Immobilization of Divalent Transition Metals from Aqueous Solutions Using Crystalline Hydrated Titania Fibers

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From a viewpoint of the treatment of high level radioactive liquid waste, the immobilization of divalent transition metal ions from aqueous solutions was studied by the use of the crystalline hydrated titania ($\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) fibers as an ion-adsorbent. The each metal ion was saturately adsorbed on the fibrous adsorbent from the aqueous solution of the divalent transition metal acetate. The adsorbed metal ions were immobilized in crystal lattices as main components of various titanate minerals after the sintering treatment. The copper ions were immobilized into the mineral assemblage of rutile, and Cu_2TiO_3 and Cu_3TiO_4 phases having a complex crystal structure. Zinc ions were fixed into the mineral assemblage of rutile and a Zn_2TiO_4 phase of the inverse spinel structure. Each metal ion of manganese, cobalt and nickel was immobilized into the same mineral assemblage of rutile and a MTiO_3 ($\text{M}=\text{Mn}, \text{Co}, \text{and Ni}$) phase of the ilmenite structure. Rutile in these immobilizers occurs as a matrix mineral in the largest amount. The leachability of each metal ion in the immobilizers was measured under normal atmospheric and hydrothermal conditions. The results of the former indicated to be very stable with high leach resistance of maximal $3.2 \times 10^{-9} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ of manganese ion, and the results of the latter also indicated to be very stable with maximal $9.1 \times 10^{-9} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ of nickel ion.

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結晶質チタニア水和物繊維による水溶液中の2価遷移金属の固定

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高レベル放射性廃液処理の観点から水溶液中の2価遷移金属イオンの固定化がイオン吸着材として結晶性チタニア水和物 ($\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) 繊維を用いて研究されている。各金属イオンは2価遷移金属酢酸塩の水溶液から吸着材に飽和吸着させた。吸着金属イオンは焼結処理により種々なチタン酸塩鉱物の主成分として格子中に固定化された。銅イオンはルチル及び複雑な結晶構造を有する Cu_2TiO_3 相と Cu_3TiO_4 相の鉱物集合体に固定化された。亜鉛イオンはルチルと逆スピネル構造の Zn_2TiO_4 相の鉱物集合体に固定化された。マンガン、コバルト、ニッケルの各金属イオンはルチルとイルメナイト構造の MTiO_3 ($\text{M}=\text{Mn}, \text{Co}, \text{Ni}$) 相の同じ鉱物集合体に固定化された。これらの固定化体中のルチルは最も多量でマトリックス鉱物として存在している。

固定化体中の各金属イオンの浸出率が大気圧及び水熱条件下で測定された。前者の結果はマンガンイオンの最大 $3.2 \times 10^{-9} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ 高浸出抵抗で非常に安定であることを示した。後者の結果はまたニッケルイオンの最大 $9.1 \times 10^{-9} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ で非常に安定であることを示した。

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Key-words : Crystalline hydrated titania fiber, Hydrated titania adsorbent, Immobilization of divalent transition metals

1. Introduction

The concept of immobilizing the radioactive elements of nuclear waste in a mineral assemblage was originally proposed by Hatch¹⁾ in 1955. Since, many immobilization processes: Supercalcine^{2),3)}, Sandia titanate base ceramic⁴⁾, Synroc^{5),6)}, and High-alumina base ceramic⁷⁾; have been developed. Especially, the Synroc which has the mineral assemblage consisting of "hollandite-perovskite-zirconollite" have received considerable attention, because the leach tests under high temperature and high pressure have been shown to be very stable^{5),6),8)}. These leach tests also suggest that the titanate minerals in the Synroc are more stable than silicate minerals such as porucite which is well known as the Cs-immobilizer. Recently, Morgan et al.⁹⁾ have reported the titania and lanthanum tailored ceramic which has the mineral assemblage consisting of pyrochlore, perovskite, monazite and fluorite, and this ceramic immobilizer has given high leach resistance.

We have previously reported a titanate base ceramic immobilized cesium or strontium¹⁰⁾⁻¹²⁾. This titanate base ceramic was produced by sintering the adsorbent in which adsorbed selectively cesium or strontium ions from an aqueous solution. The crystalline hydrated titania fibers were used as a new type adsorbent. In the present work, the immobilizations of divalent transition metal ions from aqueous solutions are studied on the base of an assemblage of titanate minerals using the same adsorbent.

