Sodium Selective Ion-Exchange Properties of Zirconium Phosphate, $\text{HZr}_2(\text{PO}_4)_3$, and Its Application for the Removal of Sodium Ions

Yasushi NAKAJIMA* and Isao YOSHIDA**

**Daiichi Kigenso Kagaku Kogyo Co. Ltd.,
Hirabayashiminami, Suminoe, Osaka 559, Japan*

***Department of Industrial Chemistry, Kumamoto Institute of Technology,
Ikeda, Kumamoto 860, Japan*

Zirconium phosphate, $\text{HZr}_2(\text{PO}_4)_3$ (NZP), in a powder form was synthesized from zirconium chloride oxide and sodium dihydrogenphosphate, and its ion exchange adsorption properties to alkali metal ions were studied. The ion-exchange adsorption partition coefficients of NZP to alkali metal ions at $\text{pH}=3.4$ were found to be 3.2×10^3 (Li^+), 4.5×10^5 (Na^+), 2.6 (K^+), 12 (Rb^+), and 380 (Cs^+) $\text{cm}^3 \text{g}^{-1}$. The results indicate that NZP has a high adsorbability to sodium ions. Mixed granules of NZP and silica sol (NZP-P) were then prepared and applied for the selective removal of sodium ions by a column adsorption method.

Keywords Sodium selective ion exchange, zirconium phosphate

Sodium-free cesium sulfate, potassium chloride, and organic solvents are important in the following industrial areas. Cesium sulfate is used as a raw material for a catalyst, which has been employed for the synthesis of phthalic anhydride from naphthalene. This catalyst has a high thermal stability and activity, but a very small amount of sodium ion poisons the activity of the catalyst. Potassium hydroxide, which is applied to a wide variety of industrial purposes, is usually produced by the electrolysis of aqueous potassium chloride solutions, and is contaminated with sodium because the electrolytic behavior of sodium chloride is similar to that of potassium chloride. Sodium-free organic solvents are important as electrorheological fluids with a high insulation resistance. To produce sodium-free cesium and potassium salts and organic solvents, we have studied the removal of sodium by the ion-exchange adsorption method.

The ion-exchange adsorption selectivity of ion-exchange resins¹ for alkali metal ions decreases according to the following sequence: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. However, the selectivity difference is not large, and the selective separation of sodium ions from other ions by an ion-exchange resin is difficult. A variety of inorganic ion-exchange materials, which have a higher thermal- and chemical stability, have been synthesized, and their ion exchange properties have been studied. For example, zeolite² and metal ion hydroxides³ are known to be representative inorganic ion-exchange materials. Their cation exchange ability is similar to that of ion-

exchange resin, and the selective separation of sodium ion is also difficult. Phosphates of quadrivalent metal ions, for example hafnium phosphate⁴, titanium phosphate^{5,6} and zirconium phosphate⁷, are known to be functional inorganic ion-exchangers, and zirconium phosphate with a layered structure^{8,9} regarded as a selective ion-exchanger is used as a catalyst carrier and others. However, since the layer distance changes, depending upon the size of the incorporated ions, its selectivity is not necessarily high.

We have synthesized zirconium phosphate, $\text{HZr}_2(\text{PO}_4)_3$ (abbreviated as NZP)¹⁰, with a crystal structure having a 3-dimensional skeleton network (Fig. 1). The $\text{O}_3\text{ZrO}_3\text{HO}_3\text{ZrO}_3$ units are linked and bound together by PO_4 .¹¹ A structure change before and after ion exchange seems, therefore, hard to occur, the size of the micropores does not change, and it is expected to show strong selectivity to ions which can enter into the pores.

In this study we investigated the ion-exchange properties of NZP for alkali metal ions. It was shown that this ion-exchange material is strongly selective to sodium ions. Further, we have prepared granules of NZP (NZP-P) to apply for the selective separation of sodium ions from other alkali metal ions with an NZP-P column.

Experimental

Reagents and solutions

Ten thousand ppm alkali metal ion standard solution. Chlo-

rides of alkali metals (Wako Pure Chemical Industries, Ltd.) were dried by heating at 110°C for 3 h, and each salt was weighed to obtain 1000 mg of alkali metal ions, and dissolved in deionized water to 1000 cm³. The standard solutions were diluted with water to concentrations for experiments.

