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Adsorption of Cobalt(II) Ions on Crystalline Hydrous Titanium Dioxide Fibers at 298 to 423 K

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The distribution of cobalt(II) ions between crystalline hydrous titanium dioxide fibers and aqueous solutions has been investigated. The adsorption behavior of cobalt(II) ions is explained in terms of their ion exchange with hydrogen-ions in the fibers. The distribution coefficients of cobalt(II) ions, K_d, increased with increasing temperature at 298—373 K. Slopes of the plots of log K_d vs. pH for 398—423 K were ca. +1.6, which was somewhat lower than those for 298—373 K: +2.0. X-Ray powder diffraction patterns indicate that the fibers hold a layer structure up to 373 K but change to anatase or its precursor above this temperature.

Many papers have been published on the treatment of radioactive wastes with inorganic ion exchangers.[1—3] The previous work in this laboratory has demonstrated that crystalline hydrous titanium dioxide fibers, $H_2Ti_4O_9 \cdot nH_2O$,[4] adsorb alkali metal ions,[5] alkaline earth metal ions,[6] and divalent transition metal ions[7] in weak acid solutions at 298 K. The logarithm of distribution coefficient, log K_d, for each metal ion increases proportionally with the pH of the aqueous phase if the concentration of hydrogen ions in the solid phase is kept substantially constant.

Removal of cobalt(II) ions from cooling water is indispensable for safe operation in an atomic power plant. The present paper deals with the adsorption of cobalt(II) ions on the hydrous titanium dioxide fibers. Distribution coefficients of cobalt(II) ions were measured as a function of pH at 298—423 K; in addition, X-ray powder diffractometry was performed to obtain information about the chemical and structural changes of the solid phase.

Experimental

Titanium dioxide used was of 99.9% purity. Distilled and deionized water was used throughout this work. All the other reagents were of analytical grade.

Crystalline potassium tetratitanate fibers, $K_2Ti_4O_9$, were synthesized by a flux method.[4] The average size of the fibers was 1 mm in length and 0.01 mm in diameter.

Figure 1 shows the flow sheet of a process for synthesizing crystalline hydrous titanium dioxide fibers. About 15 g portion of the fibers was filled in a glass column with an inner diameter of 25 mm, and washed with 20 dm³ of water to remove residual K_2MoO_4. Subsequently, 1 mol dm⁻³ hydrochloric acid was passed through the column to convert $K_2Ti_4O_9$ into an H⁺ form according to the reaction:

$$K_2Ti_4O_9 + nH_2O + 2H^+ \rightarrow H_2Ti_4O_9 \cdot nH_2O + 2K^+. \quad (1)$$

The fibers were treated with the acid solution until the concentration of potassium ions in the effluent became less than 1×10^{-5} mol dm⁻³. Potassium concentrations were measured by atomic absorption spectrophotometry. The resulting product was washed with water and dried over a saturated NaCl solution (relative humidity: 70%) to a constant weight.

Aqueous standard solutions of cobalt(II) ions were prepared by dissolving cobalt(II) chloride in water. The concentration of cobalt(II) ions was determined by EDTA titration.

Figure 2 gives the flow sheet of adsorption measurement of cobalt(II) ions on the fibers. Adsorption experiments were carried out in batchwise operations in an aluminium box thermostated at temperatures between 298 and 423 K. Twenty-cm³ stoppered glass tubes (298—373 K) or teflon tubes (398—423 K) were used to equilibrate the solid (0.1 g) with the aqueous solutions (10 cm³) containing cobalt(II) ions. The Teflon tubes were covered with an aluminium block to seal them tightly (Fig. 3). The initial concentration of cobalt(II) chloride was 1×10^{-4} mol dm⁻³,

