Long Term Stability of Yttria-Stabilized Zirconia Waste Forms - Stability for Secular Change of Partitioned TRU Waste Composition by Disintegration -

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1. Introduction

The purpose of this study is R & D on yttria-stabilized zirconia (YSZ) as waste forms used in the Partitioning - Conditioning, which is ceramic solidification and disposal of partitioned TRU wastes. This TRU waste will arise from the 4-group partitioning[1] of high level radioactive wastes. And exceptional radioisotope-institute wastes mainly composed of TRU nuclides must be treated in the same manner as the partitioned TRU wastes. Isolation of these hazardous TRU wastes from the biosphere is one of the most important concepts for the management of radioactive waste. It is necessary for the partitioned TRU wastes to be immobilized stable ceramic forms chemically and physically, because the partitioned TRU wastes almost compose of TRU nuclides which are hazardous α-emitters with extremely long half-lives.

On the viewpoint of R & D on ceramic waste forms for the partitioned TRU waste, properties of ceramic waste forms must be evaluated. It is important for as-fired ceramic waste forms to research and evaluate phase stability, chemical durability, mechanical property, thermal property etc as initial properties of waste forms. In addition long-term stability, e.g. stability for irradiation damage, stability for secular change of waste composition by disintegration etc, is also requested to ceramic waste forms. In the previous studies yttria-stabilized zirconia, alumina compounds and YSZ-alumina composite ceramics were nominated as waste forms for immobilization of the partitioned TRU waste, and characterized with emphasis on phase stability, chemical durability and compactness[2]. From the results YSZ with a fluorite-type structure of cubic system was selected as a waste form for the partitioned TRU wastes[3] and was expected to show good properties. In the last 2 years Np and/or Am-doped YSZ waste forms have been studied in JAREI. Phase stability and mechanical property of Np-doped YSZ waste forms (Np-YSZ) will be introduced in this

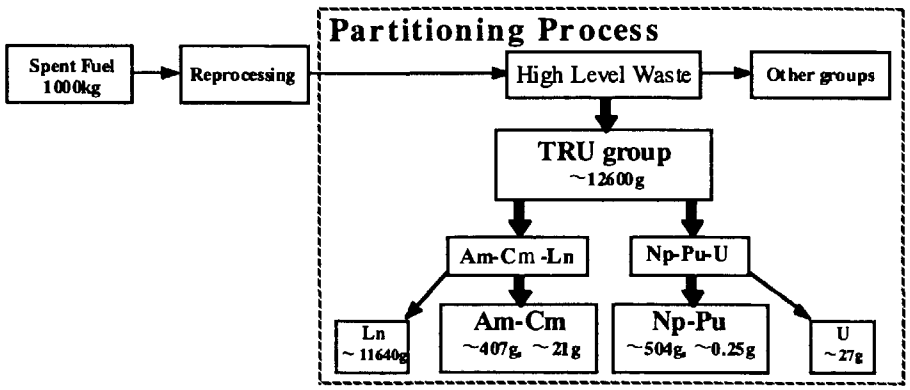

Fig. 1 Flow of TRU nuclides from spent fuel to the products in a partitioning process.
The amounts of each production per 1000 kg of spent fuel are also indicated in this figure.
All values are normalized to their oxide weights.

symposium[4]. In addition, chemical durability of Np-YSZ is under evaluation. Stability for irradiation damage of ^{244}Cm-doped YSZ waste forms, the most important term in long term stability, is now under consideration.

In this study the stability of YSZ waste forms for secular change of partitioned TRU waste composition by disintegration, one of important terms in long-term stability, is the special concern. It must be investigated and evaluated that the fluorite-type structure can be formed in YSZ waste forms with Pb and Bi, final daughters of TRU nuclides, because Zr oxide can't form solid solution in the wide range with these elements[5]. In addition quantitative understanding of effect of secular changes on the other properties, such as chemical durability, mechanical property and so on, is necessary for long-term safety assessment of final disposal.

