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A CESIUM IMMOBILIZATION FROM AN AQUEOUS SOLUTION USING THE CRYSTALLINE ADSORBER OF HYDROUS TITANIUM DIOXIDE FIBERS

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The immobilization of Cs^+ ions in a CsOH solution was studied by using the adsorber of crystalline $TiO_2 \cdot nH_2O$ fibers. The adsorbed cesium contents were in a compositional range of $Cs_xTi_6O_{12+x/2}(1.5 < x \leqslant 2)$. This cesium titanate was remade to the Cs-priderite$(Cs_xAl_xTi_{8-x}O_{16}: 1.5 < x \leqslant 2)$ of the hollandite structure type by heating after the addition of Al_2O_3. The most stable immobilizer of Cs^+ ions was obtained by sintering the mixed phases of Cs-priderite and rutile.

It is well known that the most popular procedure of the radwaste has been to incorporate active components into borosilicate glasses1), or that ^{137}Cs can be immobilized by incorporating in the crystal lattice of pollucite($CsAlSi_2O_6$) by using zeolites2)-4) or montmorillonite clays5) as a starting material. Recently, Ringwood et al.6)7) have proposed a SYNROC process, by which various components in a radwaste could be immobilized by forming dilute solid solutions with host components in a mineral assemblage consisting of three titanate phases. The titanate assemblage was proved by them to be exceptionally resistant to the hydrothermal leaching test. In this method, cesium is immobilized by forming a solid solution with barium in a titanate($BaAl_2Ti_6O_{16}$) having hollandite structure type. However, this procedure can not directly be applied to a liquid radwaste or the separation of high-level waste, and the acceptable amount of Cs in the solid solution is very small, although the process is effective for a solid radwaste. For the liquid radwaste, suitable ion-adsorber or ion-exchanger is necessary to solidify the Cs^+

ions in an aqueous solution.

In the present work, the immobilization of Cs^+ ions from an aqueous solution is investigated by using the crystalline adsoeber of hydrous titanium dioxide fibers.

Fibrous potassium titanates were prepared by the following procedure: the starting material consisting of a $K_2O\cdot 2TiO_2$ composition was melted at 1100 °C for 30 min in a 100 cm^3 Pt crucible, the melt was then taken out from a furnace, and was rapidly cooled by pouring into another metallic crucible cooled with water on bottom. Consequently, the fibrous aggregation of potassium titanates was obtained, and it was easily separated in fibers by sorking in water for several hours. The fibers were composed of the mixture phase of $K_2Ti_2O_5\cdot nH_2O$ and a small amount of $K_2Ti_4O_9\cdot nH_2O$ of 3 mm in average length, and 0.03 mm in average diameter.

Hydrous titanium dioxide($TiO_2\cdot nH_2O$) fiber was prepared by extracting K^+ ions from the obtained potassium titanate fibers with a 1 mol dm^{-3} HCl solution in order to employ as the adsorber of Cs^+ ions in an aqueous solution.

The cesium leachability of the immobilizing material in pure water was measured by using the pellet-like specimens of the size of 13 mm diameter and 1.0 mm thickness. The specimen was made by pressing the powder of the immobilizer under 25 MPa at room temperature, and then, by calcining at 1000 °C for 15 h.

The specific surface area of a pellet-like sample was determined to be approximately 5.8×10^4 cm/g by the N_2 gas adsorption method.

The hydrous titanium dioxide fibers obtained are crystalline on the x-ray diffraction pattern, and the original layer structure of $K_2Ti_2O_5$ 8) or $K_2Ti_4O_9$ 8) is kept by the existence of interlayer water 9). The solidification of Cs^+ ions

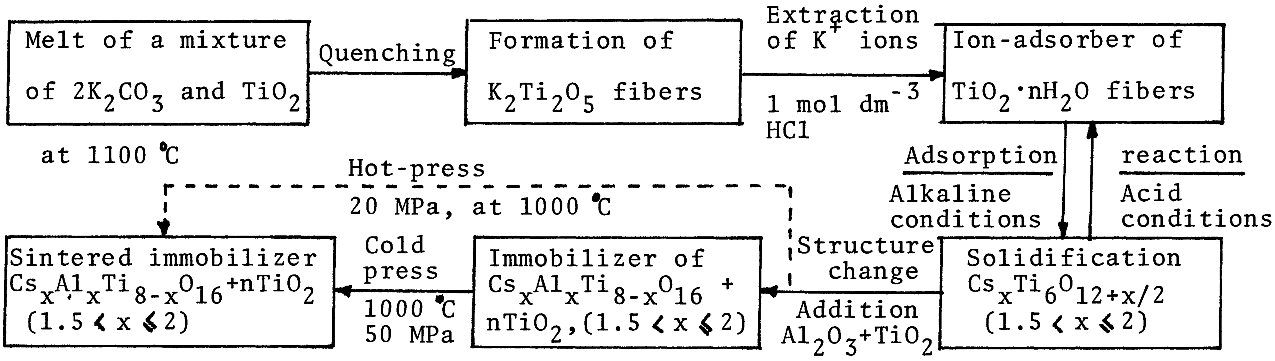

Fig. 1. Flowsheet for the immobilization of Cs^+ ions in an aqueous solution.

