JOURNAL OF MATERIALS SCIENCE 27 (1992) 5948–5952

Immobilization of barium, cadmium and antimony over titania

D. K. BHATTACHARYYA, N. C. DUTTA
Nuclear Chemistry Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Calcutta 700 064, India

A simple method of immobilization of barium, cadmium and antimony cations in crystalline titania has been studied. High uptake was observed with ^{140}Ba, ^{115}Cd and ^{125}Sb; weighable quantities of these cations were separately precipitated together with titanium hydroxide and 69.02 wt% Ba, 52.00 wt% Cd and 46.05 wt% Sb were found to be adsorbed. After calcination each of the mixed materials, the leaching of cations by immersing into de-ionized water at room temperature and by a Soxhlet apparatus at 97 °C were found to be of the order of 10^{-10} and 10^{-7} g cm^{-2} day^{-1}, respectively. X-ray powder diffraction analysis revealed that barium, cadmium and antimony cations were immobilized separately in the titania crystal lattice, which suffered some structural changes with the formation of different mineral phases.

1. Introduction

Radioactive wastes pose an alarming problem in relation to the spent nuclear fuels which are being produced from the nuclear power reactors and other sources all over the world. The immobilization of such radioactive elements in mineral assemblages and their subsequent disposal in a repository has attracted much attention in recent years. In addition to the various solid wasteforms, such as borosilicate glass [1, 2], concrete [3], silica matrix [4], high alumina tailored ceramics [5], supercalcine [6, 7], etc., the mineral assemblages with a titanate base, such as synroc [8], and the adsorption of cations such as barium [9], caesium [10], copper, zinc, manganese, cobalt, nickel [11], strontium [12] and some rare-earth metal ions [13] over hydrous titania fibres with appreciable leach-resistant properties, have also been described.

A review of the literature shows that borosilicate glass decomposes under fairly severe hydrothermal conditions, preparation of synroc is rather complicated, the concrete wasteforms have comparatively high leach rates for caesium and strontium, and the safest process for the immobilization of radioactive elements of nuclear wastes may not yet have been achieved. An ideal immobilizer to accommodate the highest amount of waste loading, and also to act as versatile adsorbent for several cations of interest with the lowest leachability and high resistance to severe hydrothermal conditions, is still being sought.

Hydrous titanium oxide has certain attractive properties which favours adsorption of many cations, but can sometimes become immobilized, particularly at high temperature with the formation of new mineral phases. Titania is fairly insoluble in acid and alkaline solutions [14], its hardness 6–6.5, melting point 1850 °C, heat of combustion 24 432 cal/eq. [15], and high chemical and radiation stability, as well as good mechanical properties, permitted its application for the removal of plutonium and certain fission products such as ruthenium, zirconium, niobium from highly radioactive solutions [16], for concentrating uranium from sea water [17], and for coprecipitating Cu^{2+} [18], In^{3+} [19], SeO_2^{2-} [20] and PO_4^{3-} [21], as well as for adsorption of Sr^{2+} [22] and Fe^{3+} [23], etc.

It was therefore expected that titanium oxide could be utilized as a very promising and stable immobilizer for many cations of interest and could withstand opposing hydrothermal conditions in the repository.

Because barium activity (^{140}Ba) with high neutron fission yield and moderately short half-life, creates some problems in respect of its safe disposal, an attempt has been made here to study the immobilization behaviour of barium in a somewhat different manner, and also to investigate whether it could be accommodated in higher quantities over titanium oxide material than those obtained by earlier workers [9]. Cadmium and antimony cations were also included in the study due to their toxic and hazardous behaviour caused by nuclear and industrial wastes.

2. Experimental procedure

^{140}Ba, ^{115}Cd and ^{125}Sb (in their chloride forms), titanium tetrachloride, and $Ba(NO_3)_2$, $Cd(NO_3)_2 \cdot 6H_2O$, Sb_2O_3, ammonia, etc. of A.R. grade, were used.

