JOURNAL OF MATERIALS SCIENCE 28 (1993) 513–517

Durability of an $La_2Zr_2O_7$ waste form in water

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The effects of time, temperature and pH on the leaching rates of an $La_2Zr_2O_7$ waste form were studied. The leaching rates of each constituent measured in deionized water and an alkaline solution (pH = 10) were less than about 10^{-5} g m^{-2} d^{-1} at 90 °C and were smaller than those in an acid solution (pH = 1) by one order of magnitude. It was found that the leaching rate of zirconium obtained after immersion for 34 days decreases with increasing temperature in an acid solution. This exceptional phenomenon is attributed to the formation and decomposition of zirconium complexes with CO_3^{2-} ligands.

1. Introduction

Solidification of transuranium (TRU) elements contained in high-level nuclear waste was the subject of this work, because they generally have very long half-lives and last for millions of years in geological period.

Zirconium is suitable as a major constituent of a TRU waste form for the following three reasons. First, Zr–O bonds in a crystal have a bond energy of about 81 kcal mol^{-1} which is relatively high compared to other metal–oxygen bonds, and they are not easily separated in water [1–3]. Second, zirconium forms an insoluble hydrate in the pH range 1.7–10.5 [4]. Third, zirconium oxide compounds with other metal cations tend to confine a considerable amount of actinide and lanthanide elements in their crystal structures [5, 6].

In our previous work, $La_2Zr_2O_7$ with a pyrochlore structure showed good durability in water [7, 8]. Because $La_2Zr_2O_7$ has a low leaching rate, it is necessary to use powdered samples in order to increase their leachable surface areas. In the present study, we examined the effects of the particle size, leachant exchange method and stirring during leaching tests on the leaching rates of each constituent, and then the durability of an $La_2Zr_2O_7$ waste form in various waters was determined.

2. Experimental procedure

Nitrates of lanthanum and zirconium were mixed with nitrates of simulated waste elements $Ce(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$ and $Sr(NO_3)_2$ at levels equal to 1.3 wt % CeO_2, 2.08 wt % Nd_2O_3, and 0.53 wt % SrO, respectively. The nitrates were dissolved simultaneously in 0.5 M HNO_3 to obtain a uniform solution. The solution was dried at 100 °C and then calcined at 700 °C to denitrate it. The calcined powder was uniaxially pressed at 500 kg cm^{-2} into pellets 2 cm diameter and 0.5 cm thick. These pellets were sintered at 1400 °C for 16 h in air and ground to powders in a mortar. The powders were classified into particle sizes of 125–250, 75–125, and < 75 μm through the sieves.

We used the leachant exchange method described below to obtain the leaching rates of each constituent. The classified powders were immersed in an HCl solution of pH = 1.0, deionized water of pH = 5.6 or an NaOH solution of pH = 10 at 40, 90 or 150 °C. The powders were immersed for a given period, and then the leachate was collected by decantation and fresh leachant was added. After leaching for about 4 days, the leachate was again collected by decantation. These operations were repeated. Part of the leachate collected by decantation was subjected to concentration measurements and the rest was filtered through a membrane of 0.45 or 0.025 μm. To examine the effect of stirring on leaching rates, the leachate was stirred for about 10 s once a day and the results after stirring were compared with those without stirring.

The acidity of the collected leachate was immediately adjusted to pH = 1 by the addition of HCl solution. Concentrations of elements in the acidified leachate were analysed by inductively coupled plasma atomic emission spectroscopy (ICP).

The extent of leaching is expressed as the leaching rate for element i (L_i) which is normalized as follows

$$L_i = C_i V/(f_i S T) \qquad (1)$$

where C_i (g m^{-3}) is the concentration of element i in the leachate, V (m^3) is the volume of the leachate, f_i is the mass fraction of element i in the unleached solid, S (m^2) is the geometric surface area of the specimen measured by the BET method, and T (d) is the leaching time during which the leachant is kept unchanged. The value of L_i is normalized to the weight fraction of element i in the bulk, and is, therefore, suitable for the comparison with those of other waste forms.

