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Simulation for Selective Removal of Potassium Ion from Concentrated Brine by Inorganic Ion Exchanger

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ABSTRACT

The calculation procedure for an adsorption breakthrough property of a high selective adsorbent was developed and investigated, based on the Kielland plot which resulted from some equilibrium adsorption experiments. Comparison between the calculated simulation using this procedure and the experimental result shows a basically good agreement.

The high selective adsorbent used in this study is a cryptomelane-type hydrous manganese dioxide, which has high selectivity to the potassium ions. This simulation procedure will be a useful indication for the potassium removal and purification process for the solution of high sodium concentration, for example, some sort of brine.

INTRODUCTION

It is important for salt manufacturing industries or chlor-alkali industries to ensure that their raw salt materials have a high degree of purity. They have researched and established purification technology for removing from raw salt materials such impurities as magnesium, calcium and sulfates (Harada and Yamori, 1967; Ueshima and Kudo, 1978; Tsukamoto, 1978). However, there is still no technology for removing potassium that is adaptable to a practical process. The potassium ingredient in the industrial raw salt material becomes caustic potash (potassium hydroxide) during the caustic soda manufacturing process, and this admixture makes the quality of the caustic soda of inferior quality. In order to avoid this, the process has therefore to be stopped just before the potassium compound is crystallized in the brine recrystallizer. For this reason, the potassium content also decreases salt manufacturing productivity. Furthermore, the natural radioactive isotope ^{40}K is present among the potassium ions. This is a serious problem as some computer chips suffer from the radiation emitted. In order to solve these problems, a method for removing the small amounts of the potassium ions from the industrial raw salt material is required.

In a previous report, the author has described a technique for selective removal of the potassium ingredient from concentrated brines (Tanaka et al., 1991). Using this technique, it is possible to achieve a potassium concentration lower than 10^{-7} M (4 ppb) in almost saturated brine.

In this paper, a simulation procedure is discussed for the selective removal of the potassium ions in brine effluted through a column filled with the adsorbent, cryptomelane-type hydrous manganese oxide (CRYMO). This adsorbent is one of the inorganic ion exchangers and has high adsorption selectivity for potassium ions.

The purification technique used in this experiment is a continuous process employing an adsorbent column. However, owing to its conspicuously high adsorption selectivity and also to the fact that its selective properties change drastically with the amount adsorbed, it has been very difficult to estimate its purification ability using established procedures. In this new simulation procedure, we have proposed a new method of estimating the continuous purification profile (called a breakthrough curve) based on equilibrium selective adsorption data for potassium ions.

Simulation of the breakthrough curve brings some great benefits. One of the most significant is that we can predict the purification abilities based on the various conditions; i.e. the brine concentra-

tion, components, amounts, and so on. This is useful information for examining industrial processes. Another benefit is that we can evaluate the adsorption property of the adsorbent. Using calculated data for various adsorption properties, the capacity and the selectivity necessary for the adsorbent became clearer. This is a valuable procedure in estimating the adsorption ability and it also leads to important information for the synthesis of new adsorbents.

ION EXCHANGER AND ITS ADSORPTION SELECTIVITY

An ion-exchange phenomenon was first recognized by Thompson (1850), namely the exchange of ammonia ions with potassium and calcium ions on the aluminosilicate constituent in soil samples. This phenomenon was studied as a means of maintaining fertilizer at those times. Zeolites and permutites were synthesized as the first ion exchangers by Gans (1905). These ion exchangers were used for water softening. Until these inventions, all the ion exchangers were made of inorganic materials.

Adams and Holmes (1935) succeeded in synthesizing ion-exchange resins which became popular because of their physical strength, chemical stability and large ion-exchange capacity.

In recent decades, interest in inorganic ion exchangers has revived because of their high radiation resistance. Zirconium phosphate, which was the inorganic ion exchanger synthesized by the research group at the Oak Ridge National Laboratory (Kraus and Philips, 1956; Kraus et al., 1958), was developed for the recovery of radioactive nuclei in nuclear reactors. Furthermore, inorganic ion exchangers with high selective adsorption, which cannot be achieved by ion exchange resins, were synthesized and developed by Abe and Ito (1965), Abe and Hayashi (1983) and Abe et al. (1985). These materials made it possible to realize a high level purification process and a selective adsorption process.

