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STUDIES OF GLASS WASTE FORM PERFORMANCE AT JAPAN ATOMIC ENERGY RESEARCH INSTITUTE

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Studies of Glass Waste Form Performance at Japan Atomic Energy Research Institute

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The recent studies of glass waste form performance at Japan Atomic Energy Research Institute can be classified into the following three categories;

(1) Study on the volatilization of radionuclides from the waste glass, which is necessary to estimate the safety in relation to operation of a storage facility.
(2) Study on the radiation (alpha-radiation) effects which have relation to the long-term stability of the waste glass.
(3) Study on the leaching behavior of actinides under the repository conditions, which is necessary to predict the long-term release rate of radionuclides from the waste glass.

In the present report, the recent results corresponding to the above categories are described.

Keywords: Nuclear Waste Glass, Volatilization, Radiation Stability, Plutonium, Neptunium, Leaching Behavior, Leached Surface Layer, Groundwater

+ Department of Reactor Fuel Examination

原研におけるガラス固化体に関する研究

日本原子力研究所東海研究所環境安全研究部
馬場　恒孝・上薗　裕史・中山　真一・田代　晋吾＋

（1989年8月3日受理）

原研における高レベル廃棄物ガラス固化体に関する最近の研究は，次の3つに大別できる。

① 貯蔵時の安全性を評価する上で重要な固化体からの放射性核種の揮発挙動に関する研究

② 固化体の長期的安定性に影響する放射線耐久性，特にα線耐久性に関する研究

③ 処分後の放射性核種漏洩量を予測するために必要な長半減期核種の浸出挙動及び処分条件下での浸出挙動に関する研究

ここでは，それぞれに関係する最近の研究成果を報告する。

東海研究所：〒319-11　茨城県那珂郡東海村白方字白根2-4
＋　実用燃料試験室

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1. Introduction

The Japan Atomic Energy Research Institute (JAERI) has contributed to the establishment of the national system for the high-level radioactive waste management with developments of safety assessment methods and accumulation of useful data. Besides, JAERI is responsible for researches of new technology to be acceptable to the Japanese environmental circumstances.

In the present document, the JAERI's studies on the properties of the nuclear waste glasses are described briefly.

2. Volatilization of ^{137}Cs and ^{106}Ru from Borosilicate Glass Containing Actual High-Level Waste [1]

In the study, attention is focused on safety in relation to operation of a storage facility. The volatilization of some radionuclides from borosilicate glass containing actual HLW generated at the Tokai Reprocessing Plant of the Power Reactor and Nuclear Fuel Development Corporation (PNC) was examined in an almost closed canister.

The HLW glass used for the present study was borosilicate glass. The reagents for the glass additives and the simulated HLW which should be converted into 1300g of oxide glass were mixed simultaneously and placed in a vitrification apparatus with about one liter of a denitrated actual HLW solution. About 50g of various oxides were assumed to come from the actual HLW solution. This mixture was calcined at about 750°C, melted at 1200°C for 2 h in the vitrification apparatus. Half the molten glass was poured into an 8.1-cm-i.d., 24.4-cm-high stainless steel canister, kept at 600°C for 2 h, and then cooled to room temperature at a cooling rate of less than 40°C/h.

The experimental details in relation to the furnace and the sampling of the air inside the canister were described in Ref.[2] (Fig.1). The following is a summary, and additional information. The furnace temperature was raised in steps from 25°C to 1000°C. The temperature rise by the decay heat of the HLW was so small in the present study that it did not affect the temperature control of the glass.

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During the course of heating, part of the air in the upper space of the canister was collected in an evacuated sampling bottle with a

volume of about 7 cm^3. An important factor is the position of the hole in the sampling needle. It should be placed in the side of the needle in order to prevent it from being blocked by silicon rubber when the needle is inserted into the sampling tube. Radioactivity from volatile elements trapped by both the sampling bottle and the sampling needle was measured by an intrinsic Ge solid state detector which has a better resolution than the NaI(Tl) detector used in the previous study [2].