In this study designed amount of wastes and YSZ powder were mixed and sintered. These waste forms were submitted to tests of phase stability, chemical durability, mechanical property and compactness. The results were compared with those of the "initial" YSZ waste forms, non-radioactive Ce and/or Nd doped YSZ samples and glass and Synroc waste forms.

2. Secular change of the partitioned TRU waste

Figure 1 shows a flow of TRU nuclides arising from reprocessing + partitioning process. Large amounts of Pu and U will be removed form high level liquid waste in a reprocessing process[6], and the waste will be partitioned to 4 groups; "TRU" group, "Sr-Cs" group, "Tc-platinum group metals" group and "the other" group. The TRU group will be separated to different 2 fraction; one is Np-Pu fraction contaminated by small amount of U and the other is Am-Cm fraction including lanthanide elements. And then U and lanthanide elements are removed from Np-Pu and Am-Cm fractions, respectively. In this case about 900 g of oxides of Np-Pu and Am-Cm fractions takes place from 1000 kg of spent fuel.

There are 4 regions in the partitioned TRU waste composition from Np-Pu and Am-Cm fractions by secular change as shown in Fig. 1. Where these compositions were calculated with reference to ORIGEN2 code[7], half lives and disintegration mechanism of the data base[8]. In

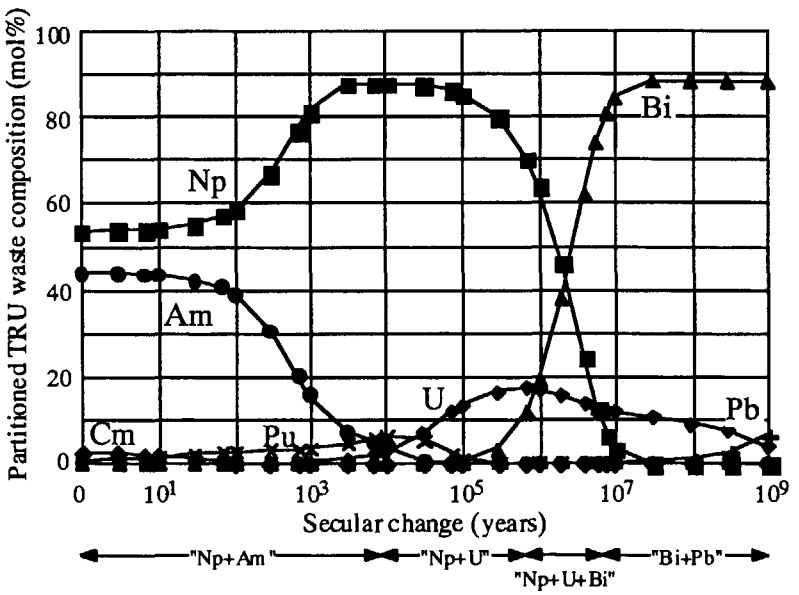

Fig. 2 Secular change of partitioned TRU waste composition ("Np-Pu" + "Am-Cm" fraction) by disintegration.

general, the "4N+1" series of TRU nuclides including ^{241}Am, ^{237}Np etc disintegrate and turn to nonradioactive ^{207}Bi, and the nuclides of other series turn to nonradioactive Pb. The first region is that only Np and Am are included in the waste illustrated by the mark "Np+Am" in Fig. 2 (0 - 10^4 years). The initial composition of the partitioned TRU waste is indicated as "0 year" of secular change, where contents of Np and Am are 53.4 mol% and 43.8 mol%, respectively. Content of Am decreases and that of Np increases by disintegration in this region. The second is the region mainly composed of Np and U as shown by the mark "Np+U" in Fig. 2 (10^4-10^5 years). In this region full amount of ^{243}Am, ^{242m}Am, ^{244}Cm and small amount of ^{237}Np disintegrate and turn to ^{235}U, ^{234}U, ^{236}U and ^{233}U, respectively, therefore the amount of total U increases. The third is of Np, U and Bi (the mark "Np+U+Bi", 10^5-10^7 years). Almost of ^{237}Np disintegrates and turns to ^{207}Bi, and the amount of U with longer half lives than ^{237}Np decreases little by little. And the fourth is of almost nonradioactive ^{207}Bi and Pb (the mark "Bi+Pb", over 10^7 years). In this study YSZ waste forms including wastes with various compositions corresponding to the "Np+Am", "Np+U" and "Np+U+Bi" regions were researched.