Titanium hydroxide was precipitated (pH 8–8.5) by ammonia from a solution of titanic chloride in HCl, completely washed free of Cl^- dried at 70 °C for ~ 20 h and ground to powder. The prepared hydrous titania was characterized by differential thermal analysis (DTA) to ensure its thermal stability, intermediate phase modification, etc., and thermogravimetric analysis (TGA) was adopted to ascertain

0022–2461

the water content using a DT-40 thermal analyzer (Shimadzu, Japan) (Fig. 1). The formula of the titania was found to be $TiO_2 \cdot 0.73\ H_2O$.

Uptake characteristics of titania were investigated with ^{140}Ba, ^{115}Cd and ^{125}Sb cations by the batch method. Each of the activities, ~ 10 000 cpm (counts per minute) in 30 ml water at pH ~ 7 were shaken for 24 h at room temperature and the β activity of the solution part was measured using a Phillips type G. M. liquid counter (mica window 2.5 mg cm^{-2}, diameter 27.8 mm). A high uptake was observed for ^{140}Ba, ^{115}Cd and ^{125}Sb (Table I). The study was then extended to macro level concentrations of barium, cadmium and antimony cations for adsorption over titania. Various proportions of barium as $Ba(NO_3)_2$, cadmium as $Cd(NO_3)_2 \cdot 6H_2O$, and antimony as Sb_2O_3 in HCl were separately mixed with a finite quantity of $TiCl_4$ in HCl solution (calculated for 1 g TiO_2) and treated with ammonia gas until precipitation (pH 8–9) was complete, then filtered, washed with de-ionized water and made free from interfering anions. The amount of adsorbed cations in each case was determined by an ultraviolet spectrophotometer from the amount of cations originally taken and from the filtrate. The maximum uptake limit for each of the barium, cadmium and antimony cations over titania was thus determined (Fig. 2). The mixed precipitates were then separately 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 different temperatures in the range 800–1200 °C for 20 h, whereby the materials turned into a compact, stable and rigid form, possibly with the formation of new mineral phases.

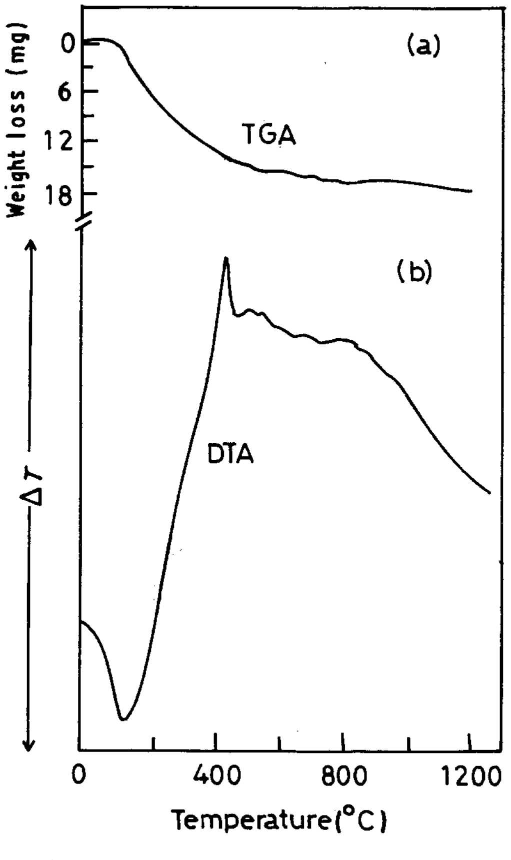

Figure 1 (a) TGA curve (range 20 mg); (b) DTA curve (range 100 mV), heating rate 20 °C min^{-1} up to 1200 °C.