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TABLE I Effects of powder size on leaching rates in deionized water at 90 °C

Particle size (μm)	Method of collection	Leaching rate ($g\,m^{-2}\,d^{-1}$)		
		Zr	La	Sr
125–250	Decantation after 3 days	1.5×10^{-6}	4.8×10^{-6}	5.9×10^{-3}
< 75		1.4×10^{-6}	4.8×10^{-6}	5.7×10^{-3}
125–250	0.45 μm filter after 3–4 days	–	1.9×10^{-5}	1.5×10^{-4}
< 75		–	1.1×10^{-5}	1.6×10^{-4}

TABLE II Effects of stirring on leaching rates in deionized water at 90 °C

Stirring	Method of collection	Leaching rate ($g\,m^{-2}\,d^{-1}$)		
		Zr	La	Sr
Day by day for 4 days	Decantation	9.3×10^{-6}	4.3×10^{-5}	1.9×10^{-4}
	Filtration[a]	$< 8.8 \times 10^{-7}$	1.3×10^{-5}	1.8×10^{-4}
No stirring	Decantation	$< 9.0 \times 10^{-7}$	1.3×10^{-5}	2.7×10^{-4}
	Filtration[a]	$< 1.2 \times 10^{-6}$	9.2×10^{-6}	2.9×10^{-4}

[a] Filtered through a 0.45 μm membrane.

3. Results

3.1. Effects of the leaching method on leaching rates

Table I shows the effects of secondary particle sizes on the leaching rates. The effect of secondary particle sizes on the leaching rates is not clearly observed. The powders used in these experiments consisted of fine crystal grains of about 1 μm diameter, and had a constant surface area of about 9 $m^2\,g^{-1}$ which was independent of secondary particle size. The leaching rates in the present experiments were calculated using the BET surface area. Troester *et al.* [9] showed that the surface areas determined by the BET method were suitable for calculating leaching rates but that those calculated from the secondary particle sizes were not. We think that when the sintered bodies containing fine grains of about 1 μm diameter are ground to powders, the specific surface area of the powders is mainly determined by the surface area of the fine grains, and the leaching rates do not depend on the secondary particle size.

The effects of stirring on leaching rates are shown in Table II. The leaching rates of zirconium and lanthanum were increased by stirring; on the other hand, that of strontium decreased. When the leachant was stirred, the leaching rates of zirconium and lanthanum were greater than those without stirring. This may be due to the separation of precipitates from the powder by the stirring.

Table III shows the effects of the leachate collection method on leaching rates. No considerable difference in the values of the leaching rates was found. However, unusually high leaching rates were sometimes observed after the decantation. This was because fine particles were taken from the leachate by decantation. Note that the time for leachates to pass through a 0.025 μm membrane was much longer than that through a 0.45 μm membrane.

Thus, the following three points were taken into account in all subsequent leaching tests.

TABLE III Effects of collecting methods on leaching rates in deionized water at 90 °C

Collecting method	Leaching rate ($g\,m^{-2}\,d^{-1}$)	
	La	Sr
Decantation	1.3×10^{-5}	1.6×10^{-4}
0.45 μm pass	1.1×10^{-5}	1.6×10^{-4}
0.025 μm pass	1.1×10^{-5}	1.6×10^{-4}

1. Classification of the particle-size distribution was not necessary when the powders consist of fine crystal grains of less than 1 μm diameter.
2. During leaching experiments, stirring was not applied.
3. The leachate was filtered through a 0.45 μm membrane.

