Sorbent	Exchanging ions $B^{z_B} - A^{z_A}$	ΔH^0 (298 K) kJ/equiv.	$T\Delta S^0$ (298 K) kJ/equiv.	Reference
Dowex-1×1	$Br^- - Cl^-$	-3.05	-0.9	[18]
Dowex-1×4	$Br^- - Cl^-$	-4.68	-1.6	[18]
Dowex-1×8	$Br^- - Cl^-$	-5.70	-2.1	[18]
Dowex-1×8	$I^- - Cl^-$	-15.9	-2.8	[59]
Dowex-1×16	$Br^- - Cl^-$	-7.04	-3.3	[18]
IRA-900	$PCP^- - Cl^-$	40.0	52.5	[62,63]
	$NS^- - Cl^-$	10.2	17.5	[62,63]
	$BS^- - Cl^-$	8.1	10.4	[62,63]

* NS^- and BS^- are naphthalene-1-sulfonate and benzene-sulfonate anions.

Table 3
Coefficients of equilibrium of ion-exchange on strong-base resins* of polysterene type at different temperatures.

Ion-exchanger	Exchanging ions $B^{z_B} - A^{z_A}$	T, °C	Solution composition		$\tilde{K}_A^B(K_A^B)$	Reference
			C_Σ (equiv./l)	C_A/C_Σ (equiv. part)		
Dowex-1×1	$Br^- - Cl^-$	9	0.5	1.6×10^{-3}	2.5	[18]
	$Br^- - Cl^-$	90	0.5	1.6×10^{-3}	1.9	[18]
Dowex-1×4	$Br^- - Cl^-$	9	0.5	1.6×10^{-3}	3.8	[18]
	$Br^- - Cl^-$	90	0.5	1.6×10^{-3}	2.5	[18]
AV-17×8, AM, Dowex-1×8	$Br^- - Cl^-$	9	0.5	1.6×10^{-3}	4.9	[18]
	$Br^- - Cl^-$	9	0.5	1.6×10^{-1}	4.8	[18]
	$Br^- - Cl^-$	25	0.5	1.6×10^{-3}	4.2	[18]
	$Br^- - Cl^-$	90	0.5	1.6×10^{-3}	2.8	[18]
	$SO_4^{2-} - Cl^-$	9	0.53	5×10^{-2}	0.09	[18]
	$SO_4^{2-} - Cl^-$	90	0.53	5×10^{-2}	0.16	[18]
	$I^- - Cl^-$	2	1.00	2.4×10^{-4}	66.4	[59]
	$I^- - Cl^-$	80	1.00	2.4×10^{-4}	12.4	[59]
	$I^- - Cl^-$	12	1.00	2.4×10^{-2}	45.0	[59]
	$I^- - Cl^-$	80	1.00	2.4×10^{-2}	15.9	[59]
Dowex-1×16	$Br^- - Cl^-$	9	0.5	1.6×10^{-3}	6.9	[18]
	$Br^- - Cl^-$	90	0.5	1.6×10^{-3}	3.5	[18]
IRA-900	$PCP^- - Cl^-$	8.5	2×10^{-3}	$(0.2-1.2) \times 10^{-1}$	(60.5)	[62,63]**
	$PCP^- - Cl^-$	35	$2 \cdot 10^{-3}$	$(0.2-1.2) \times 10^{-1}$	(271.4)	[62,63]

* Resins with benzyl-trimethyl amm006Fnum functional groups. Dowex sorbents are of gel type with 1%, 4%, 8% and 16% DVB. IRA-900 is macro-porous resin.

** PCP^- is pentachlorophenate anion.

$$v \frac{\partial c_i}{\partial x} + \varepsilon \frac{\partial c_i}{\partial t} + \frac{\partial \bar{c}_i}{\partial t} = 0, \quad i = 1, 2, 3 \dots \quad (8)$$

At $f(c_1, \bar{c}_1 \dots c_i, \bar{c}_i \dots) = 0$, $\bar{c}_i = \bar{c}_i(x, t)$ and $c_i = c_i(x, t)$.