Synthesis of zirconium phosphate (NZP). Octahydrate of zirconium chloride oxide (35.3 g) containing 10 g Zr was dissolved in 100 cm³ of deionized water, 20 cm³ of a 10% hydrofluoric acid solution and 100 cm³ sodium dihydrogenphosphate solution (5.0 g as P) were added; the solution was refluxed at 110°C for 2 weeks. The formed precipitate was collected by filtration, shaken with 100 cm³ of 3 M (1 M=1 mol dm⁻³) hydrochloric acid for 24 h, again collected by filtration, and washed with water. Then, it was heated at 600°C for one hour to obtain 23.5 g of NZP in powder form.

Preparation of granular zirconium phosphate (NZP-P). One hundred grams of NZP were mixed with 40 g of 30% silica sol and made into spherical granules (NZP-P) by Marumerizer (Fuji Paudal Co., Ltd.). The yield of the product was 33.0 g.

Adsorption tests

Batch method. The NZP or NZP-P (0.1–1.0 g) was put in 100 cm³ of 100 ppm–1000 ppm alkali metal ion solutions, and the suspensions were stirred at 25°C for 24 h. After a given time, NZP was removed by filtration; the amount of alkali metal ions remaining in the filtrate was then measured by atomic absorption spectrometry. The amount of adsorbed ions was obtained as a difference between the amount of ions added and that remaining in the solution. For NZP-P, a portion of the water phase was taken out, filtered, and the alkali metal ion concentrations were measured. The pH of aqueous phase was measured to see the effect of the pH on the ion exchange.

Column method. Ten grams of NZP-P were filled in a column (1.0 cm diameter, 30 cm length), through which either solutions containing various alkali metal ions (1000 ppm of Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺) or model solutions of cesium sulfate and potassium chloride were passed at a flow rate of 1 cm min⁻¹. The effluent was fractioned every 10 min, and its alkali metal ion content was measured.

Instruments

The pH was measured by an F-22 pH-meter (Horiba Ltd.). The alkali metal ion concentration was measured by a Z-6000 atomic absorption photometer (Hitachi Ltd.). The XRD pattern of NZP was obtained by a powder X-ray diffractometer (RINT 2220, Rigaku Ltd.).

Results and Discussion

Physical properties of zirconium phosphate

The XRD pattern of NZP, obtained by a powder X-ray diffractometer with a Cu tube bulb under a rated voltage

Fig. 1 Crystal structure of zirconium phosphate, NZP. Z: Zr, P: P, M: M⁺. A: micro pore.

of 60 kV and a rated current of 30 mA. The results agreed with JCPDS Card 38-4, showing a "Nasicon" type structure. The lattice constants are $a=8.792$ Å, $b=8.792$ Å, $c=22.91$ Å, $\alpha=90.00^\circ$, $\beta=90.00^\circ$, $\gamma=120.00^\circ$. The crystal structure is hexagonal, and the pore diameter is 2.6 Å.

Figure 1 shows a model structure of NZP; Z and P indicate the ZrO₆ octahedron and the PO₄ tetrahedron, respectively. NZP has a 3-dimensional skeleton crystal network structure and seems not to change upon an ion exchange. In fact, the XRD pattern of NZP did not change before and after an ion exchange. The pore diameter, expressed by A in the figure, is 2.6 Å, which could give a sieve type effect, resulting in strong selectivity to ions which can enter into the pores. Since NZP-P showed a similar XRD pattern as that of NZP, it is likely that the crystal structure shown in Fig. 1 remains unchanged after granulation.

Thermal balance and differential thermal analyses (TAS100, TG8110, DSC8230: made by Rigaku) of NZP were performed from room temperature to 1000°C. Up to 850°C no weight change or endo- or exothermic heat capacity change was observed.

The specific surface area and pore-size distribution of the adsorbent sample were measured by the B.E.T. method using helium and an instrument for specific surface area and pore size distribution measurements (Autosorb-1 made by Cantachrom). The pore size of NZP was 2.8 Å, agreeing with that obtained from the crystal structure (2.6 Å). The specific surface area of NZP was 3.7 m² g⁻¹ and that of NZP-P was 0.78 m² g⁻¹, ca. 1/5 of that of NZP. The decrease in the specific surface area of NZP-P can be ascribed to the influence of granulation.