In this study, we used one of the inorganic ion exchangers, CRYMO. Its selectivity is sufficient to permit separation of the potassium ions from the sodium ions in the solution phase. CRYMO has a rigid structure and does not swell in solution unlike organic ion-exchange resins. This enables recognition of potassium ions by ionic radius of the adsorption site, like the molecular sieve effect.

In the case of such a highly selective adsorbent, the question of how to express its high selectivity becomes a problem. However, the distribution coefficient Kd, expressed below, has been used in many studies:

$$Kd = \frac{\text{uptake amount in exchanger phase [mmol/g]}}{\text{concentration in solution phase [mmol/ml]}}$$

The experiment for measuring the distribution coefficient was carried out at low concentration range near the ideal conditions. However, it is difficult to apply these data to industrial processes because they normally operate at high concentrations.

Kielland (1935) presented an expression for the selectivity under specified adsorption conditions. Using this, it is possible to express the selectivity at high concentrations used in industrial processes. Kielland's selectivity coefficient is written as:

$$K_{M_b}^{M_a} = \frac{\overline{X_{M_a}}\, X_{M_b}}{\overline{X_{M_b}}\, X_{M_a}}$$

where

$$X_{M_a} = \frac{[M_a]}{[M_a] + [M_b]} \quad \text{(in solution phase)}$$

$$\overline{X_{M_a}} = \frac{[\overline{M_a}]}{[\overline{M_a}] + [\overline{M_b}]} \quad \text{(in exchanger phase)}$$

(The terms C_K and $\overline{C_K}$ in the figures have almost the same meaning to the terms X_K and $\overline{X_K}$ in their nature).

There are thought to be two extreme conditions: one is that M_a is dominant and M_b is a small value, and the other is that M_b is dominant and M_a is a small value. This coefficient represents the adsorption selectivity under both conditions in the same way, and is a very convenient coefficient for industrial estimations to use. Kielland's coefficient and a Kielland plot, in which the coefficient is represented, have their main roles in this simulation.

CALCULATION PROCEDURE

The Kielland plot, which plays an important role in this simulation, was introduced from the plot of adsorption isotherms. The adsorption isotherm is one of the graphs indicating selectivity; the X axis represents the mol ratio of the ions under study in solution phase (C_K), and the Y axis represents the ratio in the exchanger phase ($\overline{C_K}$). This graph indicates the uptake selectivity for the potassium ions at the mol fraction in the solution. In the Kielland plot, ($\overline{C_K}$) and the logarithm of Kielland's coefficient are plotted on the X and Y axes, respectively. From this relationship, we obtained the adsorption selectivity corresponding to the potassium ion adsorption ratio in the exchanger phase. This graph enables expres-

sion of the selectivity as numerical data which can be used for calculation of the simulation.

The calculation procedure is described below in detail.

1. Dividing the adsorbent column into two imaginary plates

Firstly, the adsorbent column (or tower) is divided into imaginary plates. In general, there is a large difference between the top and the bottom of the column when a solution is passed through by downflow eluting. The concept of the ideal plates is considered to have some relation to flow rate, packing density of adsorbents, size of adsorbents, shape of columns, and equilibrium degree of the adsorption. From the approximation of experimental results, two imaginary plates are postulated.

2. Deciding the adsorption capacity of the column

The maximum adsorption capacity of CRYMO was measured by batch experiment. The capacity of CRYMO was measured as 1.1 [mmol/g] at pH 11; the capacity of the column was derived from the multiplication of the capacity and the weight of CRYMO adsorbent.

3. Defining the initial conditions of the adsorbent

The CRYMO adsorbent was synthesized as an H form which has the highest potential to exchange with potassium or sodium ions. At the start of effluting, all the cations in the effluent were adsorbed, and the conditions were defined as the initial conditions.

4. Calculation of the phenomena occurring on the first imaginary plate

The calculation was performed for the distributed effluent with the selectivity parameters deduced from the Kielland plot. From this calculation, the packed condition of the adsorbed potassium in the exchanger phase and the potassium concentrations in the effluent from the first imaginary plate are estimated. The packing condition data was applied to the next distributed effluent, a feedback method. The concentration data was then used in respect of the second imaginary plate.