3.2. Effects of leaching time, temperature and pH

3.2.1. Effects of leaching time

Fig. 1 shows the leaching rates in an acid solution (pH = 1). The data in Fig. 1 show that the leaching rates in an acid solution decrease with time when the leachant is exchanged repeatedly after the initial static period of 1, 5 or 34 days. The leaching rates of strontium, lanthanum and zirconium decrease with time and then converge to constant values. The initial great decrease of leaching rates can be explained by the dissolution of unreacted or incompletely reacted constituents in the waste form. The leaching rate of strontium is highest of all the constituents and converges to about $10^{-3}\,g\,m^{-2}\,d^{-1}$. The leaching rate of lanthanum is smaller than that of strontium by one order of magnitude. Although the leaching rates of neodymium and cerium are not shown in Fig. 1, they were nearly the same as those of lanthanum. The leaching rate of zirconium is about $10^{-6}\,g\,m^{-2}\,d^{-1}$ and is the lowest of all the constituents.

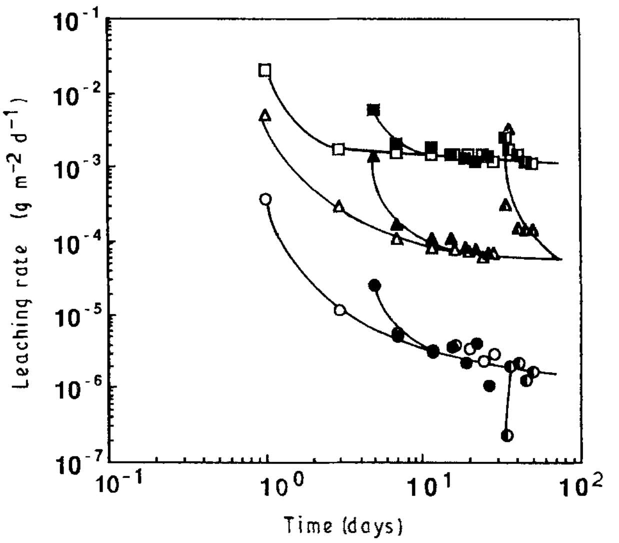

Figure 1 Leaching rates in an acid solution (pH = 1) at 90 °C after immersion for 1, 5 and 34 days. Note that leaching rates converge to approximately the same values independently of the immersion time. (○) Zr1, (△) La1, (□) Sr1, (●) Zr5, (▲) La5, (■) Sr5, (◐) Zr34, (◭) La34, (◧) Sr34.

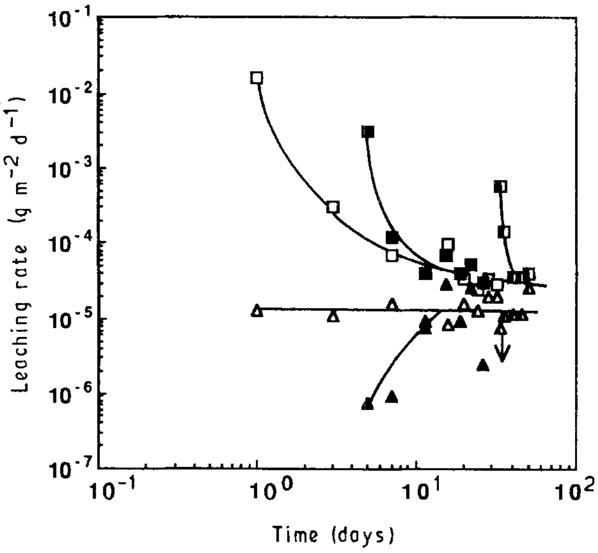

Figure 2 Leaching rates in deionized water at 90 °C after immersion for 1, 5 and 34 days. Note that leaching rates converge to approximately the same values independently of the immersion time. (△) La1, (□) Sr1, (▲) La5, (■) Sr5, (◭) La34, (◧) Sr34.