With the use of chain rule, the expression (8) can be transformed into the next one:

$$u_{c_i} = \left(\frac{\partial x}{\partial t} \right)_{c_i} = \frac{v}{\varepsilon + \partial \bar{c}_i / \partial c_i} \quad (9)$$

It shows the speed of progress of the frontier points of fixed concentration ($c_i(x, t) = const$ or $\bar{c}_i(x, t) = const$) along the column. Through the derivative $\partial \bar{c}_i / \partial c_i$, temperature influences on the speed of transference of exchange frontier points along the column.

For example, for a micro-component ($c_i \rightarrow 0$), we have:

$$u_{c_i} = u(T) = v / [\varepsilon + \Gamma_i(T)] \quad (10)$$

where $\Gamma_i(T) = \bar{c}_i / c_i$ is the equilibrium distribution coefficient (Henry's law constant).

One more dynamic effect can be distinguished [19,20]. Just imagine that as a result of some process, a concentration band of a component has been formed in some sorbent bed. This band can be a concentration peak in elution chromatography or it can be generated when some component is desorbed from the bed. Such a peak contains two waves – the first and the last frontiers. If the sorbent bed exists in some temperature zones (as minimum, two), as it is shown in Fig. 1, the effect is in the compression of the concentration peak when it is transferred from the temperature zone with lesser selectivity of ion-exchanger to a zone with the higher selectivity. Indeed, in the case of linear isotherm and $\Gamma(T_2) < \Gamma(T_1)$, it follows from the formula (10): $u_x(T_2) > u_x(T_1)$. When the peak moves along the column (Fig. 1), the points of its back-frontier cover more long distance at T_2 than the points of upper one. It leads to different speeds of frontiers of the concentration peak: it becomes more narrow and higher.

2.3. Fundamental rules regulating dual-temperature sorption and ion-exchange processes

Three rules follow from the short analysis made above.

Rule 1: As temperature changes, the distribution of components between sorbent (ion-exchanger) and solution also changes (distribution rule).

Rule 2: As temperature changes, the speed of motion of concentration wave of a component in sorption bed changes too; temperature influences on the speed and selectivity in opposite manner (rule of change of the speed of concentration frontier).

Rule 3: As concentration peak of component is transferred in sorption bed consisting of two or more temperature zones, it compresses at transfer from zone of less selectivity to the component to a zone of higher selectivity (rule of change of the width of concentration peak).

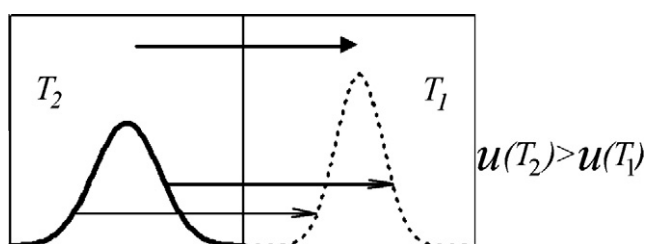


Fig. 1. Compression of concentration peak at its transition through different temperature zones of sorbent bed.

Below, we consider all the known dual-temperature methods according to these rules.

3. Methods of separation regulated by component distribution in phases

3.1. Simple cyclic process with the single effect of dual-temperature separation

This type of separation can be classified as the temperature-swung mode. The flow of original solution containing the mix of components is continuously passed through the sorbent bed at temperatures being changed from time to time. If the selectivity of sorbent to a target-component decreases with temperature, its concentration in the effluent decreases at T_1 , while enrichment is observed at T_2 . In the opposite case, reverse separation mode takes place.

Fig. 2a and b shows experimental elution curves for the process of purification of sodium chloride brine from the impurity of calcium chloride on polyacrylic and polymethacrylic cation-exchangers which demonstrate high selectivity for bivalent metals significantly increasing with the rise of temperature [4,69,70]. Purification of solution from calcium up to 10 times is observed for hot half-cycle, and more than 5 times enrichment of the effluent takes place at lower temperature. The process is useful for preparing the solutions of sodium chloride for membrane electrolysis, as well as for processing of mixed brines.