5. Calculation of the phenomena occurring on the second imaginary plate

The calculation procedure was similar to that described for the first imaginary plate, the only being that the effluent in the second plate was the one determined by calculation.

6. Plotting the breakthrough curve from the result

The simulation of the breakthrough curve was plotted from the data calculated values of the potassium concentration from the second imaginary plate.

EXPERIMENTAL

Preparation of CRYMO

CRYMO was prepared in the same way as has been reported by Tsuji and Abe (1984). The preparation flow chart is shown in Fig. 1.

CRYMO was obtained as a colloidal black precipitate by mixing the aqueous solutions of manganous sulfate and potassium permanganate. The precipitate was washed and dried. After grinding and sieving, this material was pretreated with concentrated nitric acid before use. The prepared CRYMO showed a good agreement with the reference data of chemical composition, XRD and thermal analysis.

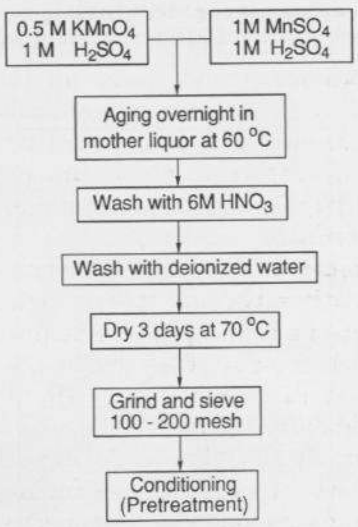

Fig. 1. CRYMO preparation.

Batch experiment

The adsorption isotherm and the Kielland plot of the CRYMO in the Na and K system were investigated by the equilibrium batch experiment.

CRYMO in 0.20 g portions were immersed in 10 ml of the solutions at 30°C. The solutions had different mol ratios of Na and K but the ionic strength was maintained at 1.0 and the terminative pH fixed at 10–11. After the adsorption equilibrium had been attained, the concentrations of Na and K in the supernatant solutions were measured by atomic absorption spectroscopy. From these data, the adsorption isotherm and the Kielland plot were drawn up. The adsorption isotherm and the Kielland plot are shown in Figs. 2 and 3, respectively.

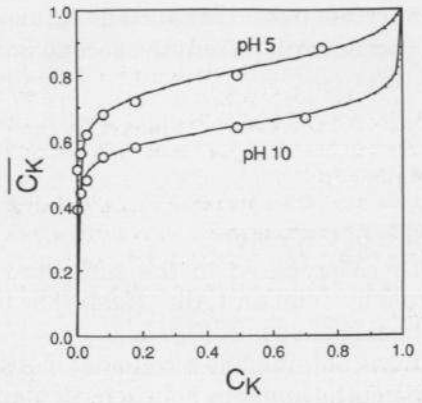

Fig. 2. Mol composition selectivity curve of CRYMO. X axis, C_K (equilibrium mol fraction in solution). Y axis, $\overline{C_K}$ (equilibrium mol fraction in adsorbent).

$$C_K = \frac{m_K}{m_{Na} + m_K}, \quad \overline{C_K} = \frac{\overline{m_K}}{\overline{m_{Na}} + \overline{m_K}}$$

(Barred symbol represents adsorbent phase).
Batch size: adsorbent, CRYMO (H type) 0.200 g, solution: ionic strength 1.0 10 ml.

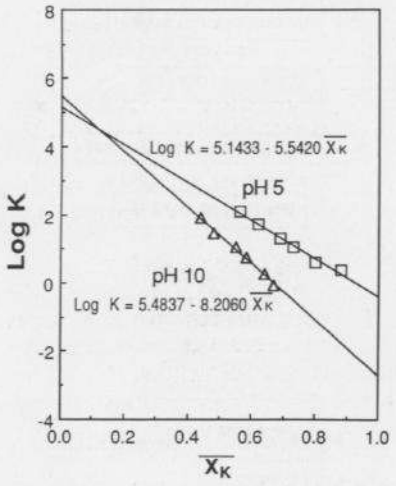

Fig. 3. Kielland plot of potassium and sodium ions on CRYMO. X axis, $\overline{X_K}$; Y axis, log K. Na and K selectivity by equilibrium batch technique. Conditions: adsorbent, CRYMO (H type) 0.200 g, solution, ionic strength 1.0 10 ml; temperature, 30°C.

