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A study of the immobilization of strontium over crystalline titania

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The immobilization of strontium over titania was carried out by the method of coprecipitation. From a preliminary study, an appreciable uptake (52.8%) of ^{90}Sr was observed over preformed titania material. A weighable amount of strontium was coprecipitated with Ti(IV) hydroxide and a maximum of ~ 34 wt% Sr was found to be adsorbed. The leachability of the mixed materials prepared by the addition of 250 and 400 mg Sr^{2+}, calcined at 1000° C, by soxhlet apparatus refluxing at 97° C and repeated seven times at intervals of 24 h, was found to be of the order of 10^{-9} and 10^{-5} $g\,cm^{-2}\,d^{-1}$, respectively. X-ray powder diffraction analysis revealed that strontium was immobilized in the crystalline matrix of rutile, which suffered some structural changes with the formation of new phases, $SrTiO_3 + Sr_2TiO_4$ and $SrTiO_3$, respectively.

1. Introduction

In the nuclear reprocessing cycle, the safe disposal of ^{90}Sr activity has always been considered a problem, owing to its long half-life, high thermal neutron fission yield and hazardous actions. The method of disposal of some such radionuclides by immobilization into a solid matrix of mineral assemblages such as borosilicate glass [1, 2], synroc [3], silica matrix [4], high alumina-tailored ceramics [5], supercalcine [6, 7], concrete [8], hydrous titania fibres [9–13], zirconia [14], titania [15], Sn(IV) and Ce(IV) oxides [16], etc., have already been reported.

A study of earlier literature [3] also reveals that titania was used as an important part of the composition in an assemblage of titanate phase synroc-C, where besides rutile itself, different minerals, such as zirconolite, hollandite perovskite, etc., contain appreciable amounts of TiO_2 which played an effective role in accommodating certain cations in different proportions. Each of these three minerals can accommodate within their structures a range of radionuclides, and perovskite ($CaTiO_3$) is particularly effective for retaining strontium where the waste loading was typically 10–20 wt %. Moreover, the rutile-like structure of Sn(IV) or Ti(IV) oxides is well known to be amenable to adopt certain metal ions which could be applied in the fields of catalytic, magnetic and electronic studies.

The possibility of decomposition of borosilicate glass under severe hydrothermal conditions, resulting in an appreciable leaching of calcium and actinides, complicated the mode of preparation for the desirable synroc variety, comparatively high leach rates for caesium and strontium in case of concrete wasteforms [8], and particularly the non-availability of suitable methods for obtaining higher waste loading of strontium in such matrices, are some of the observed limitations for utilization of any one of such matrices as a versatile immobilizer, with lowest leachability and high resistance to severe hydrothermal conditions.

Hydrous titanium oxide has some attractive physical and chemical properties [17], high chemical and radiation stability, and good mechanical properties; and it has already been applied [15] for removal of certain cations by way of coprecipitation, adsorption and immobilization. Sasaki *et al.* [12] reported the immobilization of strontium in F-type ($SrTi_6O_{13} \cdot 6H_2O$) and M-type ($SrTi_4O_9 \cdot 6.7H_2O$) titania, fairly leach-resistant wasteforms, prepared by adopting the batch technique and calcination at high temperatures with waste loadings of ~ 18 and ~ 24.6 wt %, respectively. An attempt has been made in the present work to study the immobilization behaviour of strontium from aqueous solution over titanium oxide by a coprecipitation technique in order to investigate whether this matrix alone could accommodate a higher amount of strontium waste, and also to ascertain whether the composite material could withstand opposing hydrothermal conditions in the repository.

2. Experimental procedure

^{90}Sr was procured from Harwell, UK. $Sr(NO_3)_2$, $TiCl_4$, ammonia, etc., of AR grade were used.

The preparation of hydrous titania, its characterization by differential thermal analysis (DTA) and thermo gravimetric analysis (TGA), and a tracer-level distribution study performed with ^{90}Sr by the batch technique equilibration over preformed hydrous titania, etc., were described in an earlier communication [18]. The formula of the titania used was found to

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be $TiO_2 \cdot 0.73H_2O$, and an uptake of 52.77% ^{90}Sr was observed.