Figure 2 shows the temperature-dependence of volatility of ^{137}Cs and ^{106}Ru at a fixed time of 24 hours when both nuclides are at apparent saturation concentrations. The solid line in the figure represents the data obtained in our previous work [2] in which the activation energy of about 140 kJ/mol was obtained on simulated HLW glass containing about 1.6×10^{10} Bq of ^{134}Cs. The present data shows fairly good agreement with this.

The volatility of ^{106}Ru measured at 600°C and 800°C is about one fifth that of ^{137}Cs. Since Gray [3] has pointed out that the activation energy for various elements are almost the same as each other, the air contamination of ^{106}Ru at a usual storage temperature of 400°C is also expected to be one fifth that of ^{137}Cs; thus, the normalized concentration of ^{106}Ru would be about 5×10^{-10} at 400°C. This extrapolated value may be conservative, since 400°C is below the softening point of the present glass and diffusion may not be a significant mechanism at this temperature. It should be also mentioned that the volatility of ^{106}Ru at 1000°C could not be measured; it was under the detection limit of 5×10^{-2} Bq/cm^3. This is probably an example that the backward step plays an important role; the stainless steel canister is markedly oxidized at around 1000°C and reacted with ^{106}Ru in the air inside the canister. It is also probable that RuO_4 is not stable at high temperatures, and this is one of the causes that ^{106}Ru disappeared at around 1000°C. The results described above will be published shortly [1].

3. Accelerated Alpha Radiation Stability Test [4]

An accelerated alpha radiation stability test started in connection with characterization of returnable waste forms from overseas reprocessing, and the test equivalent to 10,000 years aging of actual waste forms has been finished.

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Curium-244 and plutonium-238 were added to a simulated waste substituting transuranium elements and 90% of rare-earths (^{244}Cm: 43.3 GBq/g-glass, ^{238}Pu: 4.4 GBq/g-glass). The waste was molten with borosilicate glass in three platinum crucibles of 14 mm in diameter. Twenty-four specimens were prepared by cutting the crucibles into pieces 5 mm thick, and each specimen was stored in a helium leak-protective capsule.

Four or five specimens were taken out from the storage pits for each time-equivalent test including zero time tests. The tests were performed with a mass spectrometer, a differential scanning calorimeter (DSC), Soxhlet type leaching apparatus and a microscope for measurement of helium remained in the matrix, stored energy in the matrix, leachability and fine-structure alteration, respectively.

It was found by measuring the amount of helium released from the specimens that 97-99% of helium remained in the matrix at the room temperature. The total amount of helium generated in the specimen was obtained from the amount of helium released from the specimen kept at 600°C for 15 min and that at room temperature, because at 600°C the helium was completely depleted from the glass specimen.

Density of the specimens decreased slightly with the increase of time and the decrement of 1.1% was observed at 10,000 years equivalent (Fig.3). Regarding leachability based on the total weight losses, some fluctuating results were obtained in the initial stages of the test but subsequently the curve is flat to the 10,000 years equivalent (Fig.3). Microscopic observation also did not show any change in the microstructure. Those results seem to suggest that alpha radiation has no significant influence on the ability of glass forms to confine high-level wastes.

4. Temperature Effect on Pu Leach Rate of the Nuclear Waste Glass [5]

In the study, the ISO leach test [6] were carried out on a ^{238}Pu-doped glass and non-radioactive waste glass at temperature between 23°C and 90°C. The dissolution kinetics of the plutonium compound in the leached surface layer is examined by the leaching data.

Experimental

1) Preparation of waste glasses

Curium-244 and plutonium-238 were added to a simulated waste substituting transuranium elements and 90% of rare-earths (^{244}Cm: 43.3 GBq/g-glass, ^{238}Pu: 4.4 GBq/g-glass). The waste was molten with borosilicate glass in three platinum crucibles of 14 mm in diameter. Twenty-four specimens were prepared by cutting the crucibles into pieces 5 mm thick, and each specimen was stored in a helium leak-protective capsule.