Column experiment

The breakthrough experiment was performed in a column filled with the synthesized CRYMO of 6.5 x 0.5 cm i.d. The brine used as effluent was a solution of the solar salt made in Shark Bay (Australia). The brine was treated in advance by adding an equivalent amount of sodium hydroxide and sodium carbonate in order to exclude magnesium and calcium ions, respectively. This solution had concentrations of 5.09 M of sodium ion, 0.0024 M of potassium ion and pH 11. The flow rate was regulated to 0.5 ml/min by a high-pressure pump. The effluent was collected fractionally, and the sodium and potassium concentrations were measured by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The experimental results and the calculated results of the breakthrough curve are shown in Figs. 4 and 5, respectively. The experimental and calculated results were found to be in very good agreement. Therefore, the simulation procedure was judged appropriate. There were, however, certain points of difference between the experiment and the calculated results, i.e.:

(a) In the experiment, a final relative concentration of 1 was not achieved.

(b) The rise in the value of the relative concentration was much steeper compared with the calculated results.

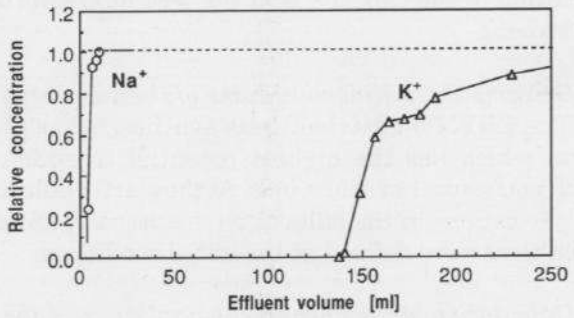

Fig. 4. Breakthrough of solar salt brine in the CRYMO column. X axis, effluent volume (ml); Y axis, relative concentration. Column size, 6.5 x 0.5 cm i.d.; absorbent, CRYMO H type mesh size 100 mm 0.9 g; flow rate, 0.5 ml/min; concentration, Na: 5.09 M, K: 0.0024 M (corresponds to relative concentration = 1).

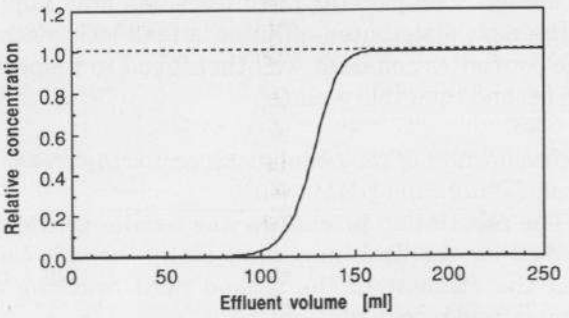

Fig. 5. Breakthrough simulation of potassium ion in solar salt brine in the CRYMO column. Simulation is founded on the same conditions as the breakthrough experiment

On the other hand, the rate-determining step is thought to be fixed by one of two situations.

1. A situation where the rate-determining step is dependent on the solid–liquid interface film dispersion: This situation occurs mainly at earlier stages because the adsorbent surface has enough potential to adsorb potassium ions.

2. A situation where the rate-determining step is determined by the inner solid dispersion: This situation occurs mainly at later stages because the surface is covered with potassium ions and so it is necessary for the inner part of the adsorbent to take up the remaining ions.

Discussion of difference (a)

This difference is thought to be related to situation 2 described above. In general, the rate of inner solid dispersion of inorganic ion exchangers is so gradual that it takes several weeks or months. In contrast, the contact time in the breakthrough experiment is very rapid and takes only a few minutes. However, the assumption in this simulation is that all the reactions reach equilibrium. However, it is impossible for inner solid dispersion to be achieved at equilibrium in these laboratory experiments. Therefore, as the inner solid dispersion remains in non-equilibrium during the column experiments, this is thought to be the reason for difference (a).