Adsorption rate and capacity for sodium ion

The effect of time on the adsorption of sodium ions by NZP and NZP-P was studied. One gram of adsorbent and 100 cm³ of a 1000 ppm-Na solution were mixed, and

Fig. 2 Adsorption rate of Na^+ by NZP and NZP-P at 25°C . Volume of Na^+ soln.: 100 cm^3 . pH of Na^+ soln.: 4–5. Initial conc. of Na^+ : 1000 ppm. Adsorption material: $\circ$, NZP; $\triangle$, NZP-P. Amount of adsorbent: 1.0 g.

then stirred in a conical flask dipped in water at 25°C . At time intervals a part of the suspension was taken, and the solid phase was separated by filtration; then, the concentration of sodium ion remaining in solution was measured. The amount of sodium ion adsorbed was calculated (Fig. 2). It can be seen that the adsorption reaction of sodium ions by NZP reaches an equilibrium in *ca.* 3 h and adsorption capacity is 45.7 mg g^{-1} (1.99 meq g^{-1}). The time necessary to reach equilibrium can be that necessary for sodium ions to diffuse in the adsorbent, because the size of the NZP pore is almost the same as that of sodium ions. For NZP-P equilibrium is reached in *ca.* 2 h, and the adsorption capacity is 24.4 mg g^{-1} (1.06 meq g^{-1}), *ca.* 1/2 of that of NZP. The decrease in the adsorption capacity of NZP-P may be due to a decrease in specific surface area.

Comparison of adsorption affinities of alkali metal ions

One hundred cubic centimeters of the mixture solution of $1.0 \times 10^{-3}\text{ M}$ alkali metal ions were mixed with 0.1 g of NZP in a 200 cm^3 conical flask dipped in water at 25°C , and stirred for 24 h. At time intervals, a portion of the suspension was taken, NZP was removed by filtration, and the concentration of each alkali metal ion remaining in the filtrate was measured. The adsorption partition coefficient, K_d , for each metal ion was obtained and the separation coefficient, α , between neighboring alkali metal ions are shown in Table 1. The partition coefficient $4.5 \times 10^5\text{ cm}^3\text{ g}^{-1}$ for sodium ion is the largest, and is substantially larger than the next largest value of $3.2 \times 10^3\text{ cm}^3\text{ g}^{-1}$ for the lithium ion. The K_d value decreases in the order of cesium, rubidium and potassium ions, and the α value between sodium ion and lithium ion is 1.4×10^2 .

Next, the ability of NZP-P to adsorb alkali metal ions was studied in a similar way at 25, 40, 60 and 80°C . The partition coefficient K_d at 24 h was obtained, and the

Table 1 Partition coefficient, K_d , and separation coefficient, α , of alkali metal ions in the ion-exchange adsorption with NZP at 25°C and $\text{pH}=3.4$

Metal ion	$K_d/\text{cm}^3\text{ g}^{-1}$	α
K^+	2.6	4.6
Rb^+	12	32
Cs^+	3.8×10^2	8.4
Li^+	3.2×10^3	140
Na^+	4.5×10^5	

Initial conc. of metal ions: $1.0 \times 10^{-3}\text{ M}$.

Volume of solution: 100 cm^3 .

NZP: 0.1 g.

Fig. 3 Partition coefficient, K_d , of alkali metal ions with NZP-P at various temperature and $\text{pH}=4-5$. Initial metal ion conc.: $1.0 \times 10^{-3}\text{ M}$. Volume of Na^+ soln.: 100 cm^3 . NZP-P: 0.1 g.

results are shown in Fig. 3 as a function of the temperature. The K_d for the sodium ion is constant at $4.8 \times 10^4\text{ cm}^3\text{ g}^{-1}$ between 25 and 80°C . It is seen that the K_d values for other metal ions are also independent of the temperature. K_d for the sodium ion is substantially larger than the next largest value for the lithium ion. The separation coefficient α between sodium and lithium ions is 1.3×10^2 , as large as that of NZP. The K_d de-

creases in the order of cesium, rubidium and potassium ions. From the K_d and α values it is clear that granulated NZP-P has similar alkali metal ion adsorption properties as those of powder NZP. NZP-P may also be applied to separate sodium ions from other alkali metal ions, because its K_d is far larger than the other ions and almost independent of the adsorption temperature.