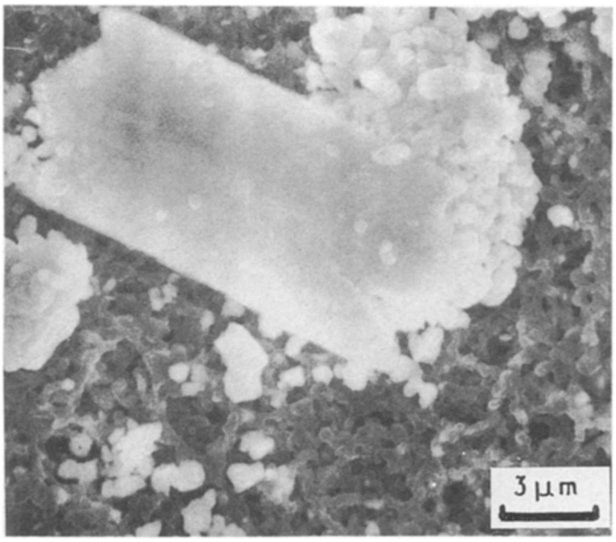

Figure 3 Scanning electron micrograph of a plate-like particle presumed to be $La_2(CO_3)_3$. It was found in the floating matter collected on a membrane filter.

The difference in the leaching rates of strontium, lanthanum and zirconium may depend on the difference in their bond energy with oxygen. The bond energy of metal–oxygen is 32 kcal g atom^{-1} for strontium 51 kcal g atom^{-1} for lanthanum and 81 kcal g atom^{-1} for zirconium [1]. The leaching rates of each constituent decrease as its bond energy increases.

Fig. 2 shows that the leaching rates of lanthanum and strontium converge to a constant value in deionized water as well as in an acid solution. The leaching rate of strontium decreases with time and is $3 \times 10^{-5}\,\mathrm{g\,m^{-2}\,d^{-1}}$ after 50 days. On the other hand, the leaching rate of lanthanum is initially small and then converges to about $1 \times 10^{-5}\,\mathrm{g\,m^{-2}\,d^{-1}}$. Because the concentrations of zirconium, cerium and neodymium in the leachate could not be measured with the ICP apparatus, their leaching rates are not shown in Fig. 2. The initial small leaching rate of lanthanum can be explained by the increase in pH which is due to the dissolution of strontium. The Eh(oxidation-reduction potential)–pH diagram for the system La–C–O–H shows that insoluble $La_2(CO_3)_3$ is stable in the pH range of > 7. Hence, the dissolution of strontium enhances the formation of $La_2(CO_3)_3$ which decreases the concentration of lanthanum ions. The particles floating on the surface of the leachate were collected on a membrane filter and were observed by SEM–EDX. Fig. 3 shows a plate-like particle which is presumed to be $La_2(CO_3)_3$ from the EDX analysis. However, note that most of the particles floating on the surface of the leachate were $La_2Zr_2O_7$.

3.2.2. *Effects of leaching temperature*

The effects of temperature on the leaching rates are shown in Figs 4–6. The leaching rates in Fig. 4 were obtained after immersion for 34 days in an acid solution. The leaching rates of lanthanum, neodymium, cerium and strontium increase slightly between 40 and 90 °C and increase considerably between 90 and 150 °C. The leaching rates of lanthanum, neodymium and cerium are almost the same as each other at 90 and 150 °C. On the other hand, that of zirconium decreases considerably between 40 and 90 °C and decreases slightly between 90 and 150 °C.

The leaching rates in Fig. 5 were obtained by the leachant exchange method; the leaching rates of lanthanum, neodymium, cerium and strontium tend to increase with increasing temperature, as observed in Fig. 4. On the other hand, the leaching rate of zirconium at 90 °C is almost the same as that at 40 °C, and the leaching rate of zirconium at 150 °C is lower than that at 90 °C by one order of magnitude.