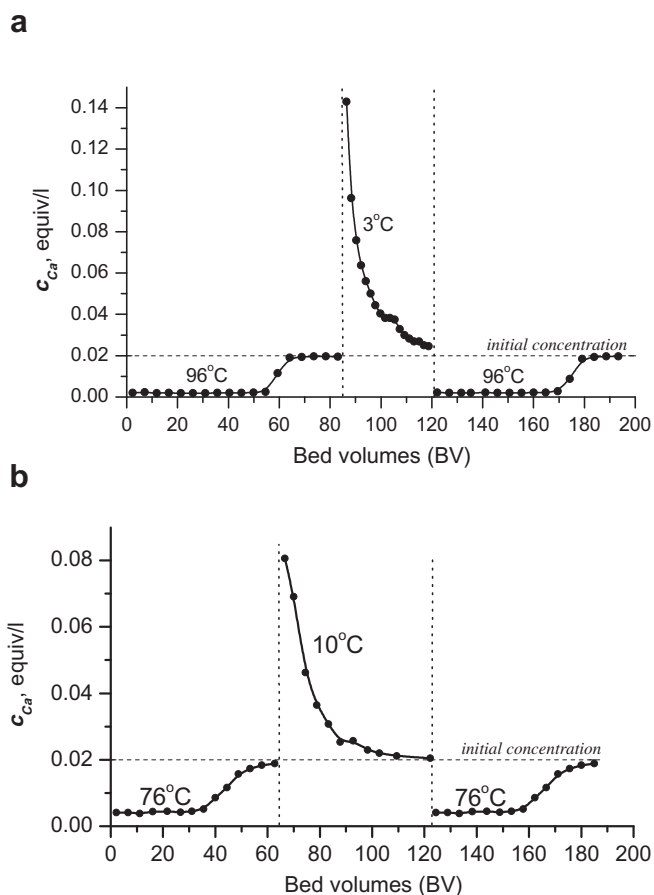


Fig. 2. Concentration histories of Ca^{2+} for ion-exchange dual temperature purification of concentrated solutions of sodium chloride from the impurities of calcium chloride. (a) Original mixture: 2.5 N NaCl–0.02 N $CaCl_2$; cation-exchanger: KB-4; (b) 2.5 N NaCl–0.02 N $CaCl_2$; Amberlite IRC 50.

The simple cyclic process can also be successfully applied for reagent-free concentration of iodides from underground brines, especially, geothermal waters, having heat potential [59]. Fig. 3a shows break-through curves for three successive cycles of the following process: the model solution of geothermal water (60 g/l of NaCl and 30 mg/l of NaI) was continuously passed through the column with strong-base anion exchanging resin AV-17. Temperature of original solution was periodically changed. It can be seen that solutions enriched with iodide more than 3.4 times (at maximal point) are produced in each hot half-cycle of the process. Cold half-cycles give exhausted effluents. It is evident that the use of two columns operating in counter-phases can provide continuous production of enriched concentrate. The important technological advantage of this process, as well as of any dual-temperature one, is that total equivalent concentration of enriched solution is not raised, but remains equal to the original content. The process can be used for utilization of poor hydro-mineral sources of iodine and can also be applied for further concentration of iodide with the use of dual-temperature cascade schemes which will be concerned below. This is demonstrated by the results pictured in Fig. 3b. Model solution of one of the expected intermediate concentrates containing 60 g/l of NaCl and 300 mg/l of NaI was treated. Maximal degree of concentration of iodide in repetitive cycles is around 3.

Another example for demonstration of the possibilities of dual-temperature method is the purification of drinking water from boron [85,86]. This problem is challenging for desalination: due to the permeability of reverse osmosis (RO) membranes for boron com-