in an aqueous solution was carried out by using the adsorber of the hydrous titanium dioxide fibers. This adsorber was immersed into a 0.5 mol dm^{-3} CsOH solution for 24 h, and then, was filtered, and was dried at 100 °C without washing. After the cesium adsorption, a composition of the adsorber was determined to be $Cs_{1.64}Ti_6O_{12.82}$ by chemical analysis. The ideal ability of adsorption for the Cs^+ ions of this adsorber seems to form Cs-hexatitanate($Cs_2Ti_6O_{13}$). The adsorption reaction may be explained;

$$6TiO_2 \cdot nH_2O + 2Cs^+ = 2OH^- = Cs_2Ti_6O_{13} \cdot nH_2O + H_2O$$

The adsorbed Cs^+ ions perhaps occupy the sites of K^+ ions vacated already in the interlayers, because they are easily extracted as well as K^+ ions in the $K_2Ti_2O_5$ in a dilute acid solution. So that, the immobilization of Cs^+ ions needs to change structurally from the Cs-hexatitanate of a layer structure type to another stable cesium titanate. It was found that Cs-priderite, $Cs_xAl_xTi_{8-x}O_{16}(1.5 < x \leq 2)$, is most suitable for this purpose among various cesium titanates. Natural priderite, $(K,Ba)_{1.33}(Ti,Fe)_8O_{16}$ 10), has an isostructure with hollandite, $BaFeMn_7O_{16}$ 11)-13), having tunnels running parallel to the c-axis by double strings consisting of the edge-sharing of TiO_6 octahedra. The Ba^{2+} ions occupy the sites in these tunnels, and can easily by replaced with various alkali metal cations. In the Cs-priderite, Cs^+ ions occupy the sites of Ba^{2+} ions in the tunnels, and Al^{3+} ions replace a portion of Ti^{4+} ions in the octahedra. The Cs-priderite was prepared by heating the stoichiometric mixture of $Cs_xTi_6O_{12+x/2}(1.5 < x \leq 2)$ and Al_2O_3 powders at the temperature above 900 °C, and was changed into the most chemically stable form with the small volume for storage by further sintering. Consequently, the immobilization of Cs^+ ions from an aqueous solution is summarized in Fig. 1.

Table 1. The leachability of cesium in the sintered immobilizers in pure water.

Sintered immobilizer (x=1.64)	Immersion time (h)	Leachability ($g/cm^2 \cdot day$)
$Cs_xAl_xTi_{8-x}O_{16}$	72	6.68×10^{-8}
$Cs_xAl_xTi_{8-x}O_{16}+2TiO_2$	48	3.66×10^{-8}
$Cs_xAl_xTi_{8-x}O_{16}+6TiO_2$	72	2.17×10^{-9}
$Cs_xAl_xTi_{8-x}O_{16}+12TiO_2$	74	6.68×10^{-9}

The leachability of Cs^+ ions from the various sintered immobilizers in pure water is summerized in Table 1. The leachability was calculated by following equation;

$$L = A/S \cdot 1/T$$

where L is the leachability ($g/cm^2 \cdot day$), A is the leached amount of cesium (g), S is the surface area (cm^2) of sample, and T is the immersion time in pure water. This equation is available to examine the additional effect of TiO_2 phase, although it is different from general equation without a weight factor of sample. As shown in Table 1, the combined phase of Cs-priderite and TiO_2(rutile or anatase) was recognized to give lower leachability than that of Cs-priderite monophase. The lowest leachability was given by sintering the mixture of $Cs_xAl_xTi_{8-x}O_{16}$($1.5 < x \leq 2$) and 6 molar of TiO_2. Namely, it is inferred that the supression of the exudation of cesium was resulted by the necking down of the structural tunnel during the sintering with the addition of TiO_2. However, the addition of large amount of TiO_2 increased the leachability of cesium, and it was observed to inhibit the formation of a dense material during the sintering.

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