The study was then extended to macro-level concentration of strontium for adsorption over titania. Various proportions of $Sr(NO_3)_2$ in water were mixed with a finite quantity of $TiCl_4$ in HCl (calculated for 0.5 g TiO_2) and bubbled with ammonia gas until precipitation was complete, then filtered, washed with de-ionized water and made free from interfering ions. The amount of adsorbed strontium in the mixed precipitate was ascertained by determination of the strontium left in the solution part as $SrSO_4$ by gravimetry, and the extent of the uptake limit for strontium over titania was thus determined (Fig. 1). The mixed precipitate was then dried at 70° C for 24 h, powdered and pelleted to 13 mm × 0.5 mm size by cold pressing under 50 MPa, calcined at 1000° C for 20 h, whereby the material turned to a compact, stable and rigid form, possibly with new mineral phases.

A separate quantity of the dried sample of the mixed precipitate was exposed to an infra red lamp for 2 h and the specific surface area was measured by a pulse chemisorb-2700 instrument, micromeritics corporation, by the BET method using purified di-nitrogen as the adsorbate.

Leach tests for the two 0.5 g calcined samples (prepared from 250 and 400 mg Sr^{2+} additions over titania) were separately performed for 7 days at intervals of 24 h in a soxhlet apparatus by refluxing at 97 °C with de-ionized water as leachant, and the leached-out solutions were analysed for strontium by atomic absorption spectroscopy. The leachability was calculated in the usual way [15]. The results are given in Table I.

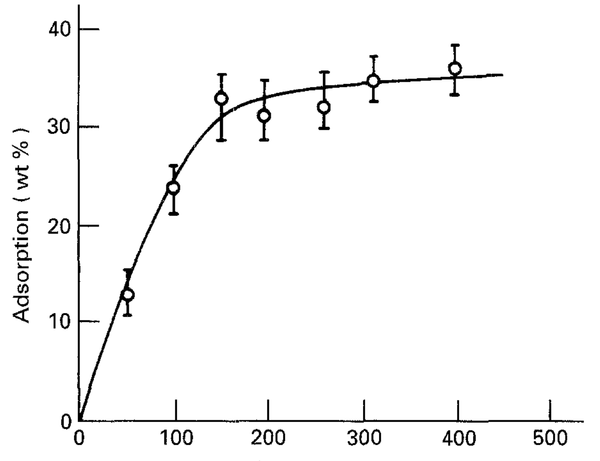

Figure 1 The extent of adsorption of strontium cations during precipitation with titanium hydroxide.

The crystalline phases of the two samples incorporating strontium were characterized by X-ray powder diffraction study with a PW 1830 Philips Automated Diffractometer with nickel-filtered CuK_α radiation ($\lambda = 0.15406$ nm) and the results are shown in Fig. 2.

3. Results and discussion

From the preliminary study of equilibration with ^{90}Sr, an uptake of 52.77% was observed over the preformed titania material. The highest uptake limit of strontium at macro-concentration obtained by coprecipitation with titanium hydroxide showed (Fig. 1) that titania could accommodate strontium with a loading of ~ 34 wt%, which is much higher, in comparison to the uptake of strontium over preformed crystalline hydrated titania fibres recorded, for F-type and M-type TiO_2 materials, to be ~ 18 and ~ 24.6 wt% by Sasaki *et al.* [12]. This may be due to the precipitation of titanium hydroxide in the presence of Sr^{2+} ions, where the primary adsorption process over the surface, and the secondary adsorption caused by high concentration is feasible, and cations might have gone into the bulk of the hydroxide gel forming an ionic cage, and become trapped. The rational compositional formula of the mixed mass was ascertained to be $SrTi_{1.5}O_4$.