Adsorption isotherm for sodium ion

The adsorption isotherm for sodium ions on NZP was obtained by a batch method. Sodium chloride solutions with six different concentrations from 100 ppb- Na^+ to 10000 ppm- Na^+ were prepared by dissolving 254 mg of sodium chloride in water with different volumes of 10 cm^3 to 1 m^3 . To these solutions 1.0 g NZP was added, and stirred for 24 h; the suspension was then filtered, and the concentration of the sodium ions remaining in the filtrate was measured. A plot of adsorption capacity, Q , vs. the equilibrium concentration, C , obeyed Freundlich's adsorption isotherm, $Q=KC^{1/n}$ (Fig. 4). The values for $1/n$ and K were obtained as 1.37×10^{-2} and 42 mg g^{-1} , respectively, from the straight line in Fig. 4.

Effect of the pH on the adsorption capacity for sodium ions

The effect of the pH on the adsorption capacity of NZP for the sodium ion was studied by a batch method in the presence of an excess of sodium ions using aqueous solutions with various pH values adjusted with hydrochloric acid and potassium hydroxide. One gram of NZP was put in 100 cm^3 of a sodium chloride solution containing 100 mg-Na^+ ; the suspension was then stirred for 24 h at 25°C . After separating the solid phase, the concentration of sodium ions remaining in the filtrate and the pH were measured. The results are shown in Fig. 5. The adsorption capacity for the sodium ion is virtually independent of the pH, from pH 1 to 11. This result indicates that NZP with P-OH as a functional group is a strong acid cation exchanger and can adsorb sodium ions even in the presence of a large excess amount of hydrogen and potassium ions. As the acidity strength of NZP, a $\text{p}K_a$ of -4.3 was obtained by the Benesi method using Hammett indicators.¹² In neutral and alkaline solutions, NZP takes up sodium ion leaving potassium chloride in the solution, as shown in Eq. (1)

where $\text{RH}_{(\text{s})}$ and $\text{RN}_{(\text{s})}$ are the solid NZP before and after ion exchange.

Adsorption of sodium ion by column method

Ten grams of NZP-P were filled in a column with a 1 cm inner diameter and 30 cm length. One hundred cubic centimeters of a sodium chloride solution containing 100 ppm-Na^+ at various pH values, adjusted with hydrochloric acid and potassium hydroxide, were passed through at flow rates of 1, 3 and $5\text{ cm}^3\text{ min}^{-1}$. The amount of adsorption was obtained by measuring the

Fig. 4 Adsorption isotherm for Na^+ by NZP at 25°C . NZP: 1.0 g.

Fig. 5 Effect of the pH on the adsorption of sodium ions at 25°C . Volume of Na^+ soln.: 100 cm^3 . Initial conc. of Na^+ : 1000 ppm . Amount of adsorbent: 1.0 g-NZP .

sodium ion concentration in the effluent, and is plotted against the pH of the sample solution in Fig. 6. It can be seen that this column quantitatively adsorbs sodium ions irrespective of the pH in the pH range 1–11 at a flow rate of $1\text{ cm}^3\text{ min}^{-1}$. At higher flow rates of $3\text{ cm}^3\text{ min}^{-1}$ and $5\text{ cm}^3\text{ min}^{-1}$, however, the amount of adsorption slightly decreases with decreasing pH at pH lower than 5. This means that the adsorption rate of NZP-P for sodium ions is influenced by the coexisting hydrogen ions. The contraction in the volume of silica gel covering NZP of NZP-P occurs by hydrogen ions in an acidic solution.

Fig. 6 Effect of the pH and flow rate on the adsorption of Na^+ with NZP-P. Column: 1.0 cm in diameter, 30 cm in length. Conc. of Na^+ sample soln.: 100 ppm. Volume of Na^+ soln. passed: 100 cm^3 . NZP-P: 10 g.

This may decrease the mobility of sodium ions and the effective surface of NZP-P in the solid phase, resulting in a decrease in adsorption, when the reaction time is shorter at a higher flow rate.

