CHEMISTRY LETTERS, pp. 1525-1528, 1980.

ADSORPTION OF CESIUM FROM AQUEOUS SOLUTIONS USING A CRYSTALLINE HYDROUS TITANIUM DIOXIDE FIBERS

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The adsorption of cesium in aqueous solutions has been studied by using an ion-exchanger of crystalline hydrous titanium dioxide fibers. Cesium can be perfectly adsorbed from alkaline solutions, and the distribution ratio of cesium is higher than that of lithium, sodium, potassium, or rubidium. This method can be applied to cesium immobilization in the radwastes under mild alkaline conditions.

The treatment of the radwastes has been studied by using various adsorbents.[1-7] Recently, Fujiki, Komatsu, and Ohta have reported[8] that cesium ions in concentrated cesium hydroxide solutions were adsorbed onto crystalline hydrous titanium dioxide fibers and that the final composition of the adsorbent was $Cs_{1.64}Ti_6O_{12.82}$. According to them, the capacity of the ion-exchanger for cesium is very high, and it is one of the most useful ion-exchangers for cesium. A high capacity and perfect uptake of cesium are prerequisites for any method for the treatment of radwastes. In the present work, cesium ions could be perfectly ion-exchanged by using the crystalline hydrous titanium dioxide fibers, and selectivity among various alkali metal ions on the adsorption was also investigated.

All of the reagents used were of analytical grade. Potassium tetratitanate fibers, $K_2Ti_4O_9 \cdot nH_2O$, were grown by the slow cooling method in a K_2MoO_4 flux melt.[9] Hydrous titanium dioxide fibers were prepared by extracting potassium from the obtained potassium tetratitanate fibers with 1 mol dm^{-3} hydrochloric acid. All the experiments for ion-exchange were carried out in a thermostatted room at 25°C. Stoppered glass tubes (volume: $2 \times 10^{-2} dm^3$) were used to equilibrate the solid and aqueous phases containing 1×10^{-3}-7×10^{-3} mol dm^{-3} cesium. The initial volume of the aqueous phase was $1\times10^{-2}dm^3$, and the amount of the solid phase was 0.1 g. The two phases were agitated by a mechanical shaker (200 r.p.m.) for three days to establish solid-liquid equilibrium and then centrifuged for three minutes at 4000 r.p.m. The cesium content in the aqueous phase was measured by atomic absorption spectrophotometer.

Figure 1 gives the dependence of the amount of adsorbed cesium on the hydrogen ion concentration. The amount of cesium uptake is proportional to the final pH value of the aqueous phase. These results indicate that extraction of potassium from the potassium tetratitanate fibers and adsorption of cesium onto hydrous titanium dioxide fibers are represented by the following equations:

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

$$H_2Ti_4O_9\cdot nH_2O + xCs^+ \rightarrow H_{2-x}Cs_xTi_4O_9\cdot nH_2O + xH^+ \quad (0 < x < 2) \qquad (2)$$

That is, the hydrous titanium dioxide fibers act as an ion-exchanger. Protons may replace potassium ions to form hydroxide ions by being attached to oxide ions in $[TiO_6]$ octahedra forming a layer structure. When cesium ions are incorporated in the hydrated fibers, they may occupy the same sites as those of interlayer potassium ions in $K_2Ti_4O_9\cdot nH_2O$.

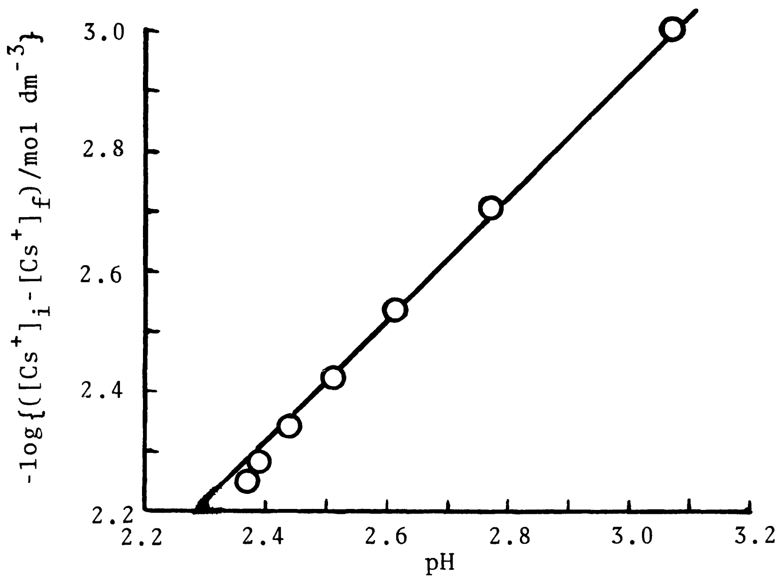

Fig.1 Dependence of Cs(I) adsorption on the final hydrogen ion concentration. The straight line has the slope of +1.

$[Cs^+]_i$: initial concentration of the aqueous phase.