TABLE I Uptake (%) of ^{140}Ba, ^{115}Cd and ^{125}Sb cations over Ti(IV) oxide (measured radiochemically)

Tracer cations	Uptake (%)
^{140}Ba (as chloride)	98.45
^{115}Cd (as nitrate)	99.30
^{125}Sb (as chloride)	87.63

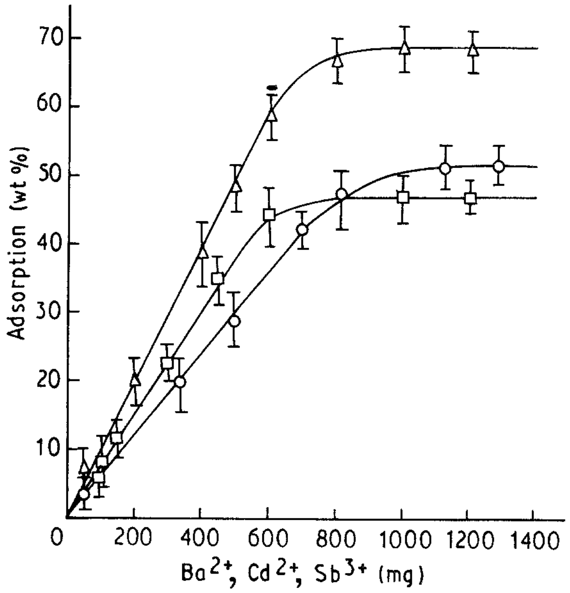

Figure 2 Extent of adsorption of (△) barium, (□) cadmium and (○) antimony cations during precipitation with titanium hydroxide.

Leaching tests for each calcined mass (0.5 g) were performed for 7 days at an interval of 24 h by immersing in deionized water at room temperature, and also separately in a Soxhlet apparatus by way of refluxing at 97 °C with deionized water as leachant; leached-out solutions were analysed spectrophotometrically, and the data obtained for the lowest leachability for the sample heated at 1200 °C for barium and cadmium, and at 1000 °C for antimony, were recorded (Table II and III).

The specific surface area of calcined titania sample was determined in a surface area analyser (BARC, Bombay, India) by the single-point BET method based on the physical adsorption of nitrogen gas by the sample at liquid nitrogen temperature, subsequent desorption at room temperature, and monitoring the changes in the nitrogen concentration; the value was determined to be 1.02×10^4 cm^2 g^{-1}.

The leachability, L_i, of the ith element was calculated from

$$L_i = M_i/C_iST\,(\mathrm{g\,cm^{-2}\,day^{-1}}) \qquad (1)$$

where M_i is the content of leached element i (g), C_i is the content of element i (g), S the specific surface area of the immobilizer (cm^2 g^{-1}), and T the immersion time (days).

Crystalline phases of different titania samples incorporating barium, cadmium and antimony cations, were characterized by studying the X-ray powder diffractograms obtained using a PW 1830 Phillips automated diffractometer with nickel-filtered CuK_α radiation (λ = 0.154 06 nm) (Fig. 3).

