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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

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To cite this Article Tanaka, Yasuo , Tsuji, Masamichi and Abe, Mitsuo(1993) 'Technology for Removing Potassium Ion from Concentrated Seawater by Electrodialysis and Solar Salt Dissolved in Brine', *Separation Science and Technology*, 28: 11, 2023 – 2034

To link to this Article: DOI: 10.1080/01496399308016731

URL: <http://dx.doi.org/10.1080/01496399308016731>

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Technology for Removing Potassium Ion from Concentrated Seawater by Electrodialysis and Solar Salt Dissolved in Brine

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ABSTRACT

Cryptomelane-type hydrous manganese dioxide (CRYMO) has a high adsorption selectivity toward potassium ions (K^+). The distribution coefficients of the highly selective adsorption are evaluated by the theoretically proven calculation method, that adsorption isotherm data and Kielland plot data are taken for granted. The calculated results and the experimental results of the adsorption isotherm show fairly good agreement for a whole range of conditions. CRYMO has been successfully applied to the caustic soda manufacturing process. The concentration of K^+ in brine for the process was lowered to less than 1 ppb. This purity is sufficient for the high quality caustic soda manufacturing process. Another advantage of CRYMO is its acidification ability for solutions. The brine is acidified with hydrochloric acid before being introduced to the electrolytic bath in the present process.

INTRODUCTION

Caustic soda (sodium hydroxide) is one of the most important raw materials for chemical industries. It is manufactured from such natural salt resources as rock salt, solar salt, and seawater. These natural salt resources usually contain small amounts of other cations. It is necessary for the caustic soda manufacturing process to exclude these impurities.

Separation techniques of coexisting alkaline earth cations from natural

2023

salt resources have been developed over many years. Magnesium ions (Mg^{2+}) and calcium ions (Ca^{2+}) are removed by precipitation with sodium hydroxide and sodium carbonate, respectively (1–5). More complete techniques for removing the small amounts of these remaining ions are adsorption techniques involving chelate resins (6–14).

Separation techniques of the potassium ion (K^+) from brines are very demanding because K^+ is transformed to potassium hydroxide in caustic soda manufacturing. This is a serious subject for manufacturers of high purity caustic soda. Studies of solvent extraction using crown ether are well known (15–17), but high cost and difficult usage prevent this reagent from spreading widely for the separation of K^+ and Na^+ . Although some obstacles exist, solvent extraction with crown ether have been examined as sensors of K^+ concentration in flow injection analysis (FIA) (18, 19) and continuous flow analysis (CFA) (20).

In this report we propose a separation process of K^+ from brine to create high purity caustic soda (Fig. 1). The main unit of the K^+ separation process is an adsorbent column filled with cryptomelane-type hydrous manganese dioxide (CRYMO). It follows the separation processes of alkaline earth metal cations. The adsorption selectivity for K^+ on CRYMO has been proven in laboratory experiments but only in a pure system and at a low concentration.

For practical application, the selectivity is examined at the higher concentrations needed for the real process. The total concentrations of the brines fed are very high, and the K^+ mole fraction is fairly low. However,

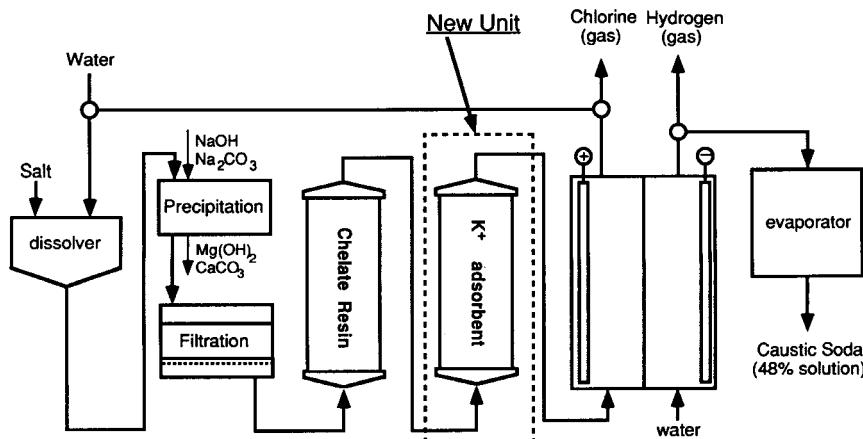


FIG. 1 Diagram of an innovative caustic soda manufacturing process.