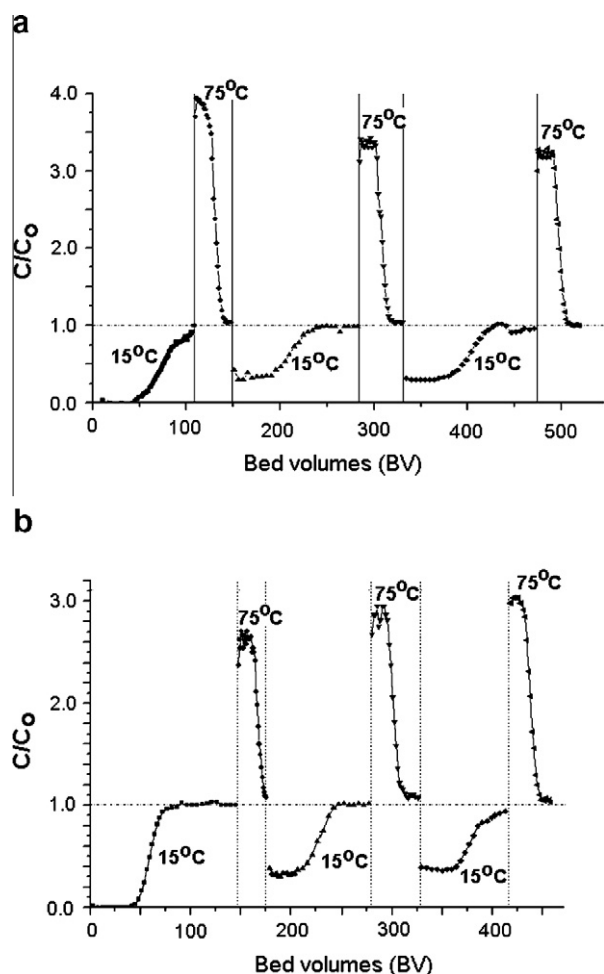


Fig. 3. Cyclic processes of I^- concentration on anionic resin AV-17x8.

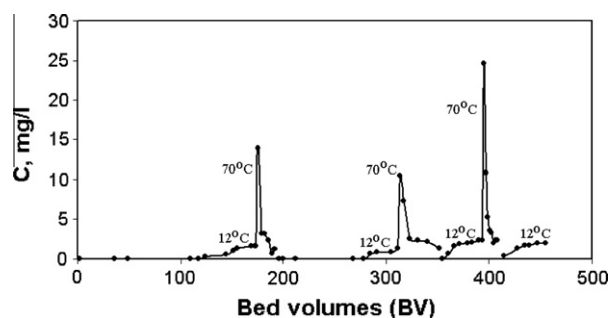


Fig. 4. Cyclic process of boron removal from the permeate of seawater desalination with the use of weak-base anion exchanging resin SB-1.

pounds, fresh water produced from seawater requires additional purification. Fig. 4 shows concentration histories for three successive cycles of the dual-temperature process. Desalinated water with total salinity 0.9 g/l, containing 1.5 mg/l of boron, was continuously passed through the column with weak-base anion exchanging resin SB-1 with N-methyl-glucamine functional groups. At sorption stage of the first cycle, the sorbent exhibits large capacity toward boron due to the extra-equivalent molecular sorption which is irreversible in dual-temperature process. Other cycles are almost repetitive.

The promising application of simple cyclic process is connected with the extraction of potassium from seawater. Investigations were carried out in many countries for development of technologies for production of potassium fertilizers from seawater with the use sorbents [87,88]. Natural zeolites like clinoptilolite happened to be most prospective ion-exchangers owing their selectivity properties, availability and cheapness [89,90]. The distribution coefficient for potassium from natural seawater on clinoptilolite is around 50 at 20 °C. It is not enough to propose a one-step technology. Problems arise with efficient and invaluable chemical agent for regeneration. Additional problem is that clinoptilolite collects from seawater some other elements including sodium, calcium and strontium which should be separated from the product. All of these problems can be resolved by the use of the specific property of clinoptilolite to change significantly the selectivity with temperature [56,57].

Fig. 5 shows the principal flow chart of the pilot plant which is installed and tested in Water Research Center of the King Abdul Aziz University (Jeddah, KSA). For realization of two-step concentration process, columns with clinoptilolite are used at each step. Thermally insulated column F1 is used in dual temperature

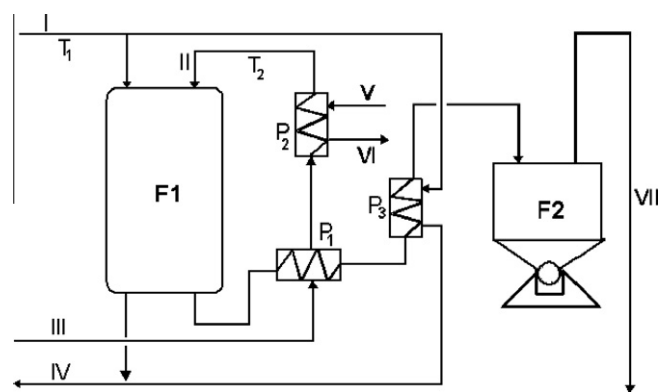


Fig. 5. Schematic flowchart of pilot unit for production of clinoptilolite-based potassium fertilizers from seawater. I, III – cold seawater, II – hot seawater, IV – exhausted water, V,VI – steam from and to power plant. F1 and F2 – sorbent beds; P1–P3 – heat-exchangers.