2. Experimental

The crystalline hydrated titania ($\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) fibers employed as an ion-adsorbent were prepared by extracting potassium ions in an acid solution from potassium dititanate ($\text{K}_2\text{Ti}_2\text{O}_5$) fibers grown directly from the melt of stoichiometric composition¹³⁾. The adsorption of a divalent transition metal ion was carried out by the batch technique; the adsorbent of 2.0 g immersed into $2 \times 10^{-1} \text{ dm}^3$ of acetic solution containing $1 \times 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$ concentration of a divalent transition metal at 25°C for 2 weeks. After adsorption process, the adsorbent was dried at room temperature and the supernatant solution was analyzed for its metal ion concentration by the EDTA titration. The amount of the adsorbed metal ions

was determined from the difference between the initial and final concentrations of the solution.

Leaching test under normal atmospheric conditions was carried out by immersing 0.2 g of the immobilizer pellet in $1 \times 10^{-2} \text{ dm}^3$ distilled water. This test was continuously repeated at an interval of one day. Hydrothermal leaching test was carried out in a closed platinum cupsule which placed in a cold seal type pressure vessel. Distilled water was used as a leachant. The leaching conditions were at 550°C for 24 h under 100 MPa.

3. Results and discussion

3.1 Adsorption behavior

Table 1 exhibits the saturated uptake, the content, the water content and the chemical composition of the adsorbent after the adsorption of each divalent transition metal ion from the aqueous solution. The order of exchange capacity of this adsorbent for the divalent transition metal ions was found to be $\text{Cu} > \text{Zn} > \text{Mn} > \text{Co} > \text{Ni}$. In this series, copper and zinc ions were especially adsorbed in large amounts. Recently, the distribution coefficient (K_d) as a function of pH for divalent transition metal ions was measured using the same adsorbent¹⁴⁾. According to the results, the plots of $\log K_d$ against pH gave a straight line, but the linear slopes were 1.3-1.5 of smaller values than 2 of theoretical value for the exchange of divalent cations. The relationship between $\log K_d$ and pH suggests that the adsorption mechanism of their metal ions on this adsorbent is accompanied by certain complex reactions. In this case, although the adsorption was carried out in high acidity of nitric solutions, the order of adsorption amount was in the same with that of the present work. This order has no relationship for the order of arrangement of ionic radii and energy of hydration. On the other hand, the order of adsorption amount for alkaline earth metal ions is known to be the same order with the increase of

Table 1. Saturated uptake of divalent transition metal ions on the layered $\text{H}_2\text{Ti}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ adsorbent fibers.

Divalent metal ions	Uptake (meq/g)	Content (wt%)	Water content (wt%)	Composition (Rational formula)
Cu	4.36	12.0	17.2	$\text{CuTi}_{4.5}\text{O}_{10} \cdot 5.1\text{H}_2\text{O}$
Zn	3.51	10.0	17.1	$\text{ZnTi}_{5.5}\text{O}_{12} \cdot 6.0\text{H}_2\text{O}$
Mn	1.78	4.7	19.4	$\text{MnTi}_{11}\text{O}_{23} \cdot 12.6\text{H}_2\text{O}$
Co	1.81	5.0	19.9	$\text{CoTi}_{11}\text{O}_{23} \cdot 13.1\text{H}_2\text{O}$
Ni	0.84	2.2	21.0	$\text{NiTi}_{25}\text{O}_{51} \cdot 30.7\text{H}_2\text{O}$

ionic radii¹⁴⁾.

3.2 Immobilization process and mineral assemblage

The immobilization was carried out by sintering the adsorbent reformed into pellet form at temperature of 1010°C or above. The pellet was produced in 13 mm diameter and 0.5 mm thickness by cold-pressing under 50 MPa for the powdered adsorbent after the adsorption process. **Figure. 1** shows the flowsheet of the immobilization process of divalent transition metals from aqueous solutions. **Table 2** exhibits the calcination conditions and the mineral phases formed on the immobilization processes. The copper ions adsorbed in the largest amount were immobilized in the mineral assemblage consisting of rutile, Cu_2TiO_3 and Cu_3TiO_4 phases. Rutile which is contained in the largest amount in the immobilizer forms a matrix texture. When the Cu-containing adsorbent was calcined at temperature below 1000°C, this adsorbent was thermally decomposed into rutile and tenorite (CuO). This is explained on the phase equilibrium relationship in the system $\text{CuO-Cu}_2\text{O-TiO}_2$ ¹⁵⁾. According to this diagram, copper titanate compounds between

