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POSSIBILITY FOR SELECTIVE REMOVAL OF CALCIUM IONS FROM BLACK SEA WATER USING THE CONTINUOUS COUNTER-CURRENT ION-EXCHANGE SOFTENING PROCESS WITH WOFATIT KS-10

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SUMMARY

A possibility for selective removal of calcium ions from Black Sea water, by means of a continuous counter-current ion-exchange process, has been investigated. The application of this method is quite suitable for this purpose. It reduces some of the disadvantages of the fixed-bed ion-exchange method to a considerable degree. By means of a suitable choice of technological parameters of the continuous counter-current ion-exchange technique, it is possible to decrease the total hardness and calcium ion content in the water up to 65% and 80%, respectively. Under optimal conditions, $Mg^{2+}/Ca^{2+} = 10$ in the softened water, and $Mg^{2+}/Ca^{2+} = 4.1$ in the non-treated water.

INTRODUCTION

Recently, the reverse osmosis, electrodialysis and evaporation methods have been used for the production of fresh water and salt concentrates from sea water. High concentrations of ions capable of forming solid deposits on the working surfaces of the apparatus cause enormous difficulties in the industrial application of these methods.

By means of selective removal of calcium ions, we can eliminate the formation not only of solid $CaCO_3$, but also of $CaSO_4$ (the formation of $CaSO_4$ is not eliminated by partial decarbonization with strong-acid injection in sea water).

Because of the extreme hardness of sea water (60–65 mgeq/l), the duration of the softening process in the conventional fixed-bed ion-exchange technique is too short. This causes both difficulties in technological servicing and extremely high consumption of reagents in the regeneration of the ion-exchange resin.

The application of the continuous counter-current ion-exchange process is quite suitable for the softening of water containing high salt concentrations, and

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particularly sea water. It reduces the disadvantages cited above to a considerable degree.

In this paper, the results obtained from Na-cation-exchange softening and selective calcium-ion removal process of Black Sea water are reported. The total hardness of the water was 64 mgeq/l and the calcium ion content was 12 mgeq/l. The experiments were done under natural conditions with Black Sea water in a semi-industrial continuous counter-current ion-exchange plant[1], filled with "Wofatit KS-10", a specially selected ion-exchange resin[2] which is a highly selective, macroporous, strong-acid cation-exchanger with a high content of a cross-linking agent (16% divinylbenzene).

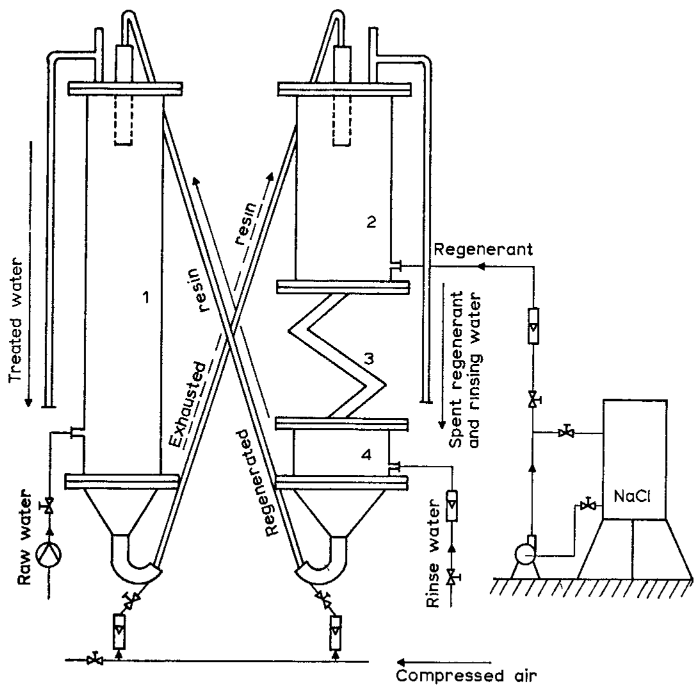

Fig. 1. Continuous counter-current ion-exchange plant. 1, Exhaustion column; 2, regeneration zone; 3, rinsing zone; 4, bottom of the rinsing zone.

EXPERIMENTAL AND RESULTS

The water to be treated enters the exhaustion column through a bottom valve and the treated water leaves it through an outlet at the top (Fig. 1). The resin enters the exhaustion column at the top and settles at the bottom whence it is continuously withdrawn and delivered to the top portion of the regeneration zone. From there the resin travels downwards first through the regeneration zone and then through the rinsing zone. From the bottom of the rinsing zone it is continuously withdrawn and fed again to the top of the exhaustion column. The regenerant is fed to a valve at the bottom of the regeneration zone and travels upwards. The rinse water is fed through a valve at the bottom of the rinsing zone and passes through the regeneration zone, diluting the regeneration solution, and leaves the regeneration zone through an outlet at the top.

TABLE I

RESULTS FROM CONTINUOUS COUNTER-CURRENT ION-EXCHANGE SOFTENING OF BLACK SEA WATER AND SELECTIVE REMOVAL OF CALCIUM IONS

Conditions: total hardness, 64 mgeq/l; calcium ion content, 12 mgeq/l, magnesium ion content, 52 mgeq/l; flow-rate of the treated water, 240 l/h; flow-rate of the rinse water, 35 l/h; flow-rate of the regeneration solution, 75 l/h; concentration of the regeneration solution, 10% NaCl.