regime: in recurred working cycles, cold seawater is passed through F1, and potassium is concentrated by clinoptilolite after that hot seawater is passed through it, and desorption of potassium takes place. The liquid concentrate, after its cooling, is used for treating the second step column F2 and producing potassium-enriched clinoptilolite. The set of heat-exchangers pictured in figure is used for heat recuperation and regulation of temperature regimes at different stages of the process. Fig. 6 demonstrates the concentration histories of K^+ and Ca^{2+} for one of the repetitive working cycles of the described process. Heating leads to 2.5 times increasing the concentration of potassium in effluent. It can be also seen, that the oppositely directed thermo-selectivity effect takes place for calcium, with the selectivity increasing with temperature. Taking into account that clinoptilolite is not selective to other macro-components of seawater [56], these thermal effects for K^+ and Ca^{2+} make it possible to achieve high concentration of potassium (more than 1 mequiv./g) in enriched sorbent of the second step.

The technology can be realized in two variants. The first one is the production of natural zeolites enriched with potassium as the chlorine-less fertilizers of “prolonged action”, as well as artificial soils [91,92] for intensive agriculture and for “green house” systems. Today, nutrient-charged zeolites are known as new commercial kind of grow mediums [92]. (see also <http://www.zeoponix.com>). For realization of the mentioned variant, exchangeable loading of clinoptilolite in special open columns (like F2 in Fig. 5) is applied. Another variant of application of such a process is the production of fertilizers of standard-type. In this case, stationary bed of clinoptilolite is used at the second step. The solution of regenerating agent, for example, ammonium nitrate can be applied for potassium desorption. In this case, liquid concentrate with the composition: 50% of KNO_3 and 50% of NH_4NO_3 can be produced for further processing. The processes described here are promising for solution of agrochemical problems in sea shore countries being short of potassium fertilizers. In this point of view, the recent publications [93–95] of researchers from Georgia (former SU republic) are interesting.

One more prospective application of temperature-swing technique is the ion-exchange process for lithium recovery from mixed brines containing lithium, sodium, and potassium with the use of zeolite-X [96]. Distinctive property of this material is strong influence of temperature on its selectivity to sodium and potassium ions as compared to lithium one. Experiments were carried out with the brine of total concentration 1 M and composition: 87% of lithium and 13% of sodium ions. Swinging mode operations between 20 °C and 97 °C provided 97% of lithium recovery at 99.8% of purity [96].

Historically, first example of simple cyclic process and one of the most known dual-temperature methods is the “Sirotherm” (CSP) developed by Bolto and co-authors [12,97,98]. The process

was introduced in industry in Australia [99]. In line with the technology, at passing “cold” brackish water through the bed of special resin containing both weak-acid cation and weak-base anion exchanging groups, desalination takes place. In working cycles, regeneration of sorbent is performed with the heated original water. At temperature changing from 20 to 80 °C, water dissociation increases approximately for 30 times, and it is the main driving force in CSP. The Sirotherm process can be efficiently realized only at using polyampholytes with special functional groups distributed on a molecular level [100–102]. Elaboration of new types of efficient and accessible sorption materials for Sirotherm process is still in the scope of interest of researchers [102,103]. The process was reviewed many times [104,105] and included in encyclopedic dictionary of named processes in chemical technology [106]. So here, we are not staying on the details of CSP.

3.2. Simple cyclic process in multi-component systems

In multi-species systems, the dual-temperature separation of two components A and B can be realized even when the separation factor α_B^A does not depend on temperature. It is sufficient that their separation factors toward third component C , i.e. α_C^A and α_C^B , change with temperature in a similar manner. In this case, temperature effects on the sum of capacities of sorbent to ions A and B . If $\alpha_B^A > 1$ and if one of these exchanging ions, for example, B , is a micro-component, it is possible to get practically significant separation effect in simple cyclic process. As it was described in works [22,107,108], such a process was performed for a system: sulfate of copper (micro-component)–sulfate of zinc–sulfuric acid with the use of weak-acid cation-exchanger Amberlite IRC-718.