3. Experimental procedure

Compositions of YSZ waste forms examined in this study are listed in Table 1. Contents of the partitioned TRU wastes included in YSZ waste forms are limited to 10 mol% to avoid extreme external exposure. Cerium and a part of Am were used as substitutes of Cm and U, respectively. Commercial powder of YSZ (TZ-8Y; Tosoh Co.Ltd) and the designed amount of waste components were mixed, calcined at 900 °C for 2 hrs and crushed in a zirconia ball mill with ethanol. After that these powders were pelletized using a uniaxial hand press and sintered at 1500 °C for 80 hrs in the stream of air.

Table 1 Composition of yttria-stabilized zirconia waste forms, in mol%*

Sample	1	2	3	4	5	6	7
Region	Initial	Np+Am		Np+U	Np+U+Bi		
Waste							
$AmO_{1.5}$	4.59	2.02	0.80	0.00	0.00	0.00	0.00
NpO_2	5.41	7.98	9.20	7.98	6.35	4.60	2.40
CeO_2	0.00	0.00	0.00	1.68	1.74	1.60	1.42
$BiO_{1.5}$	0.00	0.00	0.00	0.34	1.91	3.80	6.18
Matrix							
ZrO_2	77.13	77.13	77.13	77.13	77.13	77.13	77.13
$YO_{1.5}$	12.87	12.87	12.87	12.87	12.87	12.87	12.87
Secular change (years)	0	70	3×10^3	3×10^5	1×10^6	2×10^6	4×10^6

* Compositions of each constituent indicate the contents of each cation to total cations in mol%.

For evaluation of phase stability, crystalline phases formed in YSZ waste forms were identified by XRD method using crushed powder specimens. Lattice parameters of fluorite-type structure were calculated by Nelson-Riley method[9] using positions of peaks depending on fluorite-type structure. Volume change (ΔV, in %) of YSZ waste forms with various composition of wastes were evaluated by the equation (1). Where, a_0 is a lattice parameter, length of unit cell of fluorite-type structure, of the initial Np+Am-doped YSZ waste form (sample No.1) in nm and a_i is that of each YSZ waste form in nm. Mechanical properties of Vicker's hardness (Hv; GPa), Young's modulus (E; GPa) and fracture toughness (K_{IC}; $MPam^{1/2}$) of YSZ waste forms were measured using a micro

$$\Delta V = (a_i / a_0)^3 \quad (1)$$

$$Hv = 0.464 \cdot N / Vi_1^2 \quad (2)[10]$$

$$E = 0.45 \cdot Hv / (0.143 - Kn_2 / Kn_1) \quad (3)[11]$$

$$K_{IC} = 0.026 \cdot \sqrt{E} \cdot \sqrt{N} \cdot Vi_1 \cdot Vi_2^{-1.5} \quad (4)[12]$$

$$d_{rela.} = d_{app.} / d_{thro.} \quad (5)$$

$$d_{app.} = W_1 / (W_1 - W_2) \quad (6)$$

hardness testing machine with Vickers and Knoop indenters. Specimens used in mechanical property evaluation were cut off into pellets of 3 mm in diameter by a core drill, mounted in an acrylic holder and polished by sandpapers and diamond paste up to 1 μm. Hv, E and K_{IC} were measured by the equations of (2), (3) and (4). Where, Vi_1, Vi_2, Kn_1 and Kn_2 are lengths illustrated in Fig. 3 in meter, and N is weight loaded to indentators in N. Densities of YSZ waste forms were measured by the water displacement method using pellet specimens to evaluate compactness of YSZ waste forms by the equations of (5) and (6). Where, $d_{app.}$ is apparent density in g/cm^3, W_1 and W_2 are weights of specimens in air and in water, respectively. And $d_{rela.}$ is a relative density in % and $d_{theo.}$ is a theoretical density calculated from a_i and weight of unit cell of fluorite-type structure of each sample in g/cm^3.