Adsorption of alkali metal ion by column method

Ten grams of NZP-P was packed in a glass column with 1.0 cm inner diameter and 30 cm length. Through the column 1000 ppm of each alkali metal ion solution was passed at $1 \text{ cm}^3 \text{ min}^{-1}$. Figure 7 shows the measured concentration of alkali metal ions in the effluent against time. Sodium ions are adsorbed almost completely in *ca.* 3 h, that is *ca.* 180 cm^3 . The lithium ions are adsorbed slightly at the beginning, but come out quite early. Potassium, rubidium and cesium ions come out almost without being adsorbed. As a result, within 3 h quantitative removal of sodium from the other ions is possible. After 3 h sodium ions gradually come out. However even after *ca.* 15 h the effluent concentration is lower than the sample concentration, indicating that sodium ions were still partially adsorbed in this region. The selectivity of NZP-P to sodium and lithium ions may be ascribed to micro pores in which only sodium and lithium ions can enter. However the shorter retention of lithium than sodium ion, suggests that lithium is larger than sodium ion. It is likely that adsorbed lithium ion is not be completely dehydrated due to its strong hydration, and its hydrated radius is larger than that of sodium ion.

Recovery of sodium ion

One hundred cubic centimeters of various eluants shown in Table 2 were added to 10 g NZP-P on which 100 mg sodium ion were adsorbed, and the suspensions were stirred at 25°C for 24 h. The sodium ion concentration was measured to obtain the recovery ratio; the results are

Fig. 7 Elution curves for alkali metal ions from the NZP-P column. Column: 1.0 cm in diameter, 30 cm in length. Flow rate: $1 \text{ cm}^3 \text{ min}^{-1}$. Metal ion conc. of sample soln.: 1000 ppm. NZP-P: 10 g.

Table 2 Effects of eluants on the recovery of Na^+ on NZP-P

Eluant	Recovery, %
1 M HCl	78
2 M HCl	80
3 M HCl	93
1 M HNO_3	65
2 M HNO_3	78
3 M HNO_3	89
1 M HCl-1 M NH_4Cl	81
1 M HCl-2 M NH_4Cl	87
1 M HCl-3 M NH_4Cl	96
1 M HCl-1 M NH_4NO_3	89
1 M HCl-2 M NH_4NO_3	96
1 M HCl-3 M NH_4NO_3	100
2 M HCl-1 M NH_4Cl	100
2 M HCl-1 M NH_4NO_3	101

Na^+ adsorbed on NZP-P: 100 mg Na^+ /NZP-P 10 g.
Reaction time: 24 h.

shown in Table 2. With 1–3 M hydrochloric acid and nitric acid, the recovery % increased with the acid concentration, reaching 93% with 3 M HCl. However, with a mixture of 1–3 M ammonium chloride or nitrate and 1–2 M hydrochloric acid, the recovery % is larger, and 100% was attained with 1 M HCl-3 M NH_4NO_3 , 2 M HCl-1 M NH_4Cl , 2 M HCl-1 M NH_4NO_3 . Thus, 2 M HCl-1 M NH_4NO_3 was chosen as the eluant for recovering sodium ions with the NZP-P column. The recovery ratios of sodium ions from a column containing 100 mg sodium ion/10 g NZP-P, are listed in Table 3 for a given eluant volume and flow rate. At eluant volumes of over 200 cm^3 the recovery is almost quantitative for a flow rate of $3 \text{ cm}^3 \text{ min}^{-1}$. For optimum NZP-P column separation, the eluant is a 2 M HCl-1 M NH_4NO_3 mixed solution, and the flow rate is $3 \text{ cm}^3 \text{ min}^{-1}$.

Table 3 Effects of the eluant volume and flow rate on the recovery of Na⁺ in an NZP-P column at 25°C

Eluant vol./cm ³	Flow rate/cm ³ min ⁻¹	Recovery, %
100	1	98
100	3	95
100	5	89
200	1	101
200	3	100
200	5	98
300	1	101
300	3	100
300	5	100

Eluant: 2 M HCl-1 M NH₄NO₃.Na⁺ adsorbed on NZP-P: 100 mg-Na⁺/NZP-P 10 g.Table 4 Purification of Cs₂SO₄ and KCl by removing Na⁺ with the NZP-P column method at 25°C

Sample soln.	Ion	Before purification	After purification
Cs ₂ SO ₄	Cs ⁺	3.1%	3.1%
	Na ⁺	95 ppm	0.2 ppm
KCl	K ⁺	10.3%	9.8%
	Na ⁺	100 ppm	0.7 ppm

NZP-P: 10 g.

