

GIANFRANCO BOARI*, LORENZO LIBERTI*, ROBERTO PASSINO**

THE SIRA PROCESS FOR BRACKISH WATER DEMINERALIZATION BY ION EXCHANGE

A new ion exchange process for partial or total demineralization of brackish waters which essentially uses weak ion exchange resins has been developed. The process proved its feasibility and flexibility in several series of pilot plant tests carried out at Bari's facilities of the Italian Water Research Institute. The most suitable layout, which includes cationic, anionic and cationic beds arranged in series, and the best operating conditions are established according to the salinity and composition of the feed water. Information on results obtained on industrial plants is also given.

LIST OF SYMBOLS

<i>A</i> — strong anion concentration in the feed water, stężenie silnych anionów w dopływie	meq/dm ³ mval/dm ³
<i>C</i> — total cation concentration in the feed water, całkowite stężenie kationów w dopływie	meq/dm ³ mval/dm ³
<i>FMA</i> — free mineral acidity in the effluent from the strong cation column, wolna kwasowość mineralna w dopływie z kolumny zawierającej silny kation	meq/dm ³ mval/dm ³
<i>H</i> — total hardness concentration in the feed water twardość ogólna w dopływie	meq/dm ³ mval/dm ³
<i>M</i> — bicarbonate alkalinity concentration in the feed water, zasadowość dwuwęglanowa w dopływie	meq/dm ³ mval/dm ³
<i>X</i> — relative alkalinity recycle, i.e. flow rate ratio of the recycled effluent from the anion section to the feed water stopień recykulacji zasadowości, tj. stosunek natężenia odpływu recykulantu z kolumny anionowej do natężenia dopływu solanki	dm ³ /dm ³ dm ³ /dm ³
<i>Y</i> — relative CO ₂ recovery, i.e. the ratio of CO ₂ recycled into the anion section to the CO ₂ discharged in the product water stopień odzysku CO ₂ , tj. stosunek ilości CO ₂ recykulowanego do kolumn anionowych do ilości CO ₂ odprowadzanego wraz z oczyszczoną wodą	meq/meq mval/mval
<i>dm_r</i> ³ — resin — masa jonowymienna	dm ³ dm ³

*G. BOARI, L. LIBERTI, IRSA-CNR, Via F. De Blasio, 70122 Bari, Italy.

**R. PASSINO, IRSA-CNR, Via Reno, 1 00198 Roma, Italy.

1. INTRODUCTION

The interest toward the use of weak ion exchange resins in water desalination technology is growing continuously, due to the economic advantages resulting from their high regeneration efficiency, low rinse requirements, high exchange capacity, etc. On the other hand, the ability of such ion exchange resins is strongly influenced by the pH of solution since the exchange occurs only till the equilibrium of resin and solution pH which depends on whether an anion or cation weak resin is employed.

In desalination of brackish water the use of weak cation resins to the removal of temporary hardness is limited by the pH of the solution, while weak anion resins have usually to be placed after a strong cation section.

On the ground of the buffer capacity of the CO_2/HCO_3 system, several efforts have been made to find out processes in which only weak resins could be used for desalination of brackish waters. The DESAL process, developed by Kunin et al. [7] is adversely affected by the progressive fouling of the weak anion resin (the first in the process sequence) by iron and alkaline earth oxides, and by the tendency of the CO_2 to be desorbed during the exhaustion step. Similar poisoning problems are present in the Selmezi's process [8], where externally produced CO_2 is added to the influent. According to Hetherington in order to remove total hardness, the required amount of a synthetic NaHCO_3 solution should be added to the brackish water fed to a weak cation resin [6].

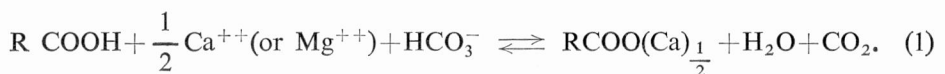
A new process, called SIRA process, which permits to employ only weak resins has been developed by the Istituto Ricerche Sulle Acque [3].