3.3. Cascade methods for multiplication of single separation effects

Multiplication of separation effects can be achieved in a cascade of single dual-temperature set-ups. Any single step gives two products: partially enriched and exhausted solutions. Depending on the task to be solved, cascade schemes can be more complex, for example, counter-current ion-exchange columns at each step can be used [39]. Not too long ago, some works appeared on cascade dual-temperature ion-exchange separation of metal ions [109], and amino-acids [110]. Cascade schemes have some limitations including high capital costs and operation problems with the regulation of multi-step process and with heat recuperation.

4. Methods regulated by the speed of motion of concentration waves along column

4.1. Parametric pumping (PP)

The principle of PP consists in passing some volume of fluid phase through the sorbent bed alternatively in direct and in opposite directions. At the end of any filtration stage the temperature is changed from the “hot” to “cold” one and vice versa. If the selectivity of ion-exchanger to a component to be removed increases with temperature, we can choose the operation condition for each cycle: $\epsilon + \Gamma(T_1) \leq v/L < \epsilon + \Gamma(T_2)$ for the column of a length L . This choice means that at passing the total volume of solution through the column at T_1 , the frontier of exchange will travel the distance equal or longer than the column length. At passing the solution through the column at T_2 , the frontier would not achieve the border of column. From cycle to cycle, the filtrate of hot stage is gradually enriched by one of the components and the filtrate of the cold stage – by another one.

Proposed by Wilhelm and co-authors [11], the principles of PP separations were considered in a lot of original works and reviews

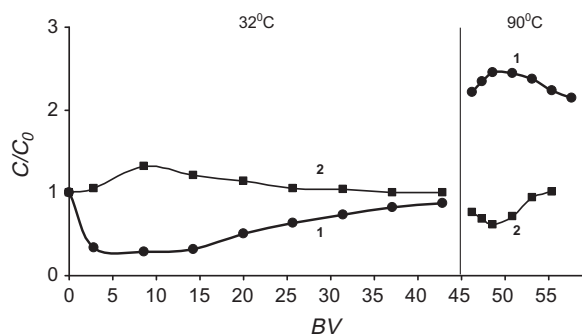


Fig. 6. Concentration histories of K^+ (1) and Ca^{2+} (2) from seawater in dual-temperature process on natural clinoptilolite.

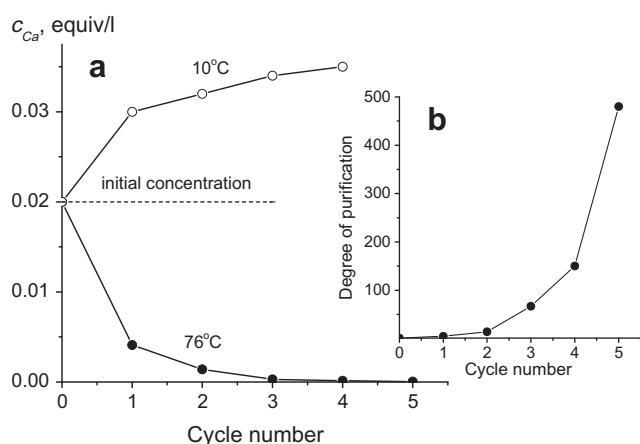


Fig. 7. Purification of sodium chloride brine from calcium chloride by dual temperature parametric pumping. Original mixture: 2.5 N NaCl and 0.02 N CaCl₂; cation-exchanger: KB-4.

for different modes: bath, recuperative, continuous and so on. So, there is no need to repeat them here. With the use of the method, practical tasks of purification of solutions and substances from organic and inorganic components [1,111–114] were solved. The method is still developed [4,38–47,115–121] and tested for many objectives including purification of drugs [121] and treatment of wastewaters for removal of phenols [118,119] and heavy metals [120]. The PP technology is described in handbooks and monographs [7,122–124]. Last 20 years gave us a number of examples showing its prospects to be introduced into chemical engineering practice.

Fig. 7 demonstrates experimental data on purification of sodium chloride brine from traces of calcium chloride on cation-exchange resin of polymethacrylic type with the use of laboratory PP set-up of closed type [5]. It is seen that five cycles of operation allow to reach the purification degree around 500.