Flow-rate of the resin (l/h)	*Total hardness and calcium ions leakage in the softened water (mgeq/l)*			*Ratio of [Mg^{2+}] to [Ca^{2+}]*	
	Total hardness	*Ca^{2+}*	*Mg^{2+}*	*Raw water*	*Softened water*
12	43.4	5.4	38.0	4.3	7.0
20	27.8	2.6	25.2	4.1	9.7
25	26.3	2.4	23.9	4.3	10.0
30	26.8	2.4	24.1	4.1	10.1
40	24.6	2.8	21.8	4.1	7.8
50	23.5	3.2	18.3	4.1	5.7
60	31.7	4.6	27.1	4.1	5.9

The experiments were carried out at different flow-rates of ion-exchange resin, because of the influence on the softening process of the amount of ion-exchange resin coming into the exhaustion column and the regeneration column. The following technological regimes of the plant have been investigated:

(1) flow-rate of the treated water, 240 l/h (linear velocity, 16 m/h);
(2) flow-rate of the rinse water, 35 l/h (linear velocity, 7 m/h);
(3) flow-rate of the regeneration solution, 75 l/h (linear velocity, 2.5 m/h);
(4) concentration of the regeneration solution 10% NaCl;
(5) flow-rate of the resin, 12, 20, 25, 30, 40, 50, and 60 l/h.

The results are given in Table I and Fig. 2.

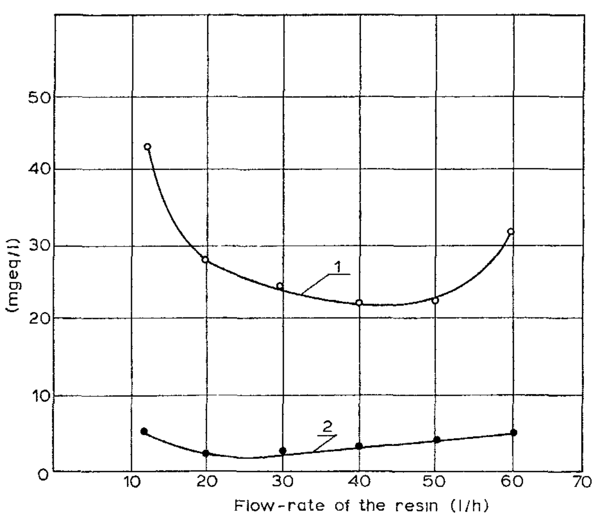

Fig. 2. The effect of variation of the resin transport flow-rate on the total hardness and calcium ion leakage in the softened water. Curve 1, average leakage of the hardness; curve 2, average leakage of the calcium ions.

As can be seen, the lowest total hardness leakage occurs at a flow-rate of the resin of *ca.* 40–50 l/h, but the lowest calcium ion leakage in the filtrate occurs at a flow-rate of the resin of *ca.* 20–30 l/h. Slower or faster flow-rates of the resin cause the same effect, an increase of the total hardness and calcium ion leakage in the treated water. The probable explanation of this phenomenon is as follows:

The entering of extremely small amounts of ion-exchange resin into the regeneration column is positive for the regeneration process, because the amount of the regenerant (NaCl) is in this case in excess of the stoichiometric amount that has to be introduced in order to regenerate the ion-exchange capacity of the resin. But even though this small portion is very well regenerated, it is not sufficient for a final removal of all the hardness ions. Thus a satisfactory decrease of the hardness under these conditions.

The entering of extremely large amounts of ion-exchange resin into the regeneration column, at the same flow-rate and concentration of the regenerant, leads to insufficiency of reagent. The larger amount of the resin cannot compensate the poorer regeneration level of the resin, and that again results in insufficient removal of hardness ions. The results show that the optimal flow-rates of the resin transport are between 25 and 40 l/h, under the conditions and technological constant parameters cited above.

The degree of decrease of the total hardness and calcium ion concentration by means of a continuous counter-current ion-exchange process and the ratio of the concentrations of Mg^{2+} and Ca^{2+} ions in both the raw (untreated) and the softened water, are given in Table I. The results show that by means of a suitable choice of technological parameters of the continuous counter-current ion-exchange technique, it is possible to decrease the total hardness *ca.* 65 % and the calcium ions content *ca.* 80 %. Under these conditions, the ratio of the concentrations of Mg^{2+} and Ca^{2+} ions is equal to 10 in the softened water. The ratio is equal to 4.1 in untreated water. The ratio of softened water to regeneration solution is equal to 3.2.

Comparative data on the content of the major ions untreated and softened Black Sea water are given in Table II.

On the basis of these results, we can draw the conclusion that during the continuous counter-current ion-exchange softening process of Black Sea water with Wofatit KS 10, it is possible to carry out a selective removal of calcium ions.

TABLE II

AVERAGE VALUES OF THE CONTENT OF THE MAJOR IONS IN THE RAW AND SOFTENED BLACK SEA WATER

Ion	*Average concentrations of the ions (mgeq/l)*	
	Raw Black Sea water	*Softened Black Sea water**
Na^+	221.3	258.8
K^+	12.5	12.5
Ca^{2+}	12.0	2.4
Mg^{2+}	52.0	24.1
SO_4^{2-}	20.6	20.6
Cl^-	241.2	241.2
HCO_3^- and CO_3^{2-}	3.4	3.4

* These results were obtained under the optimal technological conditions.

The shape of curves 1 and 2 in Fig. 2, and particularly that of curve 2, indicate that by means of a suitable variation of the exhaustion and regeneration levels of the resin it is possible to get a better selective removal of calcium ions.

CONCLUSIONS

The softening process of Black Sea water by means of continuous counter-current ion-exchange in a fluidized bed, with the strong-acid, macroporous cation-exchanger Wofatit KS 10 was investigated, and the possibility for selective removal of calcium ions established.

The conditions and parameters of the process necessary to obtain *ca.* 65% decrease of the total hardness and *ca.* 80% decrease of the calcium ion content were established. The best result obtained in these experiments was a ratio of the concentrations of Mg^{2+} and Ca^{2+} ions in the softened water equal to 10, as against a ratio of 4 in the untreated water.

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