2. DESCRIPTION OF THE PROCESS

Basic arrangement of the process is presented in Fig. 1. Its main characteristics are the following:

1. A partial recycle of the alkaline effluent from the anion column, in order to increase the temporary hardness percentage in the feed water.
2. A recovery of the CO_2 produced in the degasifier (if necessary), in order to convert all the anions into bicarbonates in the weak anion section.

Brackish water passing through the C_1 column, which contains weak cation resin, exchanges an amount of (divalent) cations equivalent to its alkalinity content, according to the reaction



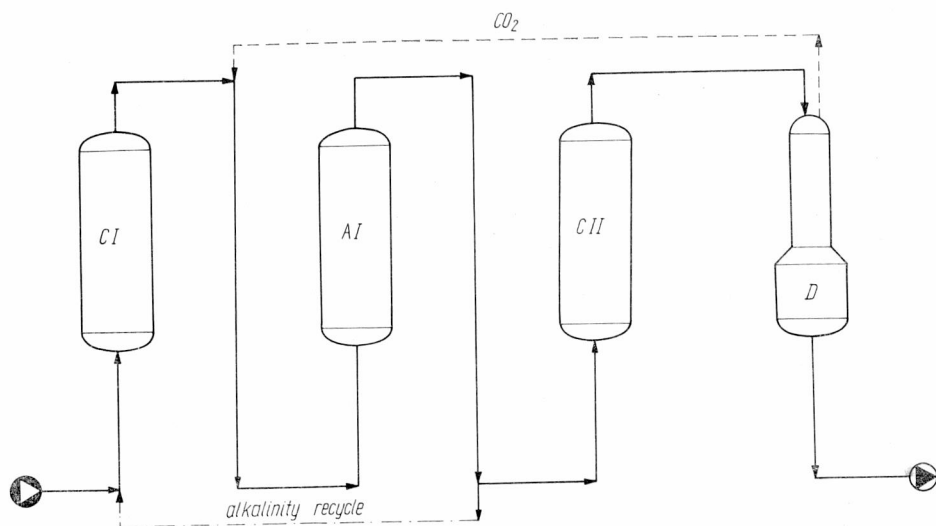


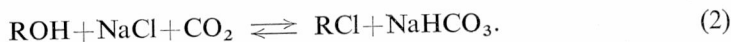
Fig. 1. Basic version of the SIRA process

(C_I – weak cation resin; A_I – weak anion resin; C_{II} – weak or strong cation resin; D – degasifier)

Rys. 1. Podstawowy wariant procesu SIRA

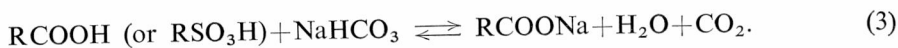
C_I – kationit słabo kwaśny; A_I – anionit słabo zasadowy; C_{II} – kationit słabo lub silnie kwaśny;
 D – odgazowywacz

The strong anions can thus be exchanged with the weak anion resin A_I , according to the reaction



A part of this effluent is recycled in order to increase the temporary hardness content of the feed water. At the same time, more CO_2 will be available for aeration (2). For many types of water, these two columns are sufficient to produce a drinkable effluent.

A third column, C_{II} , containing either weak or strong cation resin, can be used depending on the desired degree of sodium removal in the product water. Here the salinity content of the product is further reduced according to



If necessary, after a degasifier, a part of this CO_2 can be recovered to complete reaction (2).

As shown later, with common brackish waters only section C_I and A_I are usually required to produce potable water.

By a proper control of the alkalinity and CO_2 recycles, the following conditions can be satisfied:

1. Virtually no leakage of strong anions occurs from the weak anion resin which,

in turn, can be regenerated efficiently with inexpensive chemicals (NH_4OH , $\text{Ca}(\text{OH})_2$, etc.);

2. Total hardness can be removed by the first weak cation resin, monovalent ions being eventually fixed by a second cation resin. In this way, sulphuric acid at high concentration (up to 10%) can be efficaciously used as the second cationic resin regenerant saturated in the sodium form prevalently. Exhausted regenerant is diluted to about 1% and used for regeneration of the first cationic resin which removed the hardness.