CuO (or $1/2 \text{ Cu}_2\text{O}$) and TiO_2 are not recognized to exist. However, some copper titanates; Cu_2TiO_3 ¹⁶⁾, Cu_3TiO_4 ¹⁷⁾ and $\text{Cu}_2\text{Ti}_2\text{O}_5$ ¹⁸⁾ have been reported. In the present work, Cu_2TiO_3 phase which is contained in a large amount following by rutile was certainly identified by X-ray powder diffraction. This phase has been indexed as the hexagonal system, but the detailed structure is not yet clear. Another phase of small amount may be either Cu_3TiO_4 phase or $\text{Cu}_2\text{Ti}_2\text{O}_5$ phase. Because, the X-ray powder diffraction patterns of the both phases are very similar as shown in **Fig. 2**. We adopted the Cu_3TiO_4 phase at present time, because the structure and composition are certainly decided by Hayashi et al.¹⁷⁾ This crystal has the mixed valence of divalent and monovalent copper ions, and is written as another formula $\text{Cu}^{2+}(\text{Cu}^{2+}, \text{Ti})\text{O}_4$, and has the same structure as the $\delta\text{-AgFeO}_2$ crystal¹⁹⁾. The Cu^{2+} ions occupy the same sites as Ti atoms in TiO_6 octahedra and Cu^+ ions are linearly coordinated by two oxygen atoms. On the other hand, the crystal structure and composition of $\text{Cu}_2\text{Ti}_2\text{O}_5$ phase are yet uncertain, although the structure is conjectured to be crednerite ($\text{Cu}_2\text{Mn}_2\text{O}_5$) type.

Fig. 1. Flowsheet of the immobilization process of divalent transition metals from aqueous solutions.

Table 2. Calcination conditions and mineral phases on the immobilization process of divalent transition metals.

Adsorbed ions	Calcination Temp.(°C), Time(h)	Colour	Immobilizer Mineral phases	Structural type
Cu	1010 ±15 1	dark brown	TiO_2 , Cu_2TiO_3 , Cu_3TiO_4	complex
Zn	" "	white	" , Zn_2TiO_4	i-spinel
Mn	" "	brown	" , MnTiO_3	ilmenite
Co	" "	green	" , CoTiO_3	"
Ni	" "	yellowish	" , NiTiO_3	"

TiO_2 = rutile, i-spinel = inverse spinel

Fig. 2. X-ray powder diffraction pattern of the copper immobilizer.

Divalent copper oxide is reduced at high temperature, and monovalent copper oxide become stable state at temperatures above 1000°C on calcination procedure, and then reacts to form titanates. Perhaps, the solid reactions between CuO (or $1/2 \text{ Cu}_2\text{O}$) and TiO_2 seem to begin at higher temperatures than an eutectic point at 1008°C in the system $\text{CuO-Cu}_2\text{O-TiO}_2^{15)}$, and to be related to the formation of liquid phase.

The zinc ions adsorbed in large amount following after copper ions were immobilized in the mineral assemblage consisting of rutile and a cubic Zn_2TiO_4 phase which has the inverse spinel structure. Namely, the zinc ions in Zn_2TiO_4 have two kinds of sites in ZnO_4 tetrahedra and ZnO_6 octahedra. The manganese, cobalt and nickel ions were immobilized in the mineral assemblage consisting of rutile and a ATiO_3 ($A=\text{Mn, Co and Ni}$) phase which has the ilmenite structure. The A ions occupy the central sites in corner-sharing

AO_6 octahedra.

On the immobilization process, it is characterized that the solid reactions between the hydrated titania adsorbent and the adsorbed metal ions are simultaneously carried out by direct sintering reactions without preheating owing to mineralization. Namely, the mineralization of the adsorbed metal ions can be simultaneously produced by the sintering reactions. The immobilization was also tried by sintering reactions at 1100°C for 1 h, and at 1200°C for 1 h. The results gave the same mineral assemblages as those obtained at 1010°C, except the copper-containing adsorbent was semi-fused.

3.3 Leaching test

Leachability (L) was calculated from following equation :

$$L = A/C \cdot S \cdot T (\text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-2}) \quad (1)$$

where A is the amount of a leached element, C is the content of the element in immobilizer, S is the

Table 3. Leach tests of divalent transition metals in the immobilizers in distilled water leachant under normal atmospheric conditions.