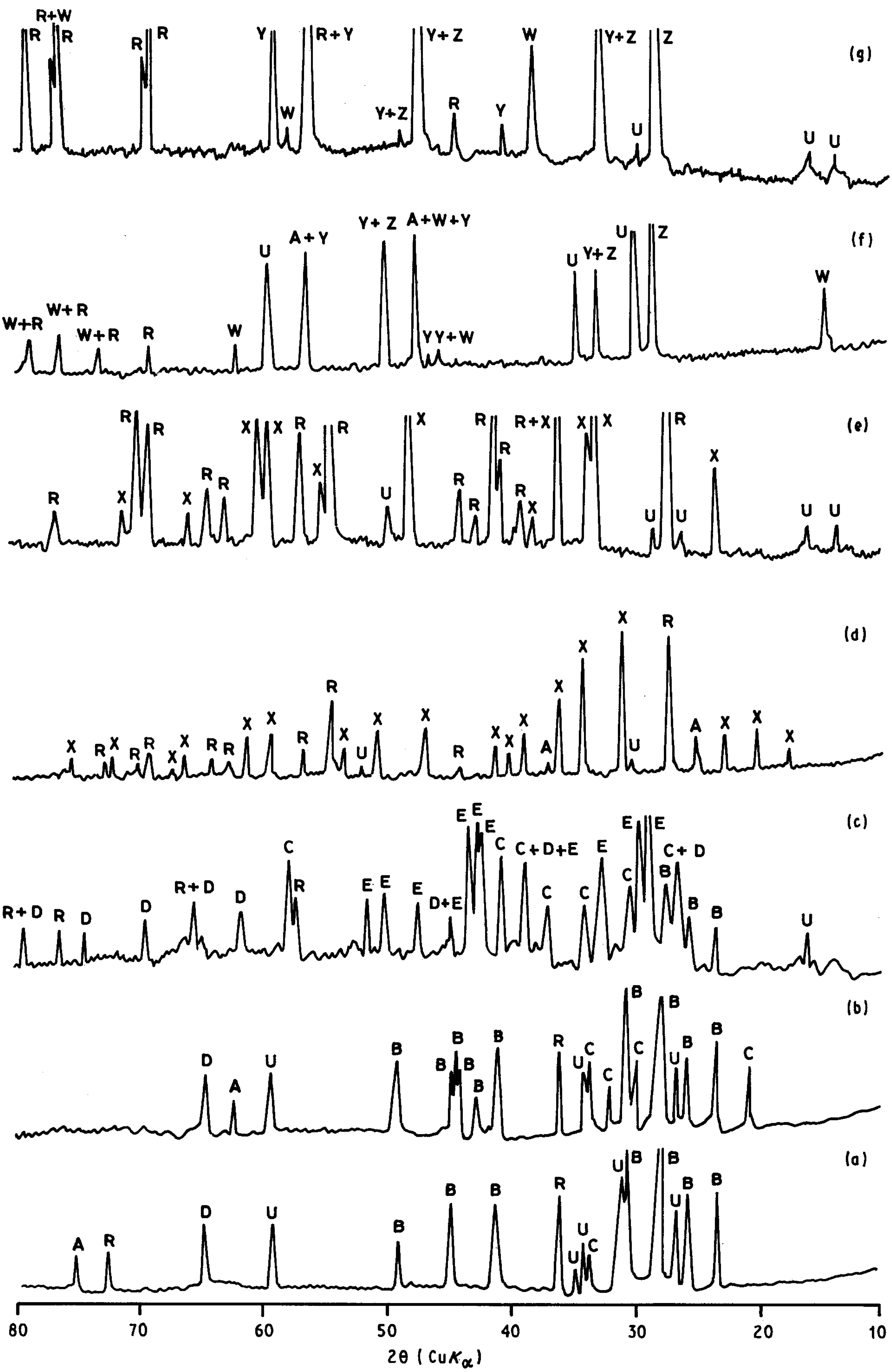

Figure 3 X-ray diffraction patterns of different mineral phases formed over titania with barium at (a) 800 °C, (b) 1000 °C, (c) 1200 °C, cadmium at (d) 800 °C, (e) 1000 °C, and antimony at (f) 1000 °C, (g) 1200 °C. B, $BaTi_5O_{11}$; C, $Ba_4Ti_{13}O_{30}$; D, $BaTiO_3$; E, $BaTi_2O_5$; X, $CdTiO_3$; W, Sb_6O_{13}; Y, $Sb_3Ti_2O_{10}$; Z, Sb_2O_3; R, rutile; A, anatase; U, unidentified.