In a variation of the basic arrangement the last part of the first weak cation resin is substituted by a strong cation resin, (Fig. 2), which is partially by-passed

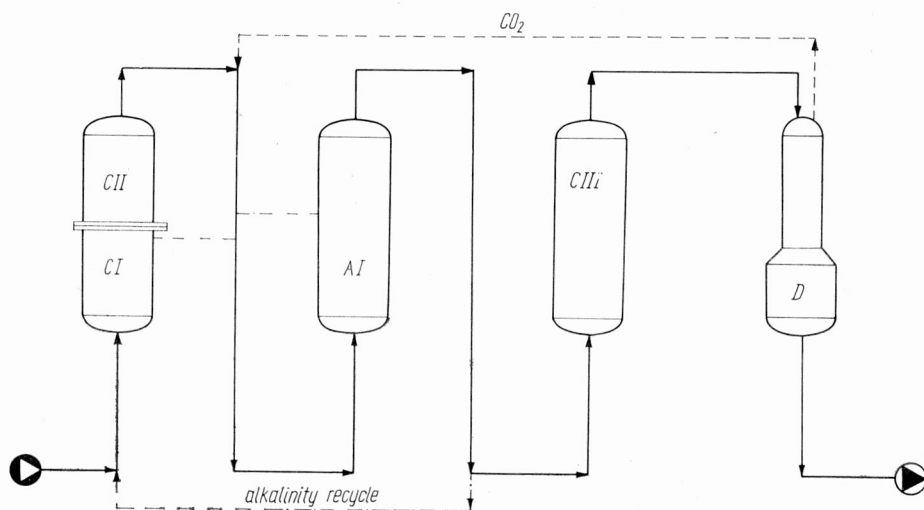


Fig. 2. Modified version of the SIRA process

(C_I – weak cation resin; C_{II} – strong cation resin; A_I – weak anion resin; C_{III} – weak or strong cation resin; D – degasifier)

Rys. 2. Zmodyfikowany wariant procesu SIRA

C_I – kationit słabo kwaśny; C_{II} – kationit silnie kwaśny; A_I – anionit słabo zasadowy; C_{III} – kationit słabo lub silnie kwaśny; D – odgazowywacz

by the softened effluent in order to obtain some NaHCO_3 leakage from the anion section. This arrangement, permits to obtain lower strong anion leakages and higher exchange capacities on the weak anion resin, due to the lower pH of its influent.

For special applications other columns can be added to this two basic arrangements. E.g. the addition of a strong anion column and/or a mixed bed is required for the production of extremely pure water.

These and other arrangements have been experimentally tested, in order to demonstrate the flexibility of the process.

3. OPTIMIZATION OF THE OPERATING CONDITIONS

The main feature of the SIRA process is its ability to produce an anion resin effluent which practically contains only sodium bicarbonate. A suitable mixing of this effluent with the brackish water allows to obtain a bicarbonate hardness ratio at least equal to one (i.e., to have only temporary hardness in the feed water), so that the whole hardness can be removed by the weak cation resin. Obviously, bicarbonates can be produced by the weak anion resin only in presence of some leakage of cations and of equivalent amounts of CO_2 . This explains the need for a by-pass when the anion column is preceded by a strong cation resin, and for an eventual recovery of the CO_2 from the final effluent.

It is evident that, for a certain type of brackish water, the CO_2 and alkalinity recycles must be correlated with the *FMA* production of the strong cation resin, in order to reach the process purposes. Considering a simple mass balance the following general correlation has been obtained.

$$Y = \frac{K}{1+X} - 1 - Z, \quad (4)$$

where $K = A/M$ and $Z = FMA/M$.