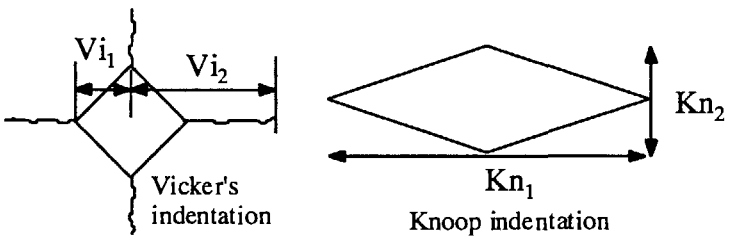

Fig. 3 Measurement of Vicker's and Knoop indentaions.

These properties were compared with the initial Np+Am-doped YSZ waste form to evaluate stability for secular change of the partitioned TRU waste composition by disintegration. In addition comparisons with Np-YSZ, Ce (nonradioactive)- and/or Nd (nonradioactive)- doped YSZ samples, and with other waste forms were attempted.

4. Results and Discussions

4.1 Phase stability

Figure 4 shows XRD patterns of the initial Np+Am-doped YSZ waste form (sample No. 1) and a Np+U+Bi-doped YSZ waste form (sample No. 7). In each pattern 9 peaks appear in the region of 20 to 100 degrees of 2θ. These peaks are evidence for the formation of fluorite-type structure in these YSZ waste forms. XRD patterns of the other 5 YSZ waste forms also indicated 9 peaks in the same region however peak positions slightly shifted because of difference of waste composition of these samples. Crystalline phases formation mainly composed of Bi were considerable because Zr oxide would not react with Bi and not form a solid solution in the wide range as mentioned before, but in this study the phases mainly composed of Bi could not be identified. From the results of XRD measurement, only fluorite-type structure could be identified in all YSZ

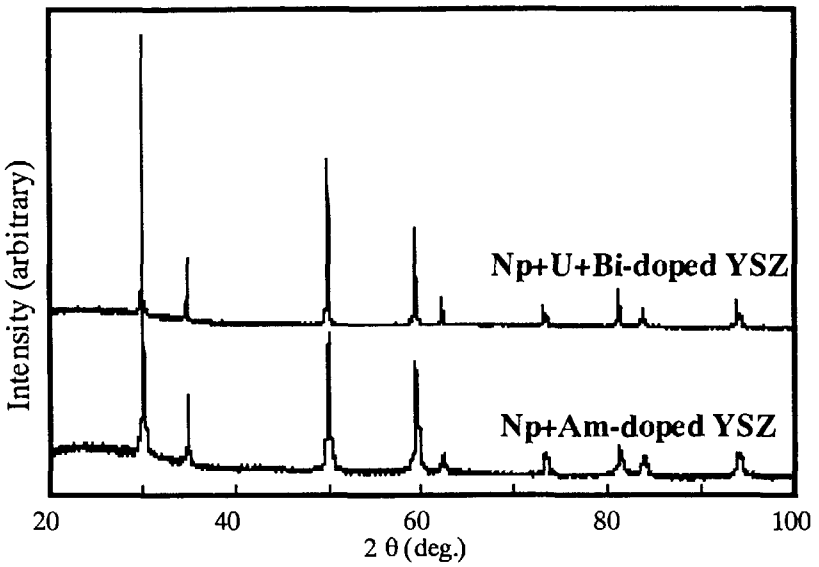

Fig. 4 XRD patterns of the initial Np+Am-doped YSZ waste form and a "Np+U+Bi"-doped YSZ waste form (sample No.7).

waste forms measured in this study. This means that the fluorite-type structure is stable for the secular change of the partitioned TRU waste composition by disintegration and that YSZ waste forms evaluated in this study is also good for phase stability. Neptunium-YSZ[4] and non-radioactive Ce and/or Nd-doped YSZ waste forms[2] also show excellent phase stability.