CRYMO retains the potential to adsorb K^+ selectively and to control the pH of the brine at favorable condition for a caustic soda manufacturing plant.

EXPERIMENTAL

Preparation of CRYMO

CRYMO was prepared by using the method described in a previous report (21). A colloidal precipitate was allowed to form by mixing aqueous solutions of 0.5 M $KMnO_4$ and 1 M $MnSO_4$ containing 1 M H_2SO_4 at 60°C. The precipitate was aged in the mother liquid at 60°C overnight. Then the product was washed with 6 M HNO_3 (0.5 L) to remove sulfuric acid by using a centrifuge (10,000 rpm, several times), and then washed with deionized water until the pH of the supernatant solution was higher than 3. The washed material was dried at 70°C for 3 days, ground, and sieved to obtain material of about 100 μm (100–200 mesh) in diameter. It is necessary to remove K^+ and SO_4^{2-} by concentrated (13 M) HNO_3 in a column operation because considerable amounts of these ions are still retained in the product. The sieved material was packed into the column, and the concentrated HNO_3 was percolated until the concentration of K^+ in the effluent was below 10^{-4} M. The washed and dried product contained K^+ of about 0.06–0.07 mmol/g.

Characterization of CRYMO

Powder x-ray diffraction (XRD) and thermal analyses (TG-DTA) were carried out on the synthesized materials. The XRD pattern was measured by Mn-filtered FeK_α radiation using a Japan Electron Optics Laboratory (JEOL) x-ray diffractometer model JDX-7E. TG-DTA was performed with a Rigaku Thermoflex model 8001 at a heating rate of 10°C/min with the reference material α - Al_2O_3 . The chemical analysis was carried out as follows: A 0.02-g portion of the synthesized material was dissolved in small quantities of a solution containing hydrogen peroxide and sulfuric acid. The solution was adjusted to a volume of 25 cm^3 , and the Mn^{2+} and K^+ contents were determined by a Seiko Instruments Inc. inductively coupled plasma atomic emission spectrophotometer model SPS 7000 and a Varian-Techtron flame atomic absorption spectrophotometer model 1200, respectively.

Ion-Exchange Isotherm

The ion-exchange isotherm was investigated by the batch equilibration technique. A 0.200-g portion of CRYMO in the H^+ form was equilibrated

at 30°C with a 10.0-cm³ solution containing Na⁺ and K⁺ at total normalities of 0.1, 1.0, and 3.4. NaOH was added to adjust the equilibrium pH to 5 or 10. After equilibration, the supernatant solution was analyzed for pH and alkali metal ions. Whenever necessary, the concentrations of Na⁺ and K⁺ in exchanger phase were also determined by the method described above.

Breakthrough Experiment

Breakthrough experiments for removing K⁺ were carried out on relatively small columns packed with CRYMO. The column sizes were 20 cm × 0.5 cm i.d. for the electrodialysis of concentrated seawater and 6.5 cm × 0.5 cm i.d. for the solar salt dissolved brine. Both brines were treated in advance by adding NaOH and Na₂CO₃ to deposit Mg²⁺ and Ca²⁺, respectively. The flow rate was regulated to 0.5 cm³/min by a Nihon Seimitsu Kagaku high pressure personal pump model NP-DX-8. The effluent from the column was collected by a drop-counting type fraction collector (Otake Works). The concentrations of K⁺ and Na⁺ in the effluent were measured by atomic absorption spectrophotometry.

Reagents and Brines

All chemicals were of analytical grade from Wako Pure Chemical Industry Ltd. (Japan) without further purification. The electrodialysis of concentrated seawater, which is the source of sodium chloride manufacturing in Japan, was supplied by Akoh Kaisui Kagaku Industry Co. Ltd. (Japan). The solar salt was produced at Shark Bay in Northern Territory, Australia.

THEORETICAL BASIS

The theoretical basis has been discussed in previous papers by Tsuji and Komarneni (22, 23) and Tsuji, Tanaka, and Abe (24).