Fig. 6 shows the effects of temperature on the leaching rates in deionized water. The leaching rate of zirconium is lower than that in an acid solution at 40

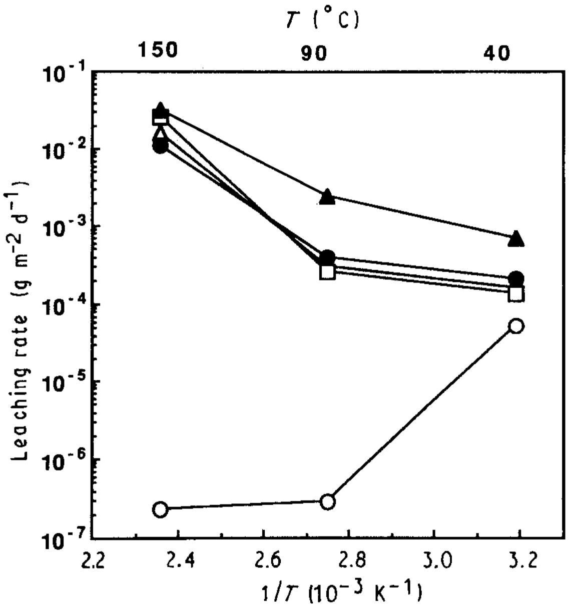

Figure 4 Leaching rate after 34 days in an acid solution (pH = 1). No exchange of leachant occurred. (○) Zr, (△) La, (□) Nd, (●) Ce, (▲) Sr.

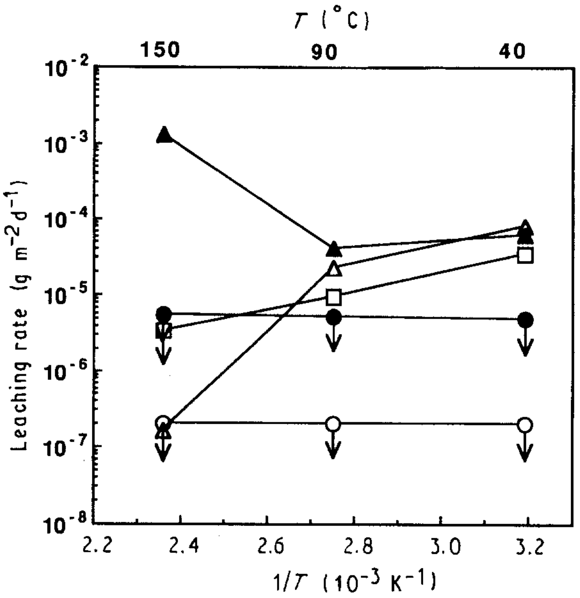

Figure 6 Leaching rate after 50 days in deionized water. (○) Zr, (△) La, (□) Nd, (●) Ce, (▲) Sr.

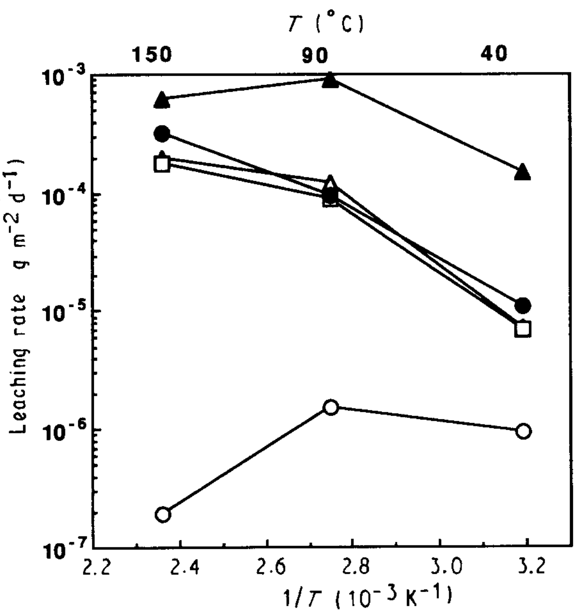

Figure 5 Leaching rate after 50 days in an acid solution (pH = 1). (○) Zr, (△) La, (□) Nd, (●) Ce, (▲) Sr.