For the volume change of YSZ waste form calculated using lattice parameters of fluorite-type structure, the results are shown in Fig. 5. The volume increased with the increase of Np content in wastes composition in the region of the "Np+Am". Maximum value of volume increase was 0.8 % in the region of "Np+U", corresponding to several 10^5 yrs, and after that the volume decreased slowly. In general, volume change may lead to the chinks or the increase of internal pressure in waste forms disposed in deep underground. The chinks will cause the increase of contact probability with underground water. Waste forms, canisters and other engineered barrier materials might be destroyed by the increase of internal pressure by waste forms and external pressure by expansion of buffer materials. On the other hand it is well known that volume of ^{244}Cm-doped Synroc increased up to 3 % by internal irradiation[13]. In this way, irradiated waste forms are expected to expand by α and recoiled particles. Therefore, it is important to evaluate that the volume change of YSZ waste forms by the secular change of compositions will act as an accelerator or a mitigator for the volume increase by α-decay damage of crystals. The result in this study means that the volume change by the secular change will accelerate the volume increase of YSZ waste

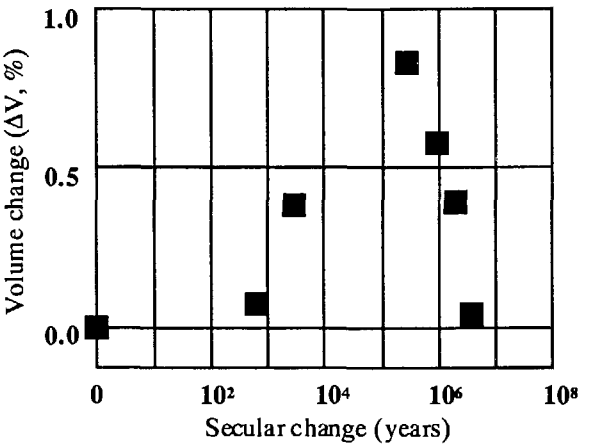

Fig . 5 Volume change of "Np+Am"-, "Np+U"- and "Np+U+Bi"-doped YSZ waste forms by the secular change of the partitioned TRU waste composition by disintegration.

forms in the regions of the "Np+Am" and "Np+U". However in the region of the "Np+U+Bi", the volume change for the secular change will act as a mitigator in the whole volume change phenomenon.

4.2 Mechanical property

Mechanical properties of Vicker's hardness (Hv), Young's modulus (E), fracture toughness (K_{IC}) of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms are illustrated in Fig. 6. In this study pelletized specimens were limited to "Np+U"- and "Np+U+Bi"-doped YSZ waste forms to avoid extremely external exposure. Hv, E and K_{IC} of these YSZ waste forms were 10 to 12 GPa, 220 to 300 GPa and about 2 $MPam^{1/2}$, respectively. It is evident that these values are independent of the secular change of the partitioned TRU wastes compositions and the averages were 11.5 GPa, 266 GPa and 1.9 $MPam^{1/2}$, respectively as shown in Fig. 6. This leads to an evaluation that the secular change of the partitioned TRU wastes composition by disintegration don't effects on mechanical properties of YSZ waste forms. Further these values were almost the same as those of Np-YSZ and those of Ce-, Nd- and Ce+Nd-doped YSZ[9] as shown in Fig. 7. In addition Hv, E and K_{IC} of YSZ waste forms were more enough than those of a glass waste form and Synroc waste forms[10],[11]. This means that mechanical properties of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms as well