The cation-exchange reaction is represented by



The equilibrium constant of this exchange reaction is defined by the following equation (25):

$$K = \frac{\overline{X}_{\text{K}}[\text{Na}^+]f_{\text{K}^+}\gamma_{\text{Na}^+}}{\overline{X}_{\text{Na}}[\text{K}^+]f_{\text{Na}^+}\gamma_{\text{K}^+}} \quad (2)$$

In the equations, barred symbols are in the exchanger phase. \overline{X}_{Na} and \overline{X}_{K} are equivalent mol fractions in the exchanger phase. $[\text{Na}^+]$ and $[\text{K}^+]$ are the concentrations in molality. γ_{Na^+} and γ_{K^+} are activity coefficients in

the solution phase. f_{Na^+} and f_{K^+} are activity coefficients in the exchanger phase. As the standard state, these coefficients are unity when the exchangers are in their pure Na^+ or K^+ forms. Also γ_{Na^+} and γ_{K^+} are unity when $[\text{Na}^+]$ and $[\text{K}^+]$ approach zero, respectively. The equivalent mol fractions are expressed as

$$X_{\text{Na}} = \frac{[\text{Na}^+]}{[\text{Na}^+] + [\text{K}^+]}, \quad X_{\text{K}} = \frac{[\text{K}^+]}{[\text{Na}^+] + [\text{K}^+]} \quad (3)$$

$$\bar{X}_{\text{Na}} = \frac{[\bar{\text{Na}}^+]}{[\bar{\text{Na}}^+] + [\bar{\text{K}}^+]}, \quad \bar{X}_{\text{K}} = \frac{[\bar{\text{K}}^+]}{[\bar{\text{Na}}^+] + [\bar{\text{K}}^+]} \quad (4)$$

The equilibrium constant are represented by

$$K = K_{\text{Na}}^{\text{K}} \frac{f_{\text{K}^+}}{f_{\text{Na}^+}} \quad (5)$$

where K_{Na}^{K} refers to the corrected selectivity coefficient (Kielland's selectivity coefficient) (26, 27):

$$K_{\text{Na}}^{\text{K}} = \frac{\bar{X}_{\text{K}} X_{\text{Na}} \gamma_{\text{Na}^+}}{\bar{X}_{\text{Na}} X_{\text{K}} \gamma_{\text{K}^+}} \quad (6)$$

The distribution coefficient (K_d) for potassium ion is defined by

$$K_d = [\bar{\text{K}}^+]/[\text{K}^+] \quad (7)$$

The total normality (TN) in the solution and the total capacity (TC) of the ion exchanger are kept constant throughout the ion-exchange reaction:

$$[\text{K}^+] + [\text{Na}^+] = \text{TN}, \quad [\bar{\text{K}}^+] + [\bar{\text{Na}}^+] = \text{TC} \quad (8)$$

Using Eqs. (3), (4) and (8), the K_d value can be expressed in terms of TC, TN, and equivalent fractions:

$$K_d = \frac{\text{TC} \bar{X}_{\text{K}}}{\text{TN} X_{\text{K}}} \quad (9)$$

Eqs. (6) and (9) can be combined to give

$$K_d = \left[\bar{X}_{\text{K}} + (1 - \bar{X}_{\text{K}}) K_{\text{Na}}^{\text{K}} \frac{\gamma_{\text{K}^+}}{\gamma_{\text{Na}^+}} \right] \frac{\text{TC}}{\text{TN}} \quad (10)$$

The K_d value at infinitesimal exchange is given by the following equation, based on Eq. (10):

$$(K_d)_{\bar{X}_{\text{K}} \rightarrow 0} = \frac{\text{TC}}{\text{TN}} \left(\frac{\gamma_{\text{K}^+}}{\gamma_{\text{Na}^+}} K_{\text{Na}}^{\text{K}} \right)_{\bar{X}_{\text{K}} \rightarrow 0} \quad (11)$$

The experiments of ion-exchange isotherms should be carried out at various ionic strengths and at various mol ratios of Na^+ and K^+ in the solution phase in order to confirm the adsorption properties (for example, K_d) at each condition. According to this calculation method, the K_d value can be calculated as a function of exchanger composition ($\text{TC}\bar{X}_K$) over a whole range of exchange, including an infinitesimal exchange.

RESULTS AND DISCUSSION

Characterization of Synthesized CRYMO

Powder x-ray diffraction and thermal analysis of synthesized CRYMO were in good agreement with those reported previously (21). The XRD data showed the lattice parameters to be $a_0 = 9.774 \text{ \AA}$ and $c_0 = 2.852 \text{ \AA}$.

The chemical composition of the synthesized CRYMO in H^+ form was determined as $\text{MnO}_2 \cdot 0.00258(\text{K}_2\text{O}) \cdot 0.390(\text{H}_2\text{O})$.