Eq. (4) shows that the relative CO_2 recovery (Y) decreases with the relative *FMA* production in the strong cation section (Z) and with the alkalinity from the anion column (X). In absence of a strong cation section before the weak anion resin (as in Fig. 1), the term Z disappears from Eq. (4), which remains still valid. According to this correlation, Fig. 3 parametrically reports Y vs. Z for different types of brackish waters, at different values of X . This diagram, which can be extended to other types of brackish waters, allows to find easily the best operating conditions of the process keeping in mind that, in order to minimize the work of the degasifier, the lowest value (eventually 0) must be chosen for Y . To avoid troubles due to regenerations with sulphuric acid, the whole hardness has to be exchanged by the first weak cation resin. To meet this condition, following value of X must be taken:

$$X \geq X_{\min} = \frac{H-M}{C-H}. \quad (5)$$

Accordingly, the highest value of Z must be chosen so that the value of Y in Eq. (4) be the lowest, provided that Z does not reach its maximum.

$$Z \leq Z_{\max} = p \frac{(C-H)}{M(1+X)}. \quad (6)$$

Here $p \leq 1$ is an empirical factor which accounts for the cation leakages obtained in strong cation resins, depending on the assumed regeneration levels. Usually

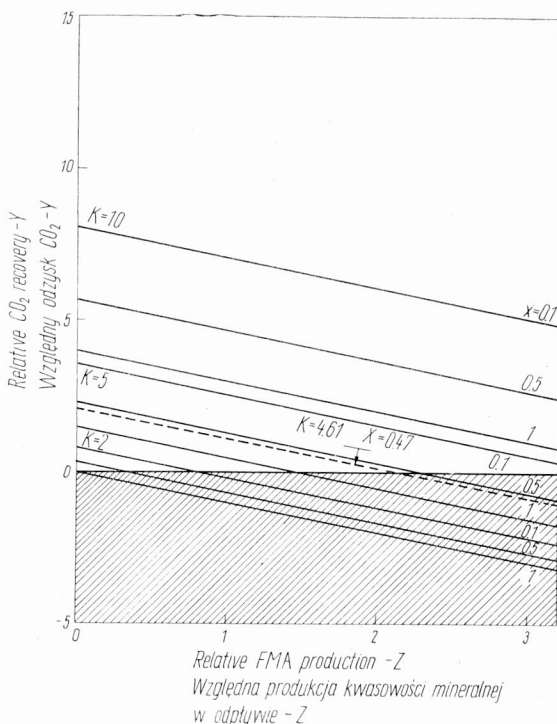


Fig. 3. Parametric correlation between CO_2 recovery (Y), FMA production (Z) and alkalinity recycle (X) in the SIRA process

Rys. 3. Współzależności między względnym odzyskiem CO_2 (Y), kwasowością mineralną w odpływie z silnie kwaśnego kationitu (Z) oraz stopniem recykulacji zasadowości (X)

$p = 0.80-1.00$. The best operating conditions will thus correspond to X and Z values which, according to limitations (5) and (6), give the lowest CO_2 recovery. Obviously, negative values of Y have no physical meaning. The dashed area in Fig. 3 simply represents cases where no CO_2 recovery is necessary ($Y = 0$), provided that a Z value corresponding to the abscissa intercept with the proper X line is adopted.

Table 1 gives the average composition of the brackish water treated in our experiments with $K = 4.61$, $X_{\min} = 0.25$ and $Z_{\max} = \frac{3.14}{1+X}$. With this water it was possible to eliminate the CO_2 recovery. From the Eq. (4) for $Y = 0$, we have obtained $X \geq 0.47$ and $Z \leq 2.14$, both values being in agreement with limitations (5) and (6) (dotted line in Fig. 3). Bearing in mind that, in order to eliminate both Y and Z , $X = 3.61 \text{ m}^3$ recycled water/ m^3 feed would be necessary, the convenience to use a strong cation section clearly results.

Table 1

Average gross composition of the used brackish water
 Ogólna charakterystyka przeciętnego składu wód odsalanych

Cations meq/dm ³		Anions meq/dm ³	
Na ⁺	33.8	Cl ⁻	36.3
Ca ⁺⁺	7.2	HCO ₃ ⁻	9.0
Mg ⁺⁺	10.0	SO ₄ ⁼	5.2

More generally, it is easy to eliminate the CO₂ recovery whenever an appreciable amount of bicarbonate (15% of total anions) is present in the brackish water. With waters, poor in bicarbonate where some CO₂ recovery cannot be avoided, *X*, *Y* and *Z* will be optimized on the basis of the degasifier and pumping energy requirements, etc.