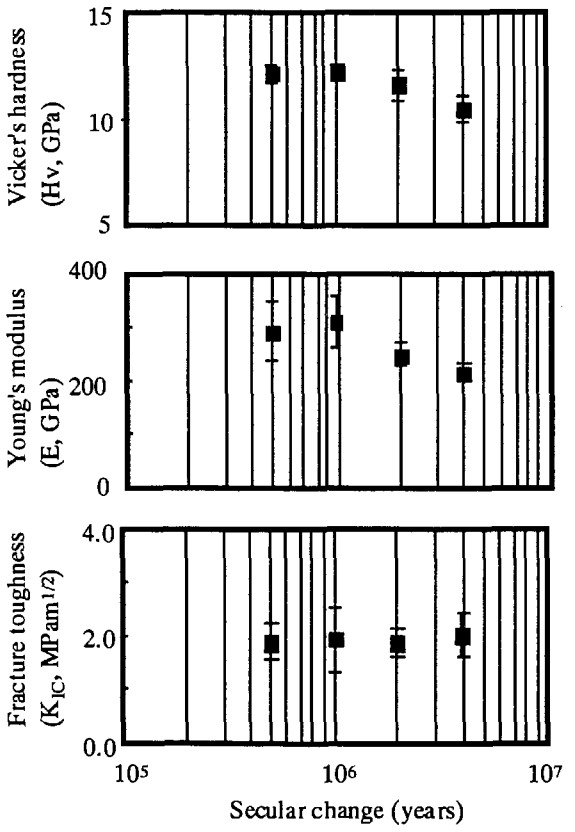

Fig. 6 Mechanical properties of Vicker's hardness (Hv), Young's modulus (E) and Fracture toughness (K_{IC}) of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms.

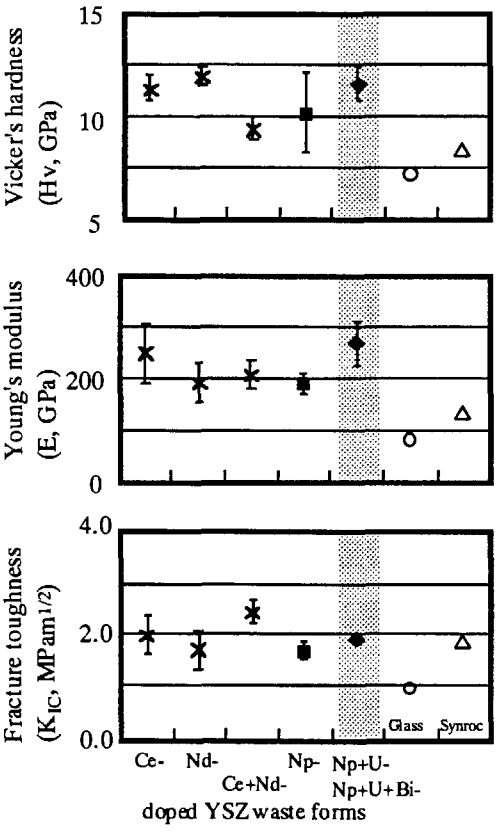

Fig. 7 Comparison of mechanical properties of Vicker's hardness, Young's modulus and fracture toughness of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms with those of Ce- and/or Nd-doped YSZ waste forms, and those of a glass and Synroc waste forms.

as Np-YSZ, Ce and/or Nd-doped YSZ were also good enough for a radioactive waste forms.

4.3 Compactness

Relative density, drela. (ratio of apparent density to theoretical density) of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms were measured. All these values were over 93 %, and the result is similar to those of Np-doped YSZ waste forms. Therefore compactness of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms are evaluated as good. However the tendency that relative densities decrease with the secular change of the partitioned TRU wastes compositions. The reason of the tendency could not be cleared in this study.

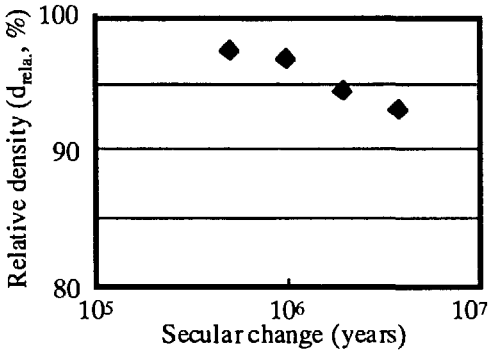

Fig. 8 Densities of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms and secular change of the partitioned TRU waste composition.