Ion-Exchange Isotherm

Ion-exchange isotherms at various ionic strengths are shown in Fig. 2. The actual experiments were examined on CRYMO in the H^+ form, but we are going to discuss the exchange system of K^+ and Na^+ . If it were to follow the experimental results, the exchange system would be discussed for a three-element exchange system, not a simple K^+ and Na^+ exchange system.

In another investigation carried out by Tanaka, Tsuji and Abe (28), this ion-exchange system was considered as a pseudobinary exchange reaction of K^+ and Na^+ . The study made comparisons of mathematically calculated simulations and experimental results of the column method with packed CRYMO in the H^+ form. The simulation was calculated based on

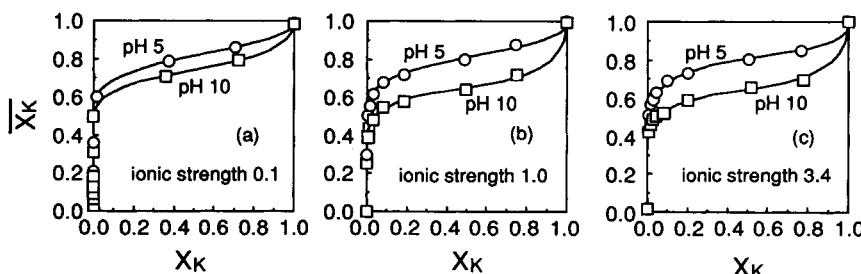


FIG. 2 Ion-exchange isotherm of Na^+/K^+ pseudobinary exchange system on CRYMO.

two assumptions: 1) Cations in solution contacting CRYMO are adsorbed, simultaneously maintaining the mol fraction in the solution phase; 2) cation species exchange between the solution phase and the exchanger phase according to the selectivity of the cation species. The calculated result showed fairly good agreement with the experimental result. On the other hand, calculation based on the assumption that CRYMO adsorbed the cation species continuously by its selectivity showed disagreement with the experimental result. This means that the mechanism of the ion-exchange reaction is supported by the first assumptions. The experimental treatment in this report considers that CRYMO's H^+ form was transformed to the Na^+ form in the earlier step. This equilibrium ion-exchange reaction can be regarded as a pseudobinary elemental ion-exchange system.

Figure 2 indicates that K^+ is adsorbed on CRYMO selectively in the solution phase, regardless of ionic strength and pH. This experimental result corroborates that CRYMO is suitable for separating K^+ at very low concentrations. The ionic strength for the electrodialysis of concentrated seawater is about 3.4, which corresponds to the experimental condition of Fig. 2(c). If this experimental result is valid for the actual brine in industrial use, CRYMO will solve the K^+ content problem in the brine of Japanese salt manufacturers, and it also creates the possibility of a new soda source for the chlor-alkali industries.

Kielland Plot

A plot of Kielland's selectivity coefficient versus \bar{X}_K is called a Kielland plot (26). Kielland plots of this experiment are shown in Fig. 3. Data of the Kielland plots were derived from the ion-exchange isotherm. There are no significant differences based on ionic strengths. There is a distinction with pH, but it is speculated that this distinction is due to a deviation of capacity at different pH values. An inorganic ion-exchanger such as CRYMO has a solid acidity property (explained as a Lewis acid). The strength of the Lewis acidity is so weak that the pH of the external solution influences the capacity of CRYMO. When the pH is increased, the ion exchanger adsorbs more cations. The difference of Kielland's selectivity between pH 5 and 10 in Fig. 3 represents the deviation of uptake capacity. The difference depends on CRYMO's maximum uptake at that pH, and it is seen in the ion-exchange isotherms for the same reason. The Kielland plot shows the essential selectivity of the adsorbent is due to its nature; it is not influenced by the ionic strength or other factors.

The region of infinitesimal exchange cannot be determined by our experimental results. It is necessary to predict the selective property in this