Immobilizer Mineral phases	Leachability ($\text{g} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$) *			
	1	2	3	4
$\text{TiO}_2, \text{Cu}_2\text{TiO}_3, \text{Cu}_3\text{TiO}_4$	$<1.2 \times 10^{-10}$	$<1.2 \times 10^{-10}$	1.4×10^{-10}	4.6×10^{-10}
" Zn_2TiO_4	0.9×10^{-10}	6.7×10^{-10}	1.0×10^{-9}	8.5×10^{-10}
" MnTiO_3	6.5×10^{-10}	3.2×10^{-9}	2.6×10^{-9}	2.6×10^{-9}
" CoTiO_3	$<0.6 \times 10^{-10}$	1.2×10^{-10}	3.0×10^{-10}	3.0×10^{-10}
" NiTiO_3	$<1.3 \times 10^{-10}$	$<1.3 \times 10^{-10}$	$<1.3 \times 10^{-10}$	2.5×10^{-10}

* Leach tests were repeated 4 times with an interval for 24 hours

Table 4. Leach tests of divalent transition metals in the immobilizers in distilled water leachant under normal atmospheric conditions.

Immobilizer Mineral phases	Fractional release *			
	1	2	3	4
$\text{TiO}_2, \text{Cu}_2\text{TiO}_3, \text{Cu}_3\text{TiO}_4$	$<9.5 \times 10^{-6}$	$<9.5 \times 10^{-6}$	1.1×10^{-5}	3.6×10^{-5}
" Zn_2TiO_4	7.3×10^{-6}	5.6×10^{-5}	8.5×10^{-5}	7.0×10^{-5}
" MnTiO_3	5.1×10^{-5}	2.6×10^{-4}	2.1×10^{-4}	2.1×10^{-4}
" CoTiO_3	$<4.2 \times 10^{-6}$	8.5×10^{-6}	2.1×10^{-5}	2.1×10^{-5}
" NiTiO_3	$<1.0 \times 10^{-5}$	$<1.0 \times 10^{-5}$	$<1.0 \times 10^{-5}$	2.0×10^{-5}

* Leach tests were repeated 4 times with an interval for 24 hours

Table 5. Leach tests of divalent transition metals in the immobilizers in distilled water leachant under hydrothermal conditions.

Immobilizer Mineral phases	S/I [*] (wt%)	Leachability ($\text{g}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$)	Fractional release
TiO ₂ , Cu ₂ TiO ₃ , Cu ₃ TiO ₄	22.3	$< 2.0 \times 10^{-10}$	$< 1.7 \times 10^{-5}$
" , Zn ₂ TiO ₃	30.9	3.4×10^{-9}	3.5×10^{-4}
" , MnTiO ₃	19.5	1.2×10^{-9}	1.2×10^{-4}
" , CoTiO ₃	20.9	$< 6.5 \times 10^{-10}$	$< 6.4 \times 10^{-5}$
" , NiTiO ₃	27.0	9.1×10^{-9}	8.9×10^{-4}

^{*}S/I = solvent/immobilizer in weight

surface area of immobilizer and T is the immersion time. The specific surface area of the immobilizer of pellet form was determined by the BET method to be $9.81 \times 10^4 \text{ cm}^2 \cdot \text{g}^{-1}$ on the average. Table 3 exhibits the leachability of each divalent transition metal in the immobilizers stated above. Table 4 shows fractional release for each metal in the immobilizers. The fractional release (F) was also calculated from following equation :

$$F = A/B \quad (2)$$

where A is the same as the A in Eq. (1) and B is the amount of an element in the immobilizer.

The chemical stability series of divalent transition metals in the immobilizers obtained from the leachability and fractional release was found to be arranged in the following order; $\text{Ni} > \text{Co} > \text{Cu} > \text{Zn} > \text{Mn}$. Although the copper ions were immobilized into complex mineral phases, the leachability gave very high leach resistance with maximal $4.6 \times 10^{-10} \text{ g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$. The leachability of manganese ions, maximal $3.2 \times 10^{-9} \text{ g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, indicates to be larger than that of cobalt or nickel ions in the same waste form of ilmenite type structure. This unstable reason of manganese ions seems to be related to the oxidation of the ions. Because the same waste form is very stable with high leach resistance under hydrothermal conditions as will be mentioned below.

The leachabilities and fractional releases under hydrothermal conditions are summarized in Table 5. The results indicate that these waste

forms are very stable with high leach resistance. The leachability of manganese ions under this condition was $1.2 \times 10^{-9} \text{ g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$ of smaller value than that under normal atmospheric condition. As shown by an example of the leach resistance of manganese ions, the conditions under low oxygen partial pressure seem to play a very important role for highly chemical stability of these immobilizers. Hydrothermal reactions are generally carried out in reducing environment.

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