$[Cs^+]_f$: final concentration of the aqueous phase.

Figure 2 shows the amount of cesium adsorption as a function of the hydroxide concentration in an aqueous solution. In these experiments, the initial cesium concentration in the aqueous phase was always kept at 5×10^{-3} mol dm^{-3} by mixing cesium chloride with cesium hydroxide solutions. The adsorption of cesium from alkaline solution was the same action as that from acidic solution in Fig. 1. The distribution ratio of cesium increased with an increase in the hydroxide concentration in the aqueous solution. For example, cesium was perfectly adsorbed into the solid phase when the aqueous phase was 5×10^{-3} mol dm^{-3} cesium hydroxide.

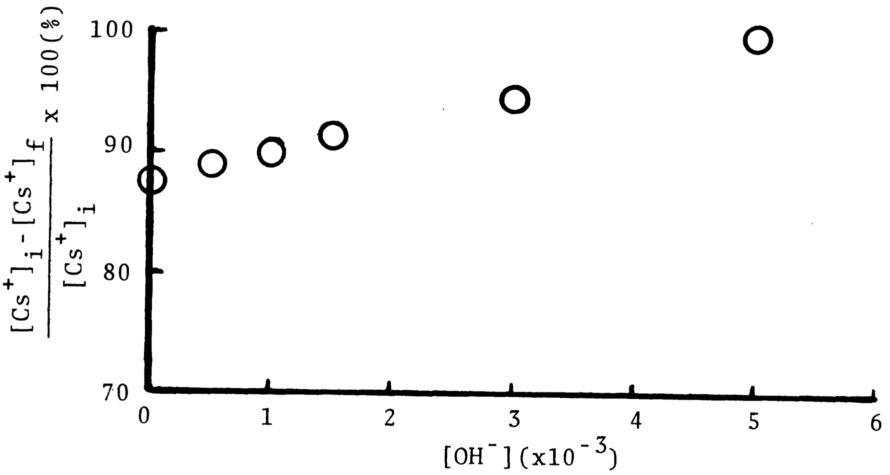

Fig. 2 Amount of cesium adsorption as a function of the hydroxide ion concentration.

Solid phase: hydrous titanate fibers.

Aqueous phase: 5×10^{-3} mol dm^{-3} Cs(OH,Cl).

The effects of other alkali metal ions (M^+) on cesium adsorption was examined by adding 1×10^{-5}-1×10^{-3} mol alkali chlorides to 10^{-2}dm^3 of a 5×10^{-3} mol dm^{-3} cesium chloride solution (Figure 3). The decrease in cesium adsorption abides by a following sequence:

$$[Rb^+] > [K^+] \gg [Na^+] > [Li^+] \quad (3)$$

From these results, the following conclusions were obtained:

1) As the hydroxide ion concentration in the aqueous phase is increased, the amount of cesium adsorption also increases.
2) Interference of cesium adsorption from other alkali metal ions is not pronounced; cesium adsorption is hardly influenced by lithium and sodium.

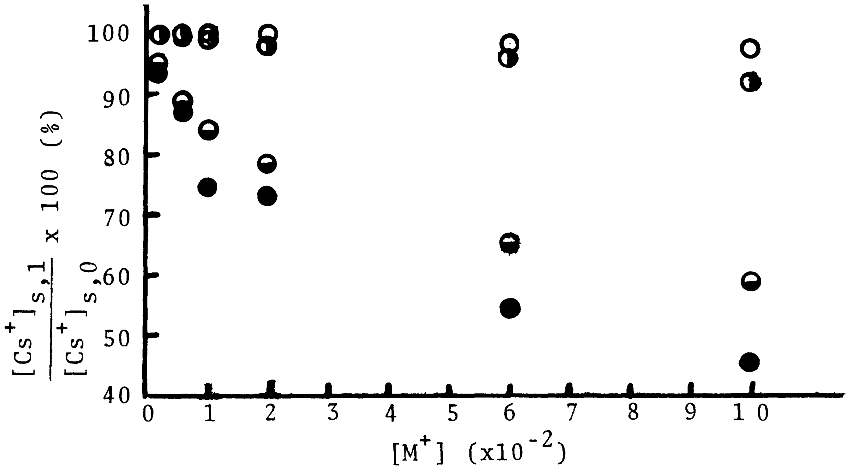

Fig.3 Effects of the addition of Li^+(○), Na^+(◑), K^+(◒), and Rb^+(●) on cesium adsorption.

$[Cs^+]_i$: 5×10^{-3} mol dm^{-3}.

$[Cs^+]_{s,0}$: cesium concentration of the solid phase in the absence of other alkali metals.

$[Cs^+]_{s,1}$: cesium concentration of the solid phase in the presence of other alkali metals.

Since radwastes are strongly acidic solutions, they need to neutralized by adding alkali hydroxide solutions prior to the treatment with this ion-exchanger. Thus, lithium or sodium hydroxide solutions are very suitable for this neutralization.

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(Received September 25, 1980)