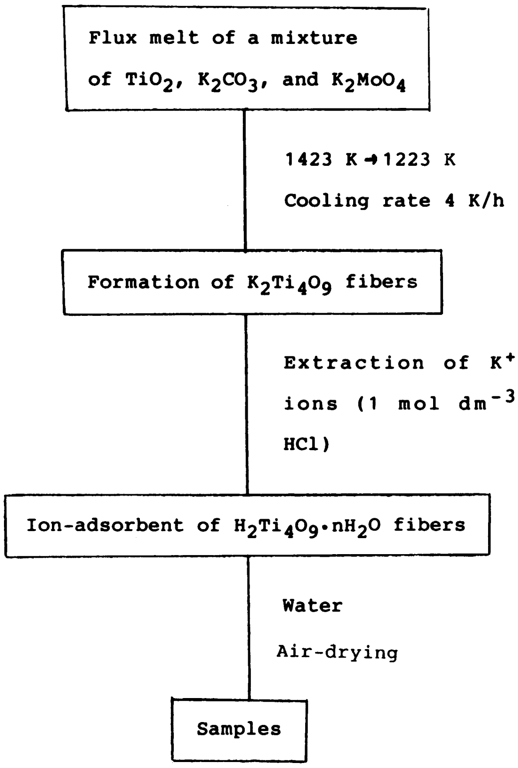

Fig. 1. Flow sheet of a process for synthesizing crystalline hydrous titanium dioxide fibers.

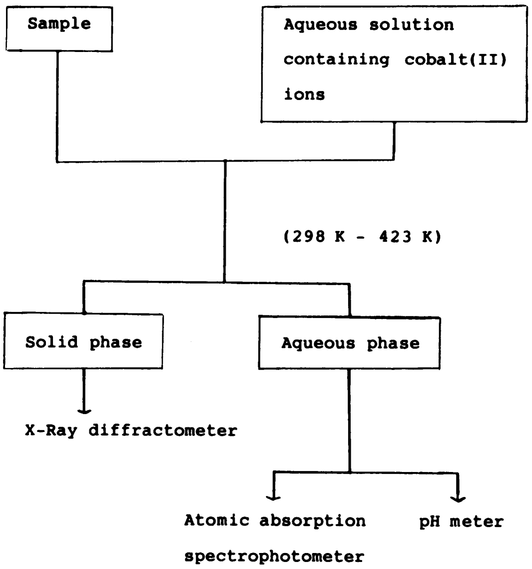

Fig. 2. Flow sheet of adsorption of cobalt(II) ions on the crystalline hydrous titanium dioxide fibers.

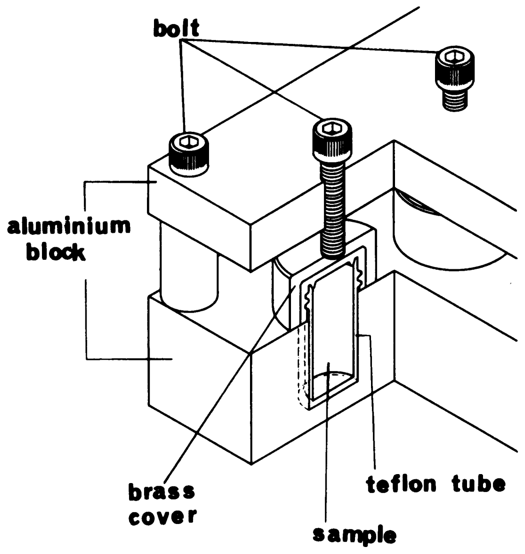

Fig. 3. Schematic diagram of the apparatus for ion exchange.

