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Temperature Dependence of Adsorption of Caesium Ions on Crystalline Hydrous Titanium Dioxide Fibers

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Synopsis. The distribution coefficient of caesium ions, K_d, measured as a function of pH at 25—100 °C, decreased with increasing temperature. Enthalpy change of the adsorption of Cs^+ on $H_2Ti_4O_9 \cdot nH_2O$ estimated from the plot of $\log K_d$ vs. T^{-1} in the range of 25—85 °C was −4.6 kcal mol^{-1}. Above 95 °C, K_d values were lower than those extraporated from the plot due to a decrease in the crystallinity of the fibers.

We have worked to develop the techniques to recover caesium ions from geothermal brine and suitable inorganic adsorbents have been investigated by revealing adsorption behavior of caesium ions in hot water.[1] The adsorbents for caesium ions in geothermal brine need selectivity for the ions and hydrothermal stability. It is known that crystalline hydrous titanium dioxide fibers, $H_2Ti_4O_9 \cdot nH_2O$, have high selectivity for caesium ions and that the distribution coefficient for alkali metal ions in weak acid solution at 25 °C increases in the order: Li<Na≪K, Rb<Cs.[2]

The present paper deals with the adsorption of caesium ions on the fibers. The distribution coefficient of caesium ions was measured as a function of pH at 25—100 °C and the enthalpy change was estimated; in addition, X-ray powder diffractometry was done for checking the structural change of fibers.

Experimental

The hydrous titanium dioxide fibers ($H_2Ti_4O_9 \cdot nH_2O$) were prepared by acid treatment of $K_2Ti_4O_9$.[3,4] Adsorption experiments were carried out in batchwise operations in a water bath thermostated at temperatures between 25 and 100 °C.

Glass ampules of 20 cm^3 capacity were used to obtain equilibrium between the solid (0.05 g) and the aqueous solution (10 cm^3) containing caesium ions. The initial concentration of caesium choride was 1 mmol dm^{-3}, and pH was adjusted with hydrochloric acid. The glass ampules were kept in the water bath, and shaken gently at intervals . The reaction time was 7 d, when the equilibrium was sufficiently attained, and then the fibers were separated by a membrane filter with 0.45 µm pores.

The concentration of caesium ions in the aqueous solution was determined by a Hitachi Z-6000 polarized Zeeman atomic absorption spectrophotometer. The pH of the solution was measured by a TOA HM5ES pH meter equipped with GS-5015C pH combination electrode. X-Ray powder patterns were obtained by a Rigaku Denki RAD-IIB diffractometer with Cu $K\alpha$ radiation.

Results and Discussion

The distribution coefficient, K_d, was calculated as

$$K_d = (C_1/\mathrm{g})/(C_2/\mathrm{cm}^3), \tag{1}$$

where C_1 is the amount of adsorbed caesium ions per 1 g of the solid, and C_2 is the concentration of caesium ions per 1 cm^3 of the aqueous solution.

Figure 1 gives the plot of $\log K_d$ vs. pH in aqueous phase for six different temperatures. As the temperature was increased, the $\log K_d$–pH lines shifted downward. The slope of $\log K_d$–pH lines was about +1 except for that at 100 °C. The adsorption of caesium ions on the fibers, therefore, can be represented by an ion-exchange reaction formula:[3]

$$\mathrm{H(s)} + \mathrm{Cs^+(aq)} = \mathrm{Cs(s)} + \mathrm{H^+\,(aq)}, \tag{2}$$

where the subscripts "s" and "aq" denote the solid and aqueous phase respectively. The equilibrium constant, K_c, of Eq. 2 is defined as

$$K_c = [\mathrm{Cs(s)}][\mathrm{H(aq)}]/[\mathrm{Cs(aq)}][\mathrm{H(s)}]. \tag{3}$$

K_c is rewritten as Eq. 4 using K_d:

$$\log K_c = \log K_d - \mathrm{pH} + \mathrm{const.} \tag{4}$$

If the K_d values for different temperatures are compared at identical pH, the enthalpy change of Cs–H ion-exchange reaction can be estimated from $\log K_d$ vs. T^{-1} plot.

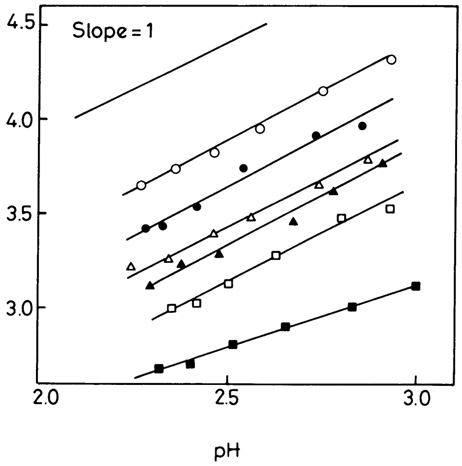

Fig. 1. Distribution coefficients of caesium ions as a function of pH in the aqueous phase at various temperatures. The ion exchanger is 0.05 g of $H_2Ti_4O_9 \cdot nH_2O$. The aqueous solution is 10 cm^3 of hydrochloric acid solution with an initial caesium concentration of 1×10^{-3} mol dm^{-3}. Temperature is (○): 25 °C, (●): 50 °C, (△): 75 °C, (▲): 85 °C, (□): 95 °C, (■): 100 °C.