4. PILOT PLANT EXPERIMENTS

Previous experiments on the laboratory plant scale, in which the arrangements of Figs. 1 and 2 were used, confirmed the feasibility of the process for the production of drinking water [5]. On the ground of these results and in order to confirm the flexibility of the process a pilot plant was built for the production of drinking or deionized water from the brackish water. (Its composition is given Table 1). At the same time, economic data for the cost evaluation of the process were collected. No CO₂ recovery was necessary throughout the experiments.

4.1. PRODUCTION OF DRINKING WATER

General arrangement shown in Fig. 2 was applied with the first column divided in two sections by a rigid screen. The following amounts of resin were employed: $C_I = 20$ dm³ of carboxylic resin; $C_{II} = 50$ dm³ of sulphonic resin; $A_I = 45$ dm³ of weak anion resin (with secondary and tertiary amino groups); $C_{III} = 10$ dm³ of carboxylic resin.

The operating conditions and the average results of this series of runs are reported in Table 2.

It must be remarked that exchange capacities up to 45 and 63.5 g CaCO₃/dm³_r for the cation and anion sections have been coupled with regeneration efficiencies higher

Table 2

SIRA process for the production of drinking water
 Parametry eksploatacyjne systemu SIRA w produkcji wody pitnej

Parameters	Cation Section		Anion Section	
Regenerant level, gCaCO ₃ /dm ³	H ₂ SO ₄	3.5%	NH ₄ OH	9.5%
Regenerant flow rate, dm ³ /dm ³ h		1.7 ^(a)		3.0
Exhaustion flow rate, dm ³ /dm ³ h		12.5		22.5
Recycle flow rate, dm ³ /dm ³ h		8.6 ^(b)		13.3
Alkalinity recycle, X, dm ³ /dm ³		0.6		0.6
Feed concentration, meq/dm ³		45.7		37.3 ^(c)
Product concentration, meq/dm ³		6.7		6.7
Cyclic production, dm ³ /dm ³		23.4		41.5
Exchange capacity, gCaCO ₃ /dm ³		45.6		63.5
Regeneration efficiency, %		96.0		90.7
Leakage, %		14.6		17.9
Rinse water consumption, dm ³ /dm ³		2.0		2.0

(a) Referred to the sulfonic resin;

(b) Referred to 70 dm³ of cations exchange resins;

(c) Strong anions only.

than 90–96%, using H₂SO₄ and NH₄OH as regenerants. Practically, only NaHCO₃ was present in the product water, with small quantities of magnesium and chlorides. Some amount of brackish water was added to the product in order to balance its salinity.

4.2. PRODUCTION OF DEIONIZED WATER

The substitution of sulphonic resin for the carboxylic one in column C_{III}, yielded in diluted product. The operating conditions and the average results of this new series of runs are given in Table 3. The volume of weak anion resin in column A_I decreased from 45 to 40 dm³. Some leakage of strong anions (about 1 meq/dm³) was noticed in the product. CO₂ being removed in a degasifier, high purity water could be obtained according to one of two methods:

a) by filtering the water through a strong anion unit (to remove silica and other strong anion leakages), and subsequently by polishing the final product on a mixed bed;

b) by treating directly this effluent on a mixed bed.