Discussion of the difference (b)

This difference is thought to arise from situation 1, described above. In view of the viscosity of the brine effluted, the small size of the column, the size of particles of adsorbent, and the slow rate of effluent, it is considered that the interface film dispersion attains approximate equilibrium. In general, the dispersion rate in the solid–liquid interface film is much more rapid for the ion exchange experimental time scale. There is no doubt that this step is thought to be equilibrated completely. This is thought to be the reason for difference (b).

In this simulation procedure, there are some problems to be solved. One is that the phenomenon of dispersion is not completely understood in the field of chemical engineering. Whatever the problems, we should endeavour to solve them and establish a more perfect procedure for this simulation. It is hoped that this simulation will contribute to the understanding of the industrial processes and chemical engineering involved.

CONCLUSION

The mathematical simulated breakthrough model of potassium extraction from high concentration and high sodium content solution is drawn up by using the Kielland's plot data analysis. This procedure will be a useful estimation for the separation industries.

REFERENCES

Abe, M. and Ito, T., 1965. The ion adsorption properties on insoluble hydrous oxides of tetra, penta and hepta valency metal. (4 ka, 5 ka oyobi 6 ka kinzoku genso no nan-yousei gansui sankabutsu no ion kyuuchaku sei.) Nippon Kagaku Zasshi, 86: 1259–1266. (in Japanese).

Abe, M. and Hayashi, K., 1983. Synthetic inorganic ion-exchangers XXXIII. Selectivities of alkali metal ions on tin(IV) antimonate cation-exchanger prepared at diferent conditions. Solvent Extrac. Ion Exchange, 1: 97–112.

Abe, M., Chitrakar, R., Tsuji, M. and Fukumoto, K., 1985. Synthetic inorganic ion-exchangers XXXIX. Synthesis of titanium(IV) antimonates and their ion exchange properties for alkali and alkaline earth metal ions. Solvent Extract. Ion Exchange, 3: 149–172.

Adams, B.A. and Holmes, E.L., 1935. Absorptive properties of synthetic resins. Part 1. J. Soc. Chem. Ind., 54: 1T–6T.

Gans, R., 1905. Zeolite und ähnliche Verbindungen, ihre Konstitution und Bedeutung für Technik und Landwirstschaft. Jahrbuch der Preussischen Geologischen Landesantalt zu Berlin, 26: 179–211.

Harada, K. and Yamori, K., 1967. Brine purification for the mercury cell process. Electrochem. Technol. 5 (3–4): 137–143.

Kielland, J., 1935. Thermodinamics of base-exchange equilibria of some different kinds of clays. J. Soc. Chem. Ind., 54: 232T–233T.

Kraus, K.A. and Phillips, H.O., 1956. Anion exchange studies. XIX Anion exchange properties of hydrous zirconium oxide. J. Am. Chem. Soc.,. 78: 249.

Kraus, K.A., Phillips, H.O., Carlson, T.A. and Johnson, J.S., 1958. Ion exchange properties of hydrous oxides. In: Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. 28: 3–16.

Tanaka, Y., Tanaka, Y., Tsuji, M. and Abe, M., 1991. Sodium–potassium separation by inorganic ion exchanger. I Potassium removal in the electrolytic soda process by cryptomelane-type hydrous manganese dioxide. (Muki ion koukantai ni yoru natoriumu to kariumu no bunri (dai 1 pou). Kuriputomeran gata gansuisanka mangan niyoru shokuen denkai koutei ni okeru kariumu no jokyo.) In: Proceeding of 42nd annual meeting of the Society of Sea Water Science, Japan. 7 pp. (in Japanese).

Thompson, H.S., 1850. On the absorbent power of soils. J. Roy. Agric. Soc. Engl., 11: 68–74.

Tsuji M. and Abe M., 1984. Synthetic inorganic ion-exchangers XXXVI. Synthesis of cryptomelane-type hydrous manganese dioxide as an ion-exchange material and their ion-exchange selectivities towards alkali and alkaline earth metal ions. Solvent Extrac. Ion Exchange, 2: 253–274.

Tsukamoto, T., 1978. Application of brine of high purity. (Koujundo ensui riyouhou.) Kokai Tokkyo Koho: 53–91151. (in Japanese).

Ueshima, H. and Kudo, T., 1978. Purification of brine for electrolysis. (Denkaiyou arukariensui no seiseihou.) Kokai Tokkyo Koho: 53–3998. (in Japanese).