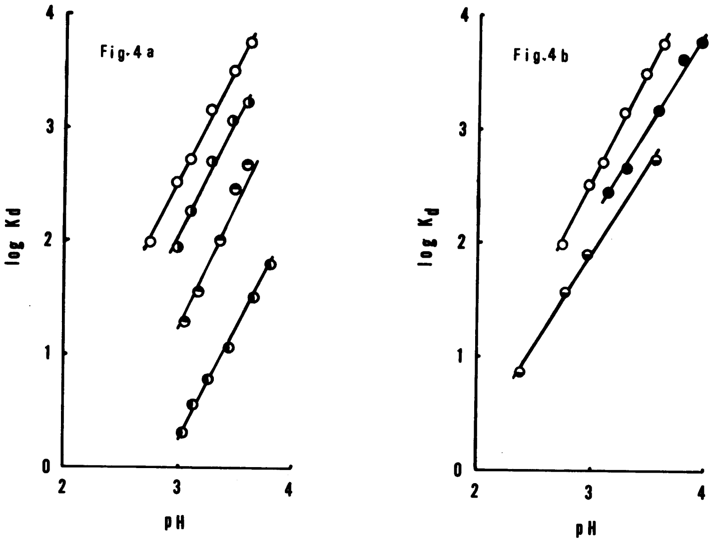

Fig. 4. Distribution coefficients of cobalt(II) ions as a function of pH in the aqueous phase at various temperatures.

The ion exchanger is 0.1 g of $H_2Ti_4O_9 \cdot nH_2O$. The aqueous solution is 10 cm^3 of hydrochloric acid solution with an initial cobalt(II) concentration of 1×10^{-4} mol dm^{-3}. Fig. 4a (◐: 298 K, ◓: 323 K, ◑: 348 K, and ○: 373 K). Fig. 4b (○: 373 K, ●: 398 K, and ◒: 423 K).

and the pH was adjusted with hydrochloric acid. The glass or teflon tubes were kept in the thermostated box, and shaken gently by hand once 1 d. The reaction times were 21 d (298 K), 10 d (323 K), or 4 d (348, 373, 398, and 423 K). Ion-exchange equilibrium was confirmed to be attained under these conditions. The fibers were separated by centrifugation for 10 min at 4000 rpm. The concentration of cobalt(II) ions in the aqueous solution was determined using a Hitachi 180—80 polarized Zeeman atomic absorption spectrophotometer. The pH of the solution was measured with a TOA HM-20E pH meter. X-Ray powder diffraction patterns were obtained by using a Rigaku Denki RAD-2B diffractometer with Cu $K\alpha$ radiation.

Results

The distribution coefficient, K_d, was calculated as

$$K_d = \frac{C_1/g}{C_2/cm^3}, \qquad (2)$$

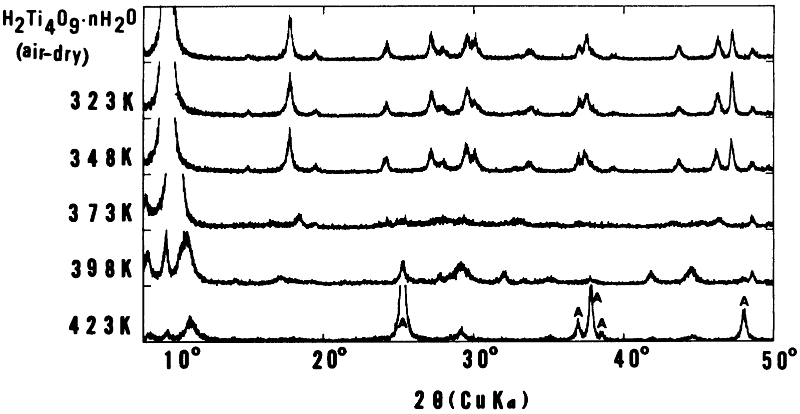

Fig. 5. X-Ray powder diffraction patterns of the solid samples treated with aqueous solutions at six different temperatures.
A: anatase.

where C_1 is the amount of adsorbed cobalt(II) ions per 1 g of the solid, and C_2 is the concentration of cobalt(II) ions per 1 cm³ of the aqueous solution.

Figure 4 gives the plots of log K_d vs. pH in the aqueous phase for six different temperatures. In these experiments, the concentration of hydrogen ions in the solid phase was held substantially constant before and after the adsorption of cobalt(II) ions. The slopes of the log K_d–pH lines were about +2 below 398 K. Figure 4 also shows that the slopes of the lines for 398 and 423 K were somewhat lower than +2. X-Ray powder diffractometry was then applied to clarify the cause of the differences in slopes (Fig. 5).