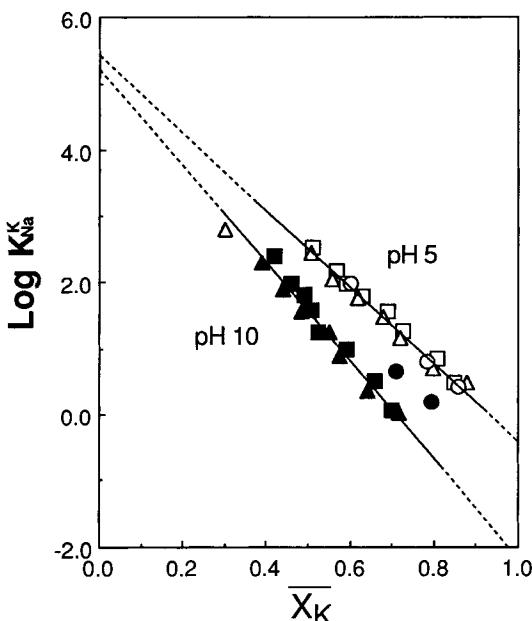


FIG. 3 Kielland plot of Na^+/K^+ pseudobinary exchange system on CRYMO. Ionic strength: 0.1 (○, ●); 1.0 (△, ▲); 3.4 (□, ■).

region by a theoretically accurate calculative procedure. The Kielland plot is an important approach to evaluating the adsorbent's selectivity.

Calculated Evaluation of the Distribution Coefficient (K_d)

Calculations for estimating K_d values were performed based on Eqs. (10) and (11). The calculated K_d values are shown in Fig. 4. The calculated K_d values are expressed by the lines and the experimental results are represented by the circles and squares. The experimental results were converted from the data of the ion-exchange isotherms. There are relatively high relationships between the calculated values and the experimental results. This means that this calculation method is valid for estimating the adsorption property of the adsorbent. The calculated curves cover the whole range of the K^+ mol ratio in solution, including the region of infinitesimal exchange. This is a region that cannot be easily determined from adsorption selectivity, especially at low ionic strength. The selectivity in the region of infinitesimal exchange is given by this calculation. These data supply important information about the adsorption selectivity at limiting conditions.

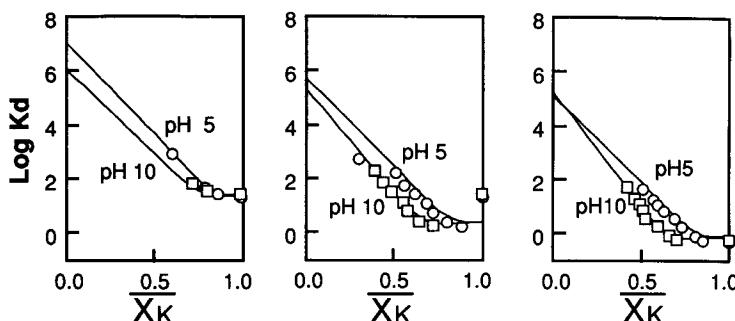


FIG. 4 Calculated K_d vs \bar{X}_K of Na^+/K^+ pseudobinary exchange system on CRYMO: (○) pH 5, (□) pH 10.

The selectivity is seen to decrease when the ionic strength is increased (Fig. 4). This fact does not indicate that the selectivity for K^+ of CRYMO becomes inferior. An inorganic ion-exchanger such as CRYMO changes its uptake amount because of the concentration in the external solution, but the change is not proportional to the ionic strength of the external solution. The rate of increase of the uptake amount is smaller than that of the ionic strength. An increase in the ionic strength of the external solution causes a decline in the K_d value. On the other hand, the selective property pointed out by the Kielland plot is represented by the lines for each pH. These results suggest that an inorganic ion exchanger has a single selective property that is independent of the conditions of the external solution. This conclusion supports the calculation method used in this paper (Eqs. 9–11).

The K_d values are seen to decrease with pH value in Fig. 4, similar to the relation between K_d and the ionic strength, but the selectivity of CRYMO is not modified by pH, either. Owing to its low Lewis acidity, CRYMO changes its apparent capacity by pH variation. The K^+ selectivity of the ion exchanger is based on its own K^+ content, regardless of the total uptake capacity. The fraction of K^+ in the uptake cations decreases at higher pH values. K_d values become lower at high pH values, even though the selective properties remain the same. This phenomenon was discussed earlier in this paper.

Breakthrough Experiment

The breakthrough experiments were carried out for the selective removal of K^+ from concentrated seawater by electrodialysis and the solar salt dissolved in brine (Figs. 5 and 6).