Flow rate: 1 cm³ min⁻¹.*Removal of a very small amount of sodium ions from cesium sulfate and potassium chloride by the NZP-P column method*

One thousand cubic centimeters of a sample aqueous solution containing 3.1% cesium and 95 ppm sodium ion was prepared by dissolving cesium sulfate and sodium chloride in water. This sample solution was passed through a column containing 10 g NZP-P at a flow rate of 1 cm³ min⁻¹. The concentration of metal ions in the effluent was 3.1% for cesium ions and 0.2 ppm for sodium ions, as shown in Table 4. This means that 99.8% of the sodium ion was removed by adsorption, while no cesium ions were adsorbed.

Removal of sodium ions from potassium chloride by a NZP-P column was performed; the results are given in Table 4. After passing a mixture solution of 10.3% potassium and 100 ppm sodium, the effluent contained 9.8% potassium and 0.7 ppm sodium, indicating that 99.3% of sodium in the sample solution was removed.

Removal of sodium ions in an organic solvent by a batch method

The removal of sodium ions in various organic solvents by NZP-P was studied. The sample organic solvents were prepared by dissolving 0.0127 g of sodium chloride

Table 5 Purification of organic solvents by removing Na⁺ with NZP-P at 20°C for 24 h

Organic solvent	Na ⁺ found in eluant/μg	Na ⁺ adsorbed by NZP-P, %
Methanol	30	100
Ethanol	29	98
1,2-Dihydroxyethane	29	98
Toluene	29	98

Na⁺ in sample solvent: 30 μg.Sample volume: 300 cm³.

NZP-P: 3.0 g.

in 500 cm³ of solvents, then by diluting them to 300 times (100 ppb-Na). Three grams of NZP-P and 300 cm³ of the sample organic solvents containing 30 μg of sodium ion were mixed and stirred for 24 h at 20°C in a 500 cm³ Erlenmeyer flask. After filtration, the collected NZP-P was added into a 100 cm³ of 2 M HCl-1 M NH₄NO₃ mixture solution as an eluant, and stirred at 25°C for 24 h. The sodium ion concentration in the eluant was measured to obtain the amount of adsorption by NZP-P; the results are given in Table 5. The amount of sodium ion in the eluants was larger than 98%, indicating that NZP-P can adsorb sodium ion in various organic solvents. This suggests that NZP-P can be used to remove sodium ions in organic solvents, to which ion-exchange resins are difficult to apply.

References

1. J. Lehto, A. Paajanen, R. Harjula and H. Leinonen, *React. Polym.*, **23**, 135 (1994).
2. T. Nabarawy and S. E. Samra, *Adsorption Sci. Technol.*, **11**, 51 (1994).
3. N. Z. Misak, H. B. Maghrawy and I. M. Elnaggar, *Solid State Ionics*, **37**, 1 (1989).
4. I. Tomita, K. Magami and H. Watanabe, K. Suzuki and T. Nakamura, *Bull. Chem. Soc. Jpn.*, **56**, 3183 (1983).
5. R. Llavona, J. R. Garcia, C. Alvarez, M. Suarez and J. Rodriguez, *Solvent Extr. Ion. Exch.*, **4**, 567 (1986).
6. S. Komarneni and R. Roy, *Adv. Ceram.*, **20**, 207 (1986).
7. E. Torracca, *J. Inorg. Nucl. Chem.*, **31**, 1189 (1969).
8. L. Kullberg and A. Clearfield, *J. Inorg. Nucl. Chem.*, **43**, 2543 (1981).
9. N. Z. Misak and E. M. Mikhail, *Z. Phys. Chem.*, **264**, 995 (1983).
10. K. Ito, T. Suzuki, M. Kawaguchi and M. Oda, *Adv. Ceram.*, **24**, 1007 (1988).
11. A. Clearfield, *Solid State Ionics*, **46**, 35 (1991).
12. H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

(Received May 9, 1996)

(Accepted October 1, 1996)