Parametric pumping technique on zeolites was shown to be efficient for separation of alkali metal ions from their mixes with the production of high-grade pure salts of one metal [117]. It is hard to be reached such a separation due to closely spaced chemical and physical properties of these ions. In experiments carried out with the use of zeolites of A and Y types, 4–6 cycles of parametric pumping were sufficient to purify lithium salts from sodium and potassium leading to 100–700 times reduction of these admixtures [117].

4.2. Method of cycling zone adsorption

“Cycling Zone Adsorption (CZA)” method was proposed in 1969 by Pigford and co-authors [125]. In this method, a number of same

sorbent beds in columns situated in series are used, and the original solution is uninterruptedly passed through these successively arranged columns. Cold columns alternate with the hot ones. By fixed time periods, after passing the fixed portion of the solution through the system, the temperatures in columns are changed, so that the cold columns become hot and vice versa. CZA method (like PP) is most suitable for purification of solutions, but they have limitations for multi-fold concentration of micro-components.

5. Separations using compression of concentration peak of target-component

5.1. Dual-temperature counter-current method

In this method the process is performed in a counter-current column that consists of two sections maintained at different temperatures. The method was firstly developed in USA and former Soviet Union in 40th and 50th with regard to hydrogen isotope separation and heavy water production [8,126,127]. In the field of ion-exchange, the method of separation of electrolyte mixtures in counter-current two-sectional columns was developed by Gorshkov and his colleagues [128] which used regulation of pH values and total concentrations instead of temperature. Baily and Tondeur [129,130] have demonstrated successful temperature-driven separation of calcium–potassium and calcium–iron ionic mixtures on polystyrene sulfonic resin.

5.2. Cyclic column method

This method was proposed by Andreev et al. [9,10] in 1961 as the process that simulates separation according to counter-current scheme but using stationary bed of ion-exchanger. That was the first dual-temperature reagent-less separation on ion-exchangers.

5.3. Method of “swinging” wave

Tikhonov predicted the possibility of a new dynamic sorption method of dual-temperature separation claimed as “swinging” wave method [16,17]. Later, Fokina, Tikhonov and one of the authors of this article elaborated theoretically and experimentally a number of variants of the method, that allow continuous concentration and separation of dissolved substances [18–21,131–133].

The simplest variant of the method can be realized, as it is shown in Fig. 8, in the set-up consisting of two identical sorption beds in columns. For example, let the selectivity decrease with temperature. At the beginning of the process, the sorbent in both columns is equilibrated with the original solution at low temperature T_1 . Then, one column is heated till T_2 and the concentration of target-component in the solution in this “hot” column increases as compared to that one in another “cold” column. Afterwards, col-

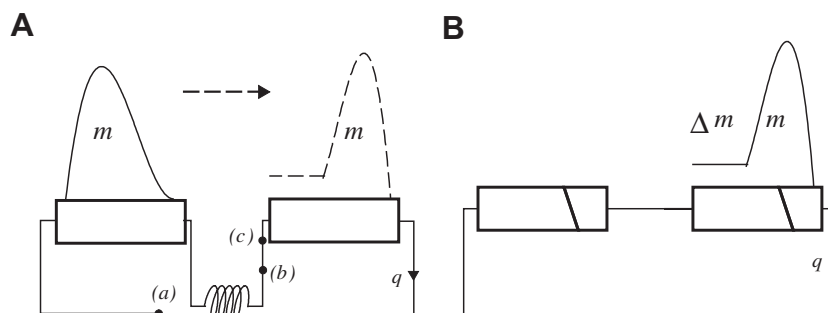


Fig. 8. Scheme of “swinging” wave method. (A) Transfer of the enriched zone from a hot column to a cold one. (B) Change of temperatures in column by a circulating flow.

umns are joined with the closed circle of liquid. The following process consists of repeating the cycles of 3 stages: shift of substance and its redistribution between columns with the use of special circulating solution, change of temperatures in columns giving the substance redistribution between the phases and the sorption of new portion of substance from the original solution. From one cycle to another, the flow direction of circulating solution is changed.

The cycle begins with the transfer of substance from the hot column to the cold one with the circulating flow of solution (Fig. 8A). The quantity of this target-component in the hot column before cycle can be called as the "accumulation value" m (in the beginning of the process $m \geq 0$). The flow q of liquid from the hot column goes into the cold one through a counter-current heat exchanger where it gives its heat to the flow of liquid withdrawal from the cold column. Heat losses are compensated by additional heating at a point (a) and cooling at a point (b). While the flow of solution with the accumulation m is transferring to the cold column, synchronous compression of the zone of accumulation and the rise of concentration in this zone take place.