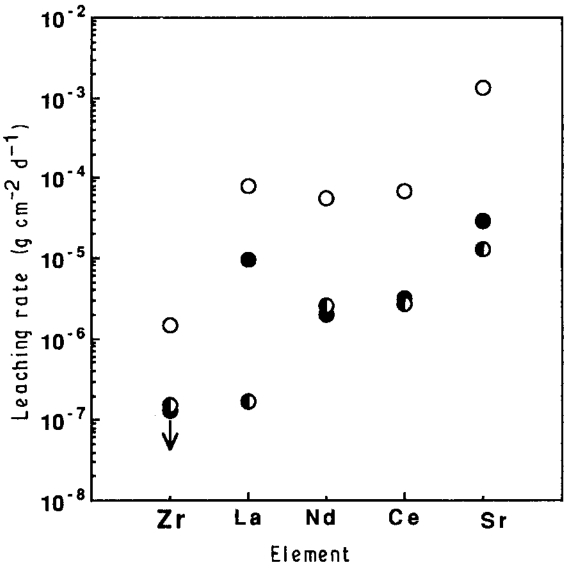

Figure 7 Leaching rate of the constituent at 90 °C after 50 days pH. (○) 1, (●) 5.6 and (◐) 10.

and 150 °C. Two explanations are possible for this phenomenon. First, the increased pH reduces the dissolution rate of $La_2Zr_2O_7$. Second, zirconium forms an insoluble hydrate layer on the powder surface in the pH range 1.7–10.5, which reduces the reaction rate of the inner part of the matrix in water.

3.2.3. *Effects of pH in leachate*

Fig. 7 shows the effects of pH on leaching rates. After samples were immersed in leachants at 90 °C for 34 days, leachants were exchanged once in 4 days and the leach rates after 50 days were obtained. In an acid solution, the leach rate of each element decreases in the order strontium > lanthanum ≃ neodymium ≃ cerium > zirconium. In deionized water and an alkaline solution, the leaching rate of each element decreases in the same order as in an acid solution except for lanthanum, and decreases more than one order of magnitude compared with those in an acid solution. The concentrations of elements in an alkaline solution were measured with the ICP–MS (mass spectroscopy) apparatus. The leaching rates of lanthanum in an alkaline solution are small in comparison with neodymium and cerium. This small leaching rate seems to be related to the formation of insoluble $La_2(CO_3)_3$.

4. Discussion

4.1. Effects of leaching temperature

As shown in Fig. 4, the leaching rates of zirconium decrease with increasing temperature in an acid solution. On the other hand, the leaching rates of lanthanum, neodymium and cerium increase with increasing temperature. In order to explain this, the following three causes were considered. First, the disintegration rate of the crystal lattice increases with increasing temperature. Second, the solubility of the constituents increases with increasing temperature. Third, the concentration of CO_3^{2-} in the leachate decreases with increasing temperature and this prohibits the formation of zirconium complexes with CO_3^{2-}. The increase of leaching rates for lanthanum, neodymium, cerium and strontium with increasing temperature (Fig. 4) is caused by the first and second effects described above. However, the decrease in the leaching rate of zirconium with increasing temperature may be related to the third effect. The unreacted or incompletely reacted zirconium in the waste form easily dissolves compared to zirconium in the $La_2Zr_2O_7$ crystal lattice. On the other hand, it is known that zirconium forms complexes with CO_3^{2-} [10], and the concentration of CO_3^{2-} in a leachate at 40 °C is much greater than that at 90 or 150 °C. Hence, during the immersion period at 40 °C, zirconium in the waste form dissolves well by the synergism effect of these two factors, namely the existence of leachable zirconium and the formation of zirconium complexes. However, as shown in Fig. 5, the greater leaching rate of zirconium at 40 °C is not found, because the affect of leachable zirconium is eliminated by the exchange of leachant.