Table 3

SIRA proces for the production of deionized water
 Parametry eksploatacyjne systemu SIRA w produkcji wody zdeminielizowanej

Parameters	Cation Section		Anion Section	
Regenerant	H ₂ SO ₄	9.5%	NH ₄ OH	3.5%
Regenerant level, gCaCO ₃ /dm ³		48.0		77.5
Regeneration flow rate, dm ³ /dm ³ h		1.7 ^(a)		3.0
Exhaustion flow rate, dm ³ /dm ³ h		18.5		32.8
Recycle flow rate, dm ³ /dm ³ h		6.3 ^(b)		12.5
Alkalinity recycle, X, dm ³ /dm ³		0.6		0.6
Feed concentration, meq/dm ³		44.6		35.8 ^(c)
Product concentration, meq/dm ³		0.1		1.0
Cyclic production, dm ³ /dm ³		19.3		38.0
Exchange capacity, gCaCO ₃ /dm ³		43.1		66.3
Regeneration efficiency, %		90.0		88.5
Leakage, %		0.2		2.7
Rinse water consumption, dm ³ /dm ³		2.0		2.0

(a) Referred to the sulfonic resin;

(b) Referred to 70 dm³ of cation exchange resins;

(c) Strong anions only.

Due to the difficulties involved with mixed bed regeneration, the introduction of a new column, according to method a) seems to be more attractive. This solution has been effectively adopted in a special series of tests, conducted in cooperation with ENEL (Italian Government Company for Electricity Production) for the production of the feed water to a high pressure boiler, using a 2500 g/m³ TDS brackish water [1].

5. INDUSTRIAL PLANTS

The pilot plant experiments confirmed the suitability of the SIRA process for various desalination problems. Moreover, it seems worth to mention the flexibility of this process, which allows not only to apply the ion exchange technology to the direct desalination of various types of brackish water, but also to utilize it as pretreatment step for other desalting techniques. Since the composition of brackish water can be modified in a weak cation step (it may be reduced to a pure NaCl solution) this process appears particularly suitable to combine it with electrodialysis. In the latter process sodium chloride can be electrically remo-

ved at lower costs than when chemical energy is employed (as in ion exchange only). Nowadays, there exist two industrial scale combined IE-ED plants, where the fundamental concepts of SIRA have been applied namely: in Mashabe i Sade (Israel), and Brindisi (Italy). For the detailed descriptions see [2] and [5].

The Brindisi plant, whose maximum capacity is 7500 m³/d (Fig. 4), has been in operation for more than two years. The average salinity of the brackish water is

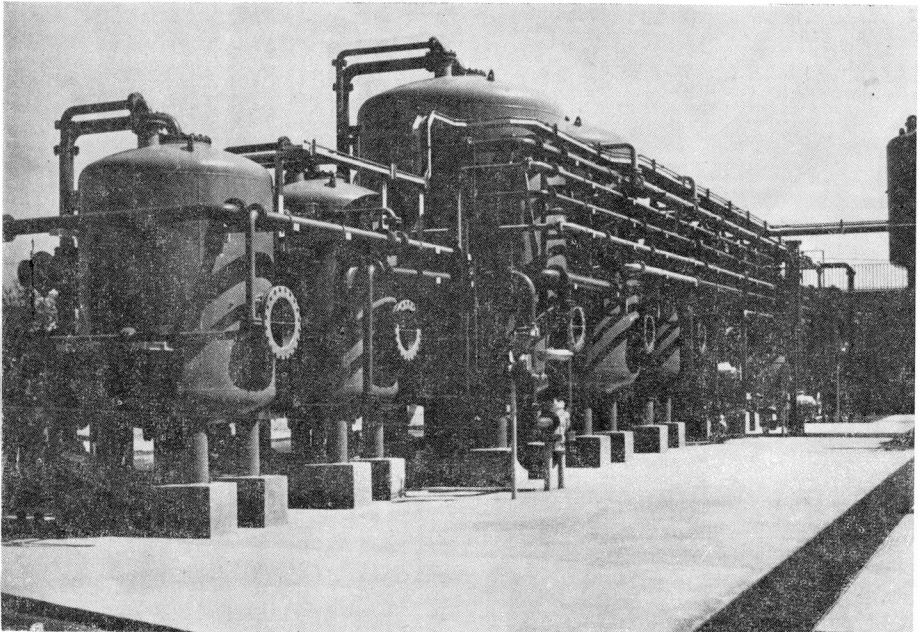


Fig. 4. Partial view of the 7500 m³/d combined ion exchange-electrodialysis SIRA plant in Brindisi
 Rys. 4. Widok zakładu odsalania wody sprężoną metodą jonitowo-elektrodialityczną SIRA w Brindisi o zdolności produkcyjnej 7500 m³/d

about 25,000 mg/dm³. 10% sulphuric acid and lime suspension are used as regenerants. Average costs of 100 lit/m³ (60 cents/1000 gals) and of 150 lit/m³ (90 cents/1000 gals) are obtained, for potable and boiler feed grade waters, respectively.