TABLE II Leachability of barium, cadmium and antimony from the immobilizer at room temperature (27 °C) by immersion in deionized water (repeated seven times at an interval of 24 h)

Main probable minerals[a]	Leachability (10^{-10} g cm^{-2} day^{-1})						
	1	2	3	4	5	6	7
$BaTi_2O_5 + Ba_4Ti_{13}O_{30} + R$	7.92	7.80	7.35	6.90	6.45	5.80	5.12
$CdTiO_3 + U_1 + R$	9.05	8.75	8.80	7.42	6.40	5.91	5.29
$Sb_3Ti_2O_{10} + U_2 + R$	6.35	6.10	5.85	5.82	5.49	5.10	4.90

[a] R = rutile, U_1 and U_2 represent the unknown phases composed of TiO_2 with the relevant cations.

TABLE III Leachability of barium, cadmium and antimony in the immobilizer, by Soxhlet apparatus at 97 °C (repeated seven times with an interval of 24 h)

Main probable minerals[a]	Leachability (10^{-7} g cm^{-2} day^{-1})						
	1	2	3	4	5	6	7
$BaTi_2O_5 + Ba_4Ti_{13}O_{30} + R$	6.32	6.05	6.15	5.75	5.13	4.95	4.82
$CdTiO_3 + U_1 + R$	7.04	7.15	6.92	6.30	5.82	4.15	4.14
$Sb_3Ti_2O_{10} + U_2 + R$	4.45	4.20	3.82	3.50	2.90	2.35	2.16

[a] R = rutile, U_1 and U_2 represent unknown mineral phases composed of TiO_2 with relevant cations.

3. Results and discussion

Fig. 1 clarifies the possible thermal behaviour of hydrous titania obtained by DTA and TGA. The DTA curve shows that an endothermic peak at ~ 100 °C was obtained due to loss of moisture from the material. The exothermic peak at ~ 400 °C with small insignificant humps nearby, is related to the modification into an intermediate phase.

From the preliminary study of equilibration with ^{140}Ba, ^{115}Cd and ^{125}Sb, a very high uptake was observed (Table I) over the freshly prepared hydrous titania material. The highest uptake limit of these ions at the macro-concentration by precipitating barium, cadmium and antimony, as well as titanium hydroxide, was then determined. The titania was found to accommodate the following loadings: 69.02 wt % Ba, 52.00 wt % Cd, and 46.05 wt % Sb (Fig. 2). The composition formulae of the mixed solid masses with adsorbed cations were ascertained to be $Ba_5Ti_{1.5}O_8$, $Cd_3Ti_{2.5}O_8$ and $Sb_4Ti_4O_{14}$.

Because of its large cation exchange properties for Na^+ ions, hydrous titanium(IV)oxide has been described [24] as a cation exchanger of great promise (3.5 meq/g at pH 13); it exhibited a strong tendency for adsorption of barium, cadmium and antimony cations, both at tracer level and also at macro-concentrations when precipitated together with titanium hydroxide.

The samples calcined in the range 800–1200 °C were subjected to leaching tests; the leachability order was found to be in the range 10^{-9}–10^{-10} and 10^{-6}–10^{-7} g cm^{-2} day^{-1} for the deionized water immersion and Soxhlet apparatus refluxing, respectively. However, the lowest leachability was observed for barium and cadmium immobilizers heated at 1200 °C and antimony immobilizer heated at 1000 °C (Tables II and III).

It should also be pointed out here that the uptake of barium over preformed crystalline hydrated titania fibres was recorded to be 15.34 and 23.37 wt % for F- and M-type materials, respectively, by Fujiki *et al.* [9], whereas in the present investigation the loading of barium was found to be substantially increased because of its co-precipitation with titanium hydroxide. The nature of the assemblage of two elements in the mixed solid mass, either by adsorption or any other mechanism, is not yet clear, although the leachability order followed the same trend as was observed by Fujiki *et al.* [9].