4.2. Effect of pH in the leachate

The leaching rate of zirconium is smallest in deionized water. In the solution saturated with ZrO_2 at 25 °C, the major ion species are $Zr_4(OH)_8^{8+}$ (10^{-3} M) at pH $= 1$, $Zr(OH)_8^-$ or $Zr(OH)_3^+$ (10^{-12} M) at pH $= 5.6$, and $Zr(OH)_8^-$ ($10^{-7.7}$ M) at pH $= 10$ [11]. The concentration of zirconium ions is small in a pH $= 5.6$ solution. In our work, the concentrations of zirconium in the leachates were 10^{-7} M at pH $= 1$, $< 10^{-8}$ M at pH $= 5.6$ (deionized water) and 10^{-8} M at pH $= 10$. The concentration of zirconium measured at pH $= 10$ was 10^{-8} M and almost the same as that in the literature ($10^{-7.7}$ M). This shows that zirconium in the leachate may be saturated. However, the concentration of zirconium measured at pH $= 1$, 10^{-7} M, is extremely low compared with data in the literature (10^{-3} M). It is known that polynuclear species such as $Zr_4(OH)_8^{8+}$ polymerize through ageing at high temperatures [10]. Because these polynuclear species have positive charges, they do not grow to a size of more than 0.45 μm and are not filtered through a 0.45 μm membrane. Thus, it is thought that low concentrations of zirconium are caused by the low dissociation rate of the $La_2Zr_2O_7$ crystal lattice.

5. Conclusion

The leaching rates of an $La_2Zr_2O_7$ waste form, containing neodymium, cerium and strontium as simulated waste elements, were measured at 40, 90 or 150 °C. The leach rates of each constituent in deionized water and an alkaline solution (pH $= 10$) decreased more than one order of magnitude than those in an acid solution. The leaching rates of lanthanum, neodymium, cerium and strontium tended to increase with increasing temperature. In contrast to this, the leaching rate of zirconium after immersion for 34 days decreased as the temperature increased. This was attributed to the decrease of a zirconium complex with CO_3^{2-} ligands which is not stable at a higher temperature. The leaching rates of zirconium, lanthanum, neodymium and cerium are less than 10^{-5} g m^{-2} d^{-1} in deionized water and an alkaline solution (pH $= 10$) at 90 °C. This shows that $La_2Zr_2O_7$ could be a superior material for immobilizing transuranic elements.

References

1. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics" (Wiley, New York, 1960) p. 99.
2. T. KAWAKUBO, H. HIRAYAMA and T. KANEKO, *Zairyo* **39** (1990) 78.
3. B. E. SCHEETZ, W. B. WHITE and S. D. ATKINSON, *Nucl. Technol.* **56** (1982) 289.
4. D. G. BROOKINS, "Eh–pH Diagrams for Geochemistry" (Spring-Verlag, Berlin, 1988) p. 116.
5. I. HAYAKAWA and H. KAMIZONO, paper presented at the "15th International Conference on Scientific Basis for Nuclear Waste Management", Strasbourg, France, on 5 November 1991.
6. T. MUROMURA and Y. HINATSU, *J. Nucl. Mater.* **151** (1987) 55.
7. H. KAMIZONO, I. HAYAKAWA and S. MURAOKA, *J. Amer. Ceram. Soc.* **74** (1991) 863.
8. I. HAYAKAWA and H. KAMIZONO, in "Proceeding of the 3rd International Symposium on Advanced Nuclear Energy Research", Mito, March 1991 p. 408. Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki.
9. J. W. TROESTER, W. P. FREEBORN and W. B. WHITE, in "Advances in Ceramics", Vol. 8, edited by G. G. Wicks and W. A. Ross (The American Ceramic Society, Columbus, Ohio, 1984) p. 247.
10. D. C. BRADLEY and P. THORNTON, in "Comprehensive Inorganic Chemistry" edited by J. C. Bailar, Jr, H. J. Emeleus, Sir Ronald Nyholm and A. F. Trotman-Dickenson (Pergamon Press, Oxford, 1973) p. 454.
11. C. F. BAES and J. R. E. MESMER, "The Hydrolysis of Cations" (Wiley, New York, 1976) p. 149.