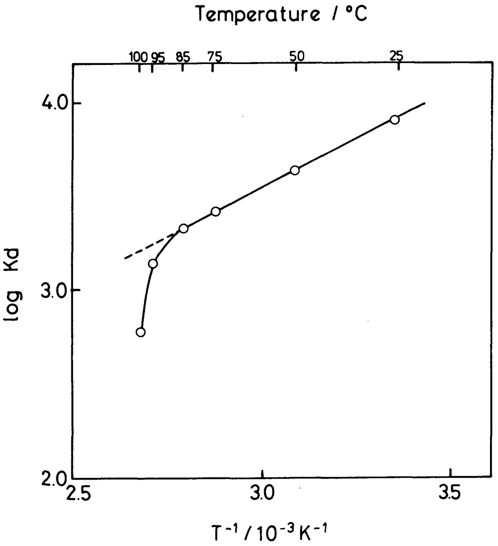

Fig. 2. Distribution coefficients of caesium ions at pH=2.5 in the aqueous phase as a function of temperature.

Figure 2 gives the plot of log K_d vs. T^{-1} at pH 2.5. The log K_d values were on a straight line in the range 25 to 85 °C as expected when enthalpy change (ΔH) is constant. And from the slope of the line, ΔH is obtained by Eq. 5:

$$\Delta H = -2.303\, R\, \mathrm{d}\log K_d/\mathrm{d}\,(1/T), \tag{5}$$

where T is the absolute temperature, and R is the gas constant.[5] The ΔH estimated from Fig. 2 in the range between 25 and 85 °C was -4.6 kcal mol^{-1}. Kraus et al. reported that the enthalpy change of ion exchange reaction between caesium ions and protons on a cation-exchange resin was -3.4 kcal mol^{-1} at 25 °C.[5] Although the enthalpy change values of the both cases are somewhat different, uni-uni valent ion exchange such as proton and caesium ion is supposed to be an exothermic reaction, irrespective of inorganic and organic ion exchangers.[6]

As shown in Fig. 2, K_d values at 95 and 100 °C were lower than those extraporated from the plot. Figure 3 gives the X-ray powder diffraction patterns of the solid treated with caesium solution at temperatures between 50 and 100 °C. The layered structure of the fibers is characterized by very strong (200) reflection with an interplanar spacing, $d(200)$, of ca. 9.1 Å.[7]

The fibers treated at temperatures below 95 °C showed almost similar diffraction patterns to those of the original fibers. This fact indicates that the structure of the fibers remains unchanged below 95 °C. Above 95 °C, however, the fibers converted into the poorly crystallized phase with an interlayer distance smaller than that of the crystalline fibers. This result agrees with that reported by Komatsu et al. in the case of adsorption of cobalt ions.[4] Consequently, the K_d value of caesium ions must be influenced only by the exothermic reaction below 95 °C. Above 95 °C, the structural change of the fibers causes the decrease of K_d in addition to the temperature effect as an exothermic reaction.

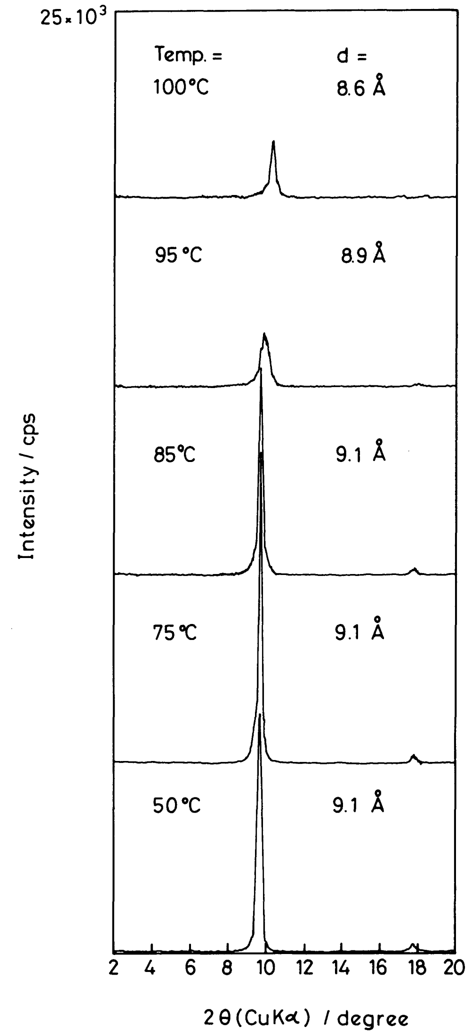

Fig. 3. X-Ray powder diffraction patterns of the solid samples treated with aqueous solutions at various temperatures.

Accordingly, the desired temperature should be below 95 °C when the fibers is utilized for an adsorbent for caesium ions from geothermal brine.

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