The fibers treated below 373 K showed almost the same diffraction patterns as the original fibers. This fact indicates that the structure of the fibers remain virtually unchanged at 348 K or below. Therefore, the adsorption of cobalt(II) ions on the fibers under these conditions can be represented by the ion-exchange reaction:

$$m\mathrm{Co}^{2+}(\mathrm{aq})+\mathrm{H_2Ti_4O_9}\cdot n\mathrm{H_2O(s)} \rightarrow 2m\mathrm{H}^{+}(\mathrm{aq})+\mathrm{Co}_m\mathrm{H}_{2(1-m)}\mathrm{Ti_4O_9}\cdot n\mathrm{H_2O(s)}, \quad (3)$$

where the subscripts "aq" and "s" denote the aqueous and solid phases, respectively, and $0<m<1$.

The layer structure of the crystalline hydrous titanium dioxide is characterized by a very strong 200 reflection with an interplanar spacing, $d(200)$, of ca. 0.91 nm.[8] The corresponding peak of the solid treated at 373 K was observed at 0.86 nm; all the other peaks disappeared almost completely. The presence of this peak suggests that the poorly crystallized phase formed at 373 K has a layer structure similar to that of hydrous titanium dioxide.

Table 1. Summary of the Values of $d(200)$ Determined by X-ray Powder Diffractometry and Distribution Coefficients of Cobalt(II) Ions at pH 3.0

Temperature K	$d(200)$ nm	K_d
298	0.91	0.22
323	0.91	1.36
348	0.91	2.10
373	0.86[a]	2.54
398	—	2.16
423	—	1.90

a) Strictly speaking, this peak cannot be assigned to the 200 reflection because this sample was not a crystalline material.

The solids treated at 373 K or below remained fibrous, but those treated at 398—423 K turned powdery. The powdery samples showed X-ray diffraction patterns different greatly from those of fibrous ones. The three reflections appeared at 8° to 12°; furthermore, the peaks of anatase-type titanium dioxide appeared, and their intensities increased with an increase in temperature of the solution. That is, a part of hydrous titanium dioxide, $H_2Ti_4O_9 \cdot nH_2O$, dehydrates to give anatase under the above conditions:

$$\mathrm{H_2Ti_4O_9}\cdot n\mathrm{H_2O} \rightarrow 4\mathrm{TiO_2}+(n+1)\mathrm{H_2O}. \quad (4)$$

The three peaks described above are assigned to an intermediate phase which is formed in the course of conversion of hydrous titanium dioxide to anatase.

Discussion

The hydrous titanium dioxide fibers have a layer structure similar to that of potassium tetratitanate.[4] Table 1 summarizes the $d(200)$ values and distribution coefficients of cobalt(II) ions at pH 3.0. As the temperature was increased between 298 and 373 K, the distribution coefficient also increased. At 373 K, the crystalline hydrous titanium dioxide fibers converted into the poorly crystallized phase with an interlayer distance considerably smaller than that of the crystalline fibers. The amount of adsorbed cobalt(II) ions must be influenced by the variations of both the temperature and structure of the fibers. It is, however, difficult to evaluate the extent to which these two factors affect the partition of cobalt(II) ions between the solid and aqueous phases.

The distribution coefficient of cobalt(II) ions reached a maximum at 373 K (Table 1). However, this temperature cannot be regarded as optimum for adsorption of cobalt(II) ions. As the temperature was raised above 373 K, the hydrous titanium dioxide changed into the intermediate phase and/or anatase to a greater extent with a result that the K_d values decreased with increasing temperature. In view of the fact that the layer structure is stable to heating in the air up to 573 K,[9] the presence of high-temperature solutions evidently accelerates both chemical and structural changes of the fibers in the closed tube. There is a fear of the unfavorable conversion of the poorly crystallized phase formed at 373 K into anatase or its precursor if minor modification in experimental conditions is made. On the other hand, the layer structure of the fibers remains almost unchanged below 373 K. Accordingly, a reaction temperature between 348 and 373 K is recommended especially when the fibers are used as an adsorbent for a long period. If the present fibers are used as an adsorbent for cobalt(II) ions, conditions under which $H_2Ti_4O_9 \cdot nH_2O$ does not change to other phases should be determined prior to adsorption runs.

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