5. Conclusions

One of the long-term stability, the stability for secular change of the partitioned TRU wastes composition by disintegration in YSZ waste forms were evaluated in this study. The results of phase stability, mechanical property and compactness were followings;

(1) Phase stability of "Np+Am"-, "Np+U"- and "Np+U+Bi"-doped YSZ waste forms could be maintained of that of the initial Np+Am-doped YSZ waste form permanently even when the composition of partitioned TRU waste changed by disintegration,

(2) secular change also accelerated volume increase of YSZ waste forms as well as α-decay damage,

(3) Hv, E and K_{IC} of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms were independent of the secular change of the partitioned TRU waste composition by disintegration,

(4) mechanical properties of YSZ waste forms were good enough as waste forms because Hv, E and K_{IC} of "Np+U"- and "Np+U+Bi"-doped YSZ waste forms were more than those of a glass and Synroc waste forms, and

(5) compactness of YSZ waste forms was good as waste forms for the partitioned TRU wastes.

From these conclusions and those from Np-doped YSZ waste forms, YSZ waste forms is expected as a host material to immobilize high concentrated TRU nuclides such as the partitioned TRU waste.

References

(1) Y.Morita and M.Kubota, "Wet partitioning and waste treatment", Radioact. Waste Res., Vol.2 (1&2), 75-83 (1996) (in Japanese).

(2) K.Kuramoto, Y.Makino, T.Yanagi, S.Muraoka and Y.Ito, "Development of zirconia- and alumina-based ceramic waste forms for high concentrated TRU elements", Proc. of "International Conference on Evaluation of Emerging Nuclear Fuel Cycle Systems (GLOBAL 95), 1838-45 (1995).

(3) K.Kuramoto, H.Mitamura, T.Banba and S.Muraoka, "Development of ceramic waste forms for actinide-rich waste", Progress in Nuclear Energy, 32 (3/4), 509-516 (1998).
(4) H.Kinoshita, K.Kuramoto, M.Uno, S.Yamanaka, H.Mitamura and T.Banba, "Phase stability of yttria-stabilized zirconia for partitioned TRU waste", JAREI-Conf. 00-00 (Proc. Of the 2nd NUCEF International Symposium, 00-00 (1998).
(5) "International centre for diffraction data", ed. by M.King et al., JCPDS, USA (1996).
(6) C.Phillips, "Operating experience of the solvent extraction processes in the thermal oxide reprocessing plant", Proc. ISEC ' 96 (Value Adding Through Solvent Extraction), Vol.1, 783-788 (1996).
(7) A.G.Croff,"ORIGEN2: A Versatile computer code for calculating the nuclide compositions and characteristics of nuclear materials," Nucl.Technol., 62, 335-52 (1983).
(8) E.Browne and R.B.Firestone, "Table of radioactive isotopes", Ed. V.S.Shirley, John Wiley & Sons Inc. (1986).
(9) C.Whiston, "X-ray method", ed. by C.Whiston, 132-164, John & Sons, New York (1985).
(10) Japan Industrial Standard (JIS) (in Japanese), R 1607 (1995).
(11) D.B.Marshall, T.Noma and A.G.Evans, "A simple method for determining elastic-modulus-to-hardness ratios using knoop indentation measurements", Commu. of Am.Seram.Soc, Oct., C-175-76 (1982).
(12) Japan Industrial Standard (JIS) (in Japanese), R 1607 (1995).
(13) T.J.White, H.Mitamura and T.Tsuboi, "Reitveld analysis of phase separation in annealed and leach tested Cm-doped perovskite", 871-878, in Scientific basis for nuclear waste management XVIII, Materials research Society, PA (1995).
(14) A.E.Ringwood et al., "Synroc"; pp. 233-334 in *Radioactive Waste Forms for the Future.* Ed. by W.Lutze and R.C.Ewing, Elsevier Science Publishing Company, New York, NY, 1988.
(15) W.Lutze and R.C.Ewing, "Summary and evaluation of nuclear waste forms"; pp. 699-740 in *Radioactive Waste Forms for the Future.* Ed. by W.Lutze and R.C.Ewing, Elsevier Science Publishing Company, New York, NY, 1988.