The leachability orders for the two samples were found to be in the range of 10^{-9} (for 250 mg Sr) and 10^{-5} (for 400 mg Sr) $g\,cm^{-2}$, d^{-1}, respectively (Table I). The data followed a fairly decreasing trend during the course of washing for 7 days for the 250 mg Sr samples, and the same trend with a slight irregularity was observed for the 400 mg Sr sample. However, both of the matrices apparently exhibited leach-resistivity of strontium.

The immobilization of strontium over a titania matrix was achieved by sintering the mixed solid mass (two samples) at 1000 °C. In the former sample (for 250 mg Sr), besides rutile, $SrTiO_3$ and $Sr_2Ti_2O_4$ phases, and in the latter (for 400 mg Sr) only rutile and $SrTiO_3$ phases, respectively, were identified in the X-ray diffraction patterns (Fig. 2). The situation in the latter case might have occurred due to a greater extent of interionic actions where the concentration of Sr^{2+} was higher and the formation of a charged cloud (ionic cage) due to secondary adsorption in multilayer forms, coulombic interactions, etc., might prohibit further interaction of Sr^{2+} with titanium (either in ionic or any other form), and as such only $SrTiO_3$ was formed in the more strontium-concentrated solution. Thus, strontium was found to be immobilized in the mineral assemblages as $SrTiO_3$ (such as perovskite) with a small amount of unidentified phases in addition to

TABLE I Leachability of strontium from the immobilizer by soxhlet apparatus at 97 °C (repeated seven times at intervals of 24 h)

Immobilizer	Leachability ($g\,cm^{-2}\,d^{-1}$)						
	1	2	3	4	5	6	7
$SrTiO_3 + Sr_2TiO_4 + R^a$	5.0×10^{-9}	3.2×10^{-9}	1.60×10^{-9}	1.91×10^{-9}	1.79×10^{-9}	1.54×10^{-9}	1.43×10^{-9}
$SrTiO_3 + R^b$	5.36×10^{-5}	1.34×10^{-5}	0.26×10^{-5}	0.80×10^{-5}	1.50×10^{-5}	1.70×10^{-5}	0.60×10^{-5}

[a,b] Immobilizers prepared by coprecipitation of [a] 250 mg Sr^{2+} and [b] 400 mg Sr^{2+} with titanium hydroxide. R = rutile.

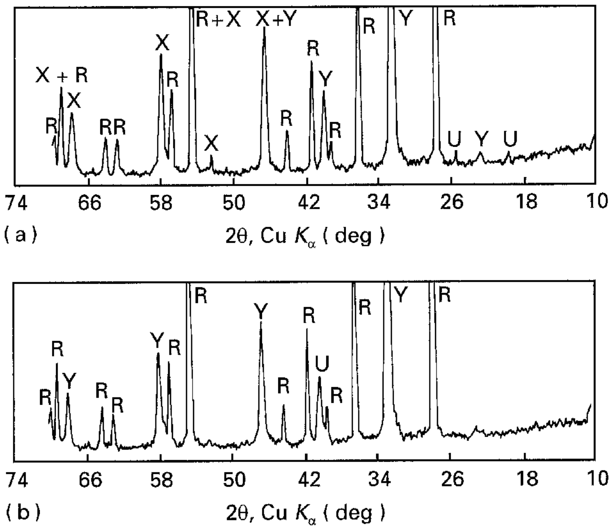

Figure 2 X-ray diffraction patterns of different mineral phases formed over titania prepared from (a) 250 and (b) 400 mg strontium, calcined at 1000° C. X = Sr_2TiO_4; Y = $SrTiO_3$; R = rutile; U = unidentified.

rutile in the former case, and a new phase of $Sr_2Ti_2O_4$ together with the above-mentioned phases, possibly due to free interaction amongst SrO and $SrTiO_3$, in the latter case, respectively.

4. Conclusion

The results taken together, indicate that adsorption of a higher amount of Sr^{2+} could be obtained by the method of coprecipitation in which strontium was immobilized in the hydrothermally stable rutile form of titania crystal lattice with high leach-resistivity, with the formation of different mineral phases. This property of titania could be well utilized for radwaste disposal purposes of ^{90}Sr, as well as for other solid-state phase studies.

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