CHEMISTRY LETTERS, pp. 957-960, 1981.

IMMOBILIZATION OF STRONTIUM FROM AN AQUEOUS SOLUTION USING THE CRYSTALLINE HYDROUS TITANIUM DIOXIDE FIBERS

Takayoshi SASAKI, Yū KOMATSU, and Yoshinori FUJIKI
National Institute for Research in Inorganic Materials
1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305

Immobilization of strontium from an aqueous solution was studied by using the two kinds of crystalline hydrous titanium dioxide fibers(C-TiHO). Strontium ions were adsorbed on the C-TiHO from an alkaline solution and its final composition was $SrTi_xO_{2x+1}\cdot nH_2O$ (x=4-6). The Sr-adsorbed C-TiHO was decomposed into the mixture phase of strontium titanate ($SrTiO_3$) and rutile (TiO_2) by calcining at 1000 °C. The sintered mixture phase was proved to be suitable as an immobilizer of strontium from the results of leaching tests under atmospheric and hydrothermal conditions.

Many processes have been proposed to immobilize high-level radwastes by using various inorganic materials. For example, borosilicate glasses1)2), zeolites3)-5), and montmorillonite clays6) have been reported as the immobilization materials. Among them, borosilicate glasses have been studied as the most promising immobilizer of radwastes. Recently, Ringwood et al.7)8) have proposed a SYNROC process, and reported its superiority over borosilicate glasses in the stability under various hydrothermal conditions. On the other hand, Fujiki et al.9)10) have reported an immobilization process by using the C-TiHO, in which Cs^+ ions were successfully immobilized as sintered mixture phase of Cs-Priderite ($Cs_xAl_xTi_{8-x}O_{16}$, x=1.6) and rutile.

In the present work, the immobilization of Sr^{2+} ions from an aqueous solution was studied by using the C-TiHO.

Two kinds of C-TiHO were prepared as described previously9)11); one is of flux growth origin (sample F) and the other is of melt growth origin (sample M). The leachabilities of strontium for the immobilizers were calculated from the Eq. 1:

$$L = \frac{A}{C \cdot S \cdot T} \qquad (1)$$

where L is the leachability($gcm^{-2}day^{-1}$), A is the amount of strontium leached(g), C is the strontium content in the immobilizer, S is the surface area of immobilizer(cm^2) and T is the immersion time(day). Here A was measured by atomic absorption spectrophotometry and S was determined by N_2 gas adsorption method. The powdered immobilizer was sintered by calcining at 1000 °C for 20 hours after cold-pressing under 50 MPa. Leaching tests under atmospheric conditions were carried out by immersing the sintered immobilizer(∿1g) of disk form (13 mm diameter x 2 mm thick) in 1×10^{-2} dm^3 distilled water. The leachant was changed every 24 hours, and both concentration of strontium and pH of leachant were measured. This procedure was repeated for 20 days. Hydrothermal leaching tests were carried out as follows; the sintered immobilizers (∿0.02g) were sealed in gold tubes with 5×10^{-4} dm^3 distilled water. The tubes were put in the standard pressure vessel and kept at 600 °C and 100 MPa for 24 hours.