The immobilization process was carried out by sintering the titania accommodated with cations at 800 °C and above. Barium ions were found to be immobilized in the mineral assemblages, consisting of the largest amount of $BaTi_5O_{11}$, small amounts of $Ba_4Ti_{13}O_{30}$ and $BaTiO_3$ followed by rutile and minor quantities of anatase, as corroborated from the X-ray diffraction peaks, obtained while heated at 800 °C for 20 h, which shows the total transformation of anatase to rutile has not yet occurred (Fig. 3a). When calcination was carried out at 1000 °C for 20 h, the mineral assemblage was found to suffer further transformation; it showed an increase in $Ba_4Ti_{13}O_{30}$ phase as well as the other phases mentioned above, with rutile and trace amounts of anatase. The existence of anatase is in agreement with the observations of Fujiki *et al.* [9], obtained by calcination for 1 h at the same temperature, although $BaTi_4O_9$ phase could not be identified from the X-ray diffraction pattern (Fig. 3b). On increasing the temperature to 1200 °C and heating for the same period, a new phase of $BaTi_2O_5$ has been found in large quantities. It appears that the $BaTi_5O_{11}$ phase might have decomposed to $BaTi_2O_5$ and TiO_2 (rutile). All the anatase phase was changed into a thermodynamically stable rutile form; other phases remained qualitatively the same with a small increase in $BaTiO_3$ (Fig. 3c). These results are in distinct contrast to those obtained by Fujiki *et al.* [9], who reported $BaTi_4O_9$ phase with rutile at the same temperature. However, their calcination was performed only for 1 h and the weight per cent adsorption of barium ions was less than that obtained by us. The difference may be attributed to the process of adsorption; Fujiki *et al.* adopted a batch technique of equilibration, whereas the present study used co-precipitation. It is thus quite possible that the calcination at 1200 °C suitably immobilizes barium in the crystal lattice of the rutile form of titania.

A similar investigation on cadmium-accommodated titania, calcined at 800 °C for 20 h, indicated the mineral assemblage contains mostly $CdTiO_3$ and rutile, with a small quantity of the anatase form of titania and traces of unidentified substances (Fig. 3d). It is also clear here that a partial conversion of anatase to rutile phase has taken place. However, complete transformation of anatase to rutile was observed at 1200 °C by heating for the same duration with the largest amount of $CdTiO_3$ including a few unidentified peaks (Fig. 3e). Because $CdTiO_3$ is the only phase so far reported on cadmium-bearing TiO_2, and the possibility of obtaining rutile (the more stable form of titania) is more certain at 1200 °C, as was observed in the barium immobilizer, the intermediate heating at 1000 °C was not attempted.

It has been reported [25] in antimony-doped titania, conversion of anatase to rutile commences in the temperature range 500–800 °C. In a previous study we also have found the presence of anatase phase at 1000 °C in barium and cadmium immobilizers. Here the calcination was performed at 1000 °C and above. The formation of a variety of phases is indicated by X-ray powder diffraction analysis on heating at 1000 °C (Fig. 3f). The contributions were due to $Sb_3Ti_2O_{10}$, a small quantity of Sb_6O_{13} and Sb_2O_3, rutile and anatase forms of TiO_2, with an unidentified phase corresponding to the maximum intensity of absorption. The matrix when heated to 1200 °C for the same duration changed to a softer texture, showing further phase modifications, in somewhat different proportions (Fig. 3g). The contributions of these phases appear to be due to Sb_2O_3, although a slight change of *d*-values and their corresponding intensities, was noted. Thus it is clear that the antimony cation has not been fully accommodated in the titania crystal lattice. Probably this might be the reason why the sample was found to be somewhat soft due to concomitant segregation and partial volatilization of antimony after calcination at 1200 °C. However, the substance still requires a detailed crystallographic investigation. It is apparent that although anatase phase (less stable than rutile) existed at 1000 °C, as described, the immobilization of antimony could best be performed at 1000 °C.

4. Conclusions

The results obtained above, taken as a whole, indicate that barium, cadmium and antimony cations were immobilized in the hydrothermally stable titania crystal lattice with the formation of different mineral phases. This property could well be utilized for radwaste disposal purposes and for other similar studies.