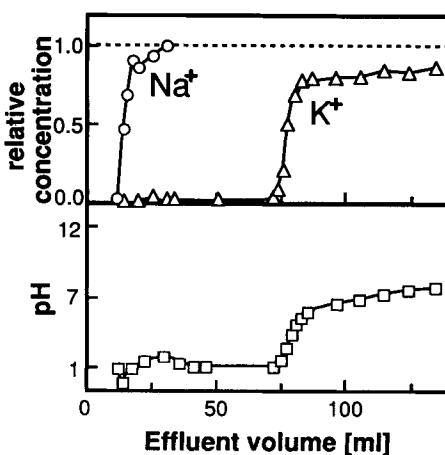


FIG. 5 Breakthrough curve of Na^+ and K^+ (above) and pH (below) of concentrated seawater by electrodialysis on the CRYMO column. Column: 20×0.5 cm i.d., CRYMO H^+ form, 8.5 g size, 100 μm . Solution and flow rate: concentrated seawater by electrodialysis 0.5 mL/min. Concentration: Na^+ , 3.65 M; K^+ , 0.105 M (corresponding to a relative concentration of 1).

The total uptake capacity of K^+ during the breakthrough experiments (breakthrough capacity: BC) can be evaluated by multiplying the apparent uptake capacity (AC) and the K^+ uptake ratio on the adsorbent (\bar{X}_K).

$$\text{BC} = \text{AC} \times \bar{X}_K$$

The CRYMO varies its AC according to the pH, so the AC should be chosen with the same pH value as that of the solution introduced into the column (29). The K^+ uptake ratio on CRYMO is indicated by the ion-exchange isotherm curve of the K^+/Na^+ pseudobinary exchange system.

The calculated value shows fairly good agreement of this breakthrough curve with the experimental results of the column operation (Table 1).

From an industrial standpoint, the K^+ concentration in the effluent flowing out of the CRYMO column before the breakthrough point is reached is lower than the detection limit of atomic adsorption spectrophotometry (10^{-6} mol/L). The purities of brines treated by the CRYMO column are sufficient for use in the chlor-alkali industries. Moreover, the pHs of the treated brines are controlled to about 1–3. In caustic soda manufacturing, it is necessary to acidify the brines before introducing them to the electrolytic cell with hydrochloric acid in the present process. The acidification avoids scale formation, impurity generation, and electrolytic efficiency deterioration. By adopting CRYMO as a high-performance

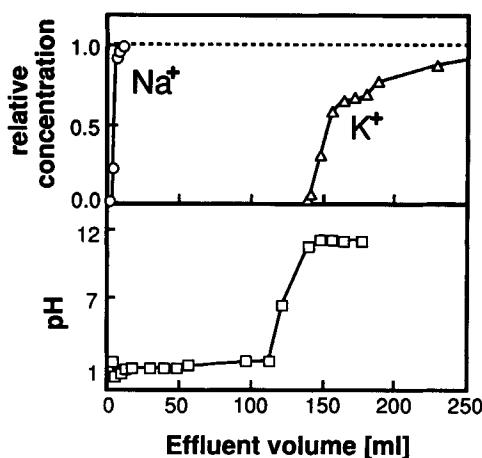


FIG. 6 Breakthrough curve of Na^+ and K^+ (above) and pH (below) of solar salt dissolved brine on the CRYMO column. Column: 6.5×0.5 cm i.d., CRYMO H^+ form, 0.9 g size, 100 μm . Solution and flow rate: solar salt dissolved brine, 0.5 mL/min. Concentration: Na^+ , 5.09 M; K^+ , 0.0024 M (corresponding to a relative concentration of 1).

K^+ remover in the electrolytic soda process, a high purity caustic soda producing system will be realized and the acidifying operation will be included.

CONCLUSION

The technology for removing potassium ion with CRYMO has been proven to be a beneficial process for the manufacture of high purity caustic

TABLE 1
Calculated Uptake of K^+ by the Columns

	Apparent uptake capacity ^a (AC)	Potassium uptake ratio (X_K)	Adsorbent amount in the columns by weight (g)	Calculated K^+ uptake value (AC)(X_K)(wt)	Experimental results of K^+ uptake
Concentrated seawater by electrodialysis	1.2 meq/g (pH 2)	0.6 (Fig. 2)	8.5	5.1 meq	~6.3 meq
Solar salt dissolved brine	1.2 meq/g (pH 2)	0.5 (Fig. 2)	0.9	0.54 meq	~0.36 meq

^a Apparent uptake capacity data are from Ref. 29.

soda. The brines treated by this method contain almost no K^+ , and they are controlled to appropriate pHs for successive treatments.

CRYMO has so high a selectivity toward the potassium ion that it is difficult to determine the selectivity in the region of infinitesimal exchange.

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Received by editor November 2, 1992