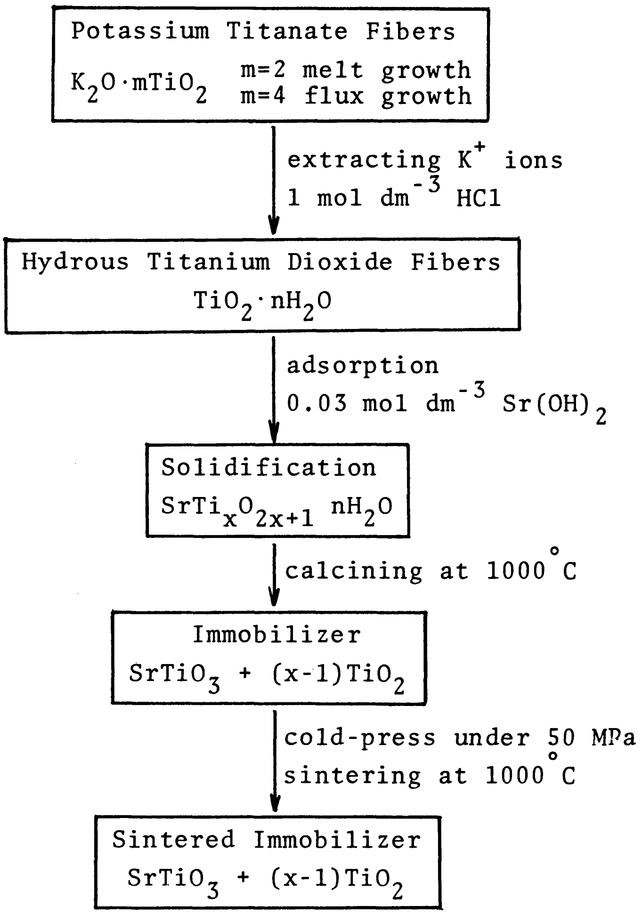

Fig. 1. Flowsheet of an immobilization process of strontium

Figure 1 shows the flowsheet of an immobilization process of strontium using the C-TiHO. The adsorption of Sr^{2+} ions was carried out batchwise; 2g of C-TiHO was immersed in a 1 dm^3 of 0.03 mol dm^{-3} strontium hydroxide solution for 6 days. In this period, the solution was changed twice. By chemical analysis, the compositions of Sr-adsorbed sample F and sample M were determined to be $Sr_{1.04}Ti_6O_{13.04} \cdot 6.74H_2O$ and $Sr_{0.94}Ti_4O_{8.94} \cdot 6.71H_2O$, respectively.

These Sr-adsorbed C-TiHO must be transformed into the most stable compounds. Among various phases of strontium titanates, the strontium titanate ($SrTiO_3$) of perovskite structure was found to be suitable. Transformation from the Sr-adsorbed

C-TiHO to strontium titanate ($SrTiO_3$) was attained by heating the former at 1000 °C. In this case, they were decomposed into two phases of strontium titanate ($SrTiO_3$) and rutile following to Eq. 2:

$$\begin{array}{lll} \text{Sample F} & SrTi_6O_{13}\cdot 6.7H_2O \longrightarrow SrTiO_3 + 5TiO_2 + 6.7H_2O \\ \text{Sample M} & SrTi_4O_9\cdot 6.7H_2O \longrightarrow SrTiO_3 + 3TiO_2 + 6.7H_2O \end{array} \quad (2)$$

So that, the immobilizers of strontium are composed of mixture phase of strontium titanate ($SrTiO_3$) and rutile.

Table 1 gives the leachabilities and fractional releases of strontium for these immobilizers in distilled water under atmospheric conditions for 24 hours. It was found that both immobilizers were chemically very stable, though the leachability of sample M was somewhat higher than that of sample F.

Figure 2 shows the time-dependence of pH values of leachants for 20 days with changing leachant every day. Although an initial pH value of distilled water was about 5.5, equilibrium pH values varied in the range of 6-8. This pH change is caused by the leaching of strontium and explained from following Eq. 3:

$$Sr\text{-}R + 2H_2O \rightleftharpoons H_2\text{-}R + Sr^{2+} + 2OH^- \quad (3)$$

where Sr-R and H_2-R represent the form of immobilizer before and after strontium leaching.

Table 2 gives the leachabilities and fractional releases of strontium for sintered immobilizers under hydrothermal conditions. Compared to the results in Table 1, the leachabilities under hydrothermal conditions are about three times as large as those under atmospheric conditions for both