Acknowledgements

The authors thank the Analytical Chemistry Division, BARC, Bombay, India, for providing facilities for surface area measurements, Professor B. Ghosh, Head, L.T.P. Division, SINP, and Mr D. K. Ghosh, Central Glass and Ceramic Research Institute, Calcutta, for X-ray diffraction patterns.

References

1. T. B. BERNADZIKOWSKI, J. S. ALLENDER, J. A. STONE, D. E. GORDON, T. H. GOULD Jr and C. F. WEST III, *Amer. Ceram. Soc. Bull.* **62** (1983) 1364.
2. *Idem., ibid.* **62** (1983) 1390.
3. L. R. DOLE, J. G. MOORE, G. CROGERS, G. A. WEST, H. E. DEVNEY, M. T. MORGAN, E. W. McDANIEL and J. H. KESSLER, "Cementitious Radioactive Waste Hosts Formed Under Elevated Temperatures and Pressures (FUETAP Contrets)" in "Scientific Basis for Nuclear Waste Management" edited by S. V. Topp (North Holand, New York, 1982), pp. 555–93.
4. N. YAMASAKI, K. YANAGISWA, S. KANAHARA, M. NISHIOKA, K. MATSUOKA and J. YAMAZAKI, *J. Nucl. Sci. Technol.* **21**(1) (1984) 71.
5. P. E. D. MORGAN, D. R. CLARKE, C. M. JENTZEN and A. B. HARKER, *J. Am. Ceram. Soc.* **64** (1981) 249.
6. N. TSUNODA, *Ceram. Jpn* **12** (1977) 913.
7. R. TERAI, *ibid.* **16** (1981) 916.
8. A. E. RINGWOOD, "Safe Disposal of High Level Nuclear Reactor Wastes" (Australian National University Press, Canberra, 1978).
9. Y. FUJIKI, YU. KOMATSU and T. SASAKI, *Yogyo-kyokai-shi* **94**(3) (1986) 313.
10. Y. FUJIKI, YU. KOMATSU and N. OHTA, *Chem. Lett.* (1980) 1023.
11. Y. FUJIKI, T. SASAKI and YU. KOMATSU, *Yogyo-kyoki-shi* **93**(5) (1985).
12. T. SASAKI, YU. KOMATSU and Y. FUJIKI, *Chem. Lett* (1981) 957.
13. Y. FUJIKI, T. SASAKI and YU. KOMATSU, *Yogyo-kyoki-shi* **95**(5) (1987).
14. C. HEITNER-WIRGUIN and A. ALBU-YARON, *J. Appl. Chem. (Lond.)* **15** (1965) 445.
15. B. HOPKINS, "Chapter in the Chemistry of Less Familiar Elements", Vol. 1 (Stipes, Champaign, IL, 1939).
16. V. VESELY and V. PEKAREK, *Talanta* **19** (1972) 219–262.
17. N. J. KEEM, *J. Brit. Nucl. Energy* **7** (1968) 178.
18. V. I. PLOTINIKOV and V. L. KOCHETKOV, *Izv. Akad. Nauk. Kaz. SSR Ser. Fiz-Mat.* **5** (1967) 66.
19. I. N. MAKATOVA and A. I. MUN, *ibid.* **19** (1969) 74.
20. V. I. PLOTNIKOV and E. G. GIBOVA, *ibid.* **5** (1967) 58.
21. *Idem., ibid.* **5** (1967) 57.
22. H. W. LEVI and E. SCHIEWER, "Radiochim" **5** (1966) 126.
23. I. V. RISKIN and T. VELIKOSLAVINSKAYA, *Zh. Prikl. khim (Leningrad)* **42** (1969) 1400.
24. Y. INOUE and H. YAMAZAKI, *J. Nucl. Sci. Technol.* **24** (1987) 462.
25. F. J. BERRY and P. M. GOGARTY, *J. Chem. Soc. Dalt. Trans.* (1988) 2161.

Received 30 September 1991
and accepted 17 February 1992