The second stage is the change of temperature of two columns. To do this, the heat exchanger is turned off (Fig. 8B) and the circulating solution passes until the hot column becomes cold and vice versa. The redistributions of the substance between solution and sorbent in both columns occur. In column from the right which became hot one, partial desorption takes place and solution gets additional quantity Δm of target-component. Left column becomes exhausted one.

The third stage of the cycle is feeding the set-up with the target-component from the original solution situated externally. In order to make it, exhausted left column is excluded from the system and cold original solution is passed through it till the equilibrium, i.e., till the absorption Δm of the target-component. Then, this column is again included into the system that becomes ready for next cycle, but with the opposite direction of the flow of circulating solution and with the opposite transfer of enriched zone between columns.

When these cycles are repeated several times the concentration band of the target-component swings from the left to right and vice versa accumulating gradually the component and increasing its concentration. When the necessary degree of enrichment is achieved, the preparation part of the process becomes completed. In working part, the product solution is picked up from the system at the moments of passing the peak of the component through the point (c). The product solution with repetitive characteristics is withdrawn in recurring mode.

For exclusion of "break-times" from the process, three columns can be used, with first, second or third one being periodically fed by original solution.

Fig. 9 shows the experimental results on bromide concentration from seawater in the three-column set-up with the strong basic anion-exchanger of polystyrene type. For a comparison, theoretical predictions performed earlier [19] are given. For 30 successive operating cycles, the concentration of bromide in its peak grows 80 times. This big number of cycles represents the preparatory stage of accumulation of micro-component. After this stage, the withdrawal of the concentrated bromide solution (productive stage) may go infinitely long. Evaluation of some technological parameters showed that output of the plant charged with 1 ton of sorbent corresponds to annual production of solution containing 1.2 tons of bromine with the energy consumption 10^8 kJ at heat losses about 15%.

Swinging wave method which was demonstrated can be called a method of "close" mode in which the stages of transfer of wave and feeding with the target-component from the original solution are separated. For micro-components, these stages can be combined. Technological advantage of such an open mode is in the fact

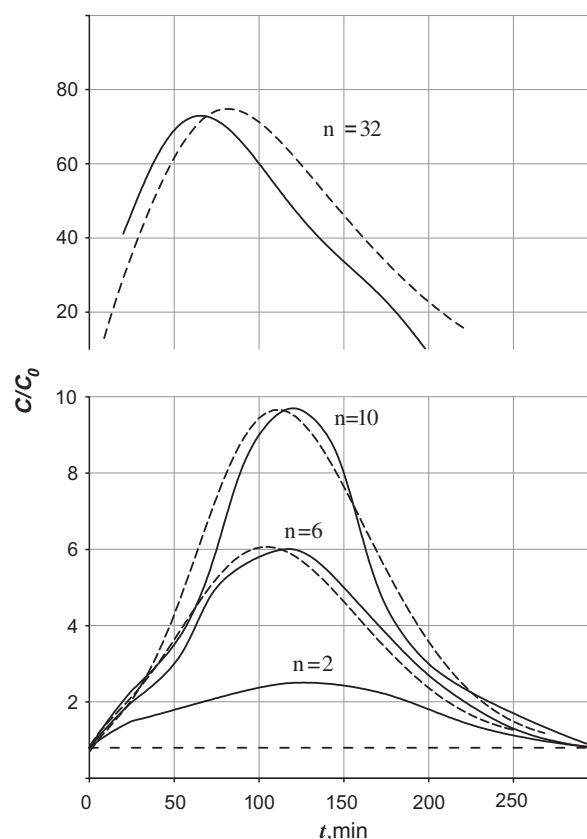


Fig. 9. Experimental (strong) and theoretical curves of Br^- concentration from seawater by swinging wave method. n -the number of treatment cycle.

that non-stop cyclic process can be realized on two columns without use of recycling solution. A set-up with such a scheme was installed in pilot plant for complex processing of seawater [24,134–137]. The process was realized in adiabatic regime with the use of waste heat of evaporating module of the plant.

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