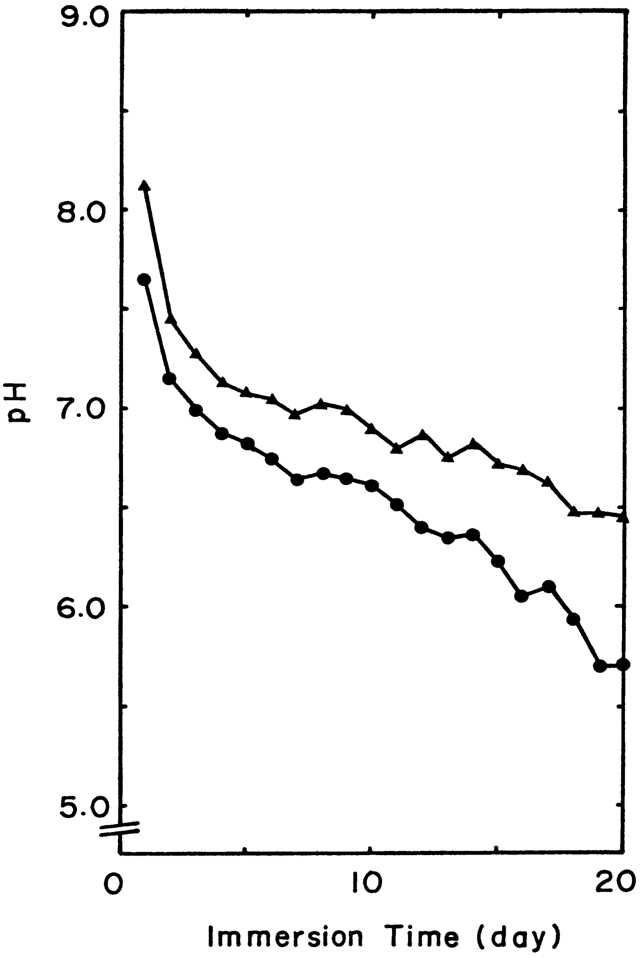

Fig. 2. Time-dependence of pH values of leachants.

● Sample F ▲ Sample M

Leachant: distilled water 10 ml

sample F and sample M. And similarly to the case in Table 1, the leachability of sample F is lower than that of sample M. This difference seems to be related to the amount of rutile in the sintered immobilizers.

Table 1. Leachabilities of strontium for sintered immobilizers in distilled water under atmospheric conditions for 24 hours.

Adsorber	Immobilizer	Leachability ($gcm^{-2}day^{-1}$)	Fractional Release
Sample F	$SrTiO_3 + 5TiO_2$	1.4×10^{-10}	1.2×10^{-5}
Sample M	$SrTiO_3 + 3TiO_2$	3.6×10^{-10}	3.8×10^{-5}

Table 2. Leachabilities of strontium for sintered immobilizers in distilled water under hydrothermal conditions at 600 °C and 100 MPa for 24 hours.

Adsorber	Immobilizer	Leachability ($gcm^{-2}day^{-1}$)	Fractional Release
Sample F	$SrTiO_3 + 5TiO_2$	4.0×10^{-10}	3.4×10^{-5}
Sample M	$SrTiO_3 + 3TiO_2$	1.3×10^{-9}	1.3×10^{-4}

References

1) IAEA, Technical Reports Series, No. 187, IAEA, Vienna (1979).
2) US-ERDA, ERDA-76-43 (1976).
3) T.Kanno, H.Mimura and T.Kitamura, Nippon Genshiryoku Gakkai Shi, 18, 518 (1976).
4) T.Kanno and H.Mimura, ibid., 19, 113 (1977).
5) H.Mimura and T.Kanno, ibid., 19, 170 (1977).
6) D.M.Strachan and W.W.Schulz, Ceram. Bull., 58, 865 (1979).
7) A.E.Ringwood, S.E.Kesson, N.G.Ware, W.O.Hibberson and A.Major, Nature, 278, 219 (1979).
8) A.E.Ringwood, S.E.Kesson, N.G.Ware, W.O.Hibberson and A.Major, Geochem. J., 13, 141 (1979).
9) Y.Fujiki, Y.Komatsu and N.Ohta, Chem.Lett., 1980, 1023.
10) Y.Komatsu and Y.Fujiki, ibid., 1980, 1525.
11) Y.Fujiki and N.Ohta, Yogyo Kyokai Shi, 88, 111 (1980).

(Received April 15, 1981)