CONCLUSIONS

The tests carried out on a pilot plant have confirmed the feasibility of the SIRA process and its flexibility in production of drinking or demineralized water, using brackish waters up to 3000 g/m³ TDS.

Due to the use of weak resins, the consumptions of regenerants, which funda-

mentally affects the cost of water treatment with more than 1000 g/m³ TDS, can be held below 110% of stoichiometry.

The most suitable arrangement and the optimum operating conditions can be established by means of simple parametric equations on the basis of the hardness and alkalinity of the brackish water, and strong anion content.

The upper concentration limit for the application of the process is obviously determined by economic reasons. In our experiments, in which the concentration of brackish water was 2500 g/m³ TDS, total cost ranged within of 100–150 lit/m³ (60–90 cents/1000 gals) depending on the final quality of the product water. Although the range of cost of the process described is the same as for other desalination techniques (electrodialysis, reverse osmosis, etc.); but considering its ability to produce completely deionized water (in contrast to the latter techniques) the SIRA process can be recommended to the treatment of brackish water.

SYSTEM SIRA DEMINERALIZACJI WÓD ZASOLONYCH METODĄ JONOWYMIENNA

Opracowano modyfikację jonowymiennego procesu SIRA do częściowej lub całkowitej demineralizacji wód słonych przy użyciu słabych jonitów. Liczne badania przeprowadzone przez Włoski Instytut Badawczy Gospodarki Wodnej stacji doświadczalnej w Bari wykazały pełną przydatność i elastyczność modyfikacji tego procesu. Na podstawie składu i stopnia zasolenia wody surowej opracowano najbardziej odpowiedni schemat technologiczny odsalania złożony z ustawionych szeregowo wymienników: kationowy—anionowy—kationowy. Praca zawiera także wyniki realizacji procesu w pełnej skali technicznej.

VOLLENTSALZUNG STARK MINERALISIRTER WÄSSER MITTELS DES IONENAUSTAUSCHVERFAHRENS SIRA

Man erarbeitete eine Abwandlung des Ionenaustauschverfahrens SIRA zu einer Teil- bzw. Vollentsalzung mittels schwacher Ionenaustauscher. Zahlreiche Versuche auf der Versuchsstation Bari des Italienischen Instituts für Wasserwirtschaft haben die Anwendbarkeit und Elastizität des modifizierten Verfahren voll erweisen. Anhand der Zusammensetzung und des Salzgehaltes des Rohwassers hat man folgende Reihenfolge der Austauscher für eine Vollentsalzung vorgeschlagen: Kationenaustauscher — Anionenaustauscher — Kationenaustauscher. Der Beitrag beinhaltet u.a. die Resultate die im technischen Maßstab des o. genannten Verfahren erhalten wurden.

СИСТЕМА SIRA ДЕМИНЕРАЛИЗАЦИИ ЗАСОЛЕННЫХ ВОД ИОНООБМЕННЫМ МЕТОДОМ

азработана модификация ионообменного процесса SIRA для частичной или полной деминерализации соленой воды при использовании слабых ионитов. Многочисленные испытания, проведенные опытной станцией Итальянского Института Водного Хозяйства в Bari показали полную пригодность и гибкость новой модификации этого процесса. На основе

состава и степени засоленности сырой воды разработана наиболее соответствующая технологическая схема обессоливания, составленная из расположенных последовательно обменников: катионный—анионный—катионный. В работе изложены результаты осуществления процесса в полном техническом масштабе.

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