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Experimental

1) Preparation of waste glasses

Two kinds of waste glasses with a similar composition were prepared, separately. The non-radioactive simulated waste glass, which was melted in a platinum crucible at 1150°C for two hr, was annealed at 550°C for one hr in a graphite mold and slowly cooled down to room temperature. The ^{238}Pu-doped glass was prepared using the mixture of powdered simulated waste glass and plutonium oxide ($^{238}PuO_2$) in a platinum crucible of 14 mm in diameter under the same heating conditions as above. The content of PuO_2 was 1.35 wt% (^{238}Pu: 6.6×10^9 Bq/g-glass). The compositions of both waste glasses are shown in Table 1. The test specimens (14 $mm^{\phi} \times 8$ mm^{t}) of both glasses were prepared by cutting and polishing.

2) Leach test method

ISO type leach test [6] were carried out in distilled water. The leach containers of Teflon were used for all tests. The ratio of surface area to leachant volume (SA/V) was 0.1 cm^{-1}. Tests were conducted at temperatures between 23°C and 90°C for up to 64 days. A single specimen of non-radioactive simulated waste glass and five separate specimens of ^{238}Pu-doped glass were independently immersed in leachant at each test temperature. These specimens were cleaned by ultrasonic washing with ethyl-alcohol for 10 min, and dried at 110°C for one hr. After predetermined intervals each specimen was withdrawn from the leach container and immediately transferred to a new leach container filled with fresh leachant. Solution analyses were carried out for the leachates of non-radioactive simulated waste glass using the inductively coupled plasma spectroscopy (ICP) and the atomic absorption spectroscopy (AAS). Plutonium-238 concentrations were determined through a combination of gas flow proportional counting and surface barrier spectrometry techniques.

The pH of leachate was measured with a pH meter of TOA Electronics Ltd., Model HM-10K.

Results and Discussion

In the case of short-term leaching, in which the protective effect of the leached surface layer is neglected, the dissolution of the glasses in aqueous solution can be described as a first order reaction proposed by Rimstidt and Barnes [7]:

$$SiO_2(s) + 2H_2O(l) = H_4SiO_4(aq). \quad (1)$$

Assuming this first order reaction, the dissolution rate r(t) is:

$$r(t) = \frac{V}{SA}\frac{dc_{Si}}{dt} = k(c_{Si,sat} - c_{Si}) \ , \qquad (2)$$

where V is the volume of solution [m^3], SA is the surface area of specimen [m^2], c_{Si} is the concentration of Si in solution [g/m^3], t is the time [sec], k is the rate constant [m/sec] and $c_{Si,sat}$ is the saturated concentration of Si in solution [g/m^3]. In the case of $c_{Si} \ll c_{Si,sat}$, Eq.(3) is obtained from Eq.(2) and the following equation, $NL_{Si} = c_{Si} \cdot V \cdot MG/(SA \cdot MG_{Si})$, where NL_{Si}, MG and MG_{Si} are the normalized elemental mass loss of Si, the mass of glass specimen and the atomic mass of Si in the specimen, respectively.

$$\frac{d(NL_{Si})}{dt} = k \cdot c_{Si,sat}\frac{MG}{MG_{Si}} \ . \qquad (3)$$

The integrated form of Eq.(3) is

$$NL_{Si} = k \cdot c_{Si,sat}\frac{MG}{MG_{Si}}\, t = k't \ , \qquad (4)$$

where $k' = k \cdot c_{Si,sat}\ MG/MG_{Si}$ [$g/(m^2 sec)$].

If the equation (4) is applied to the present leaching data, the rate constant k' can be obtained in term of $g/(m^2 day)$ and their temperature dependency can be calculated. Figure 4 shows the normalized elemental mass loss of Si, NL_{Si}, in the initial stages of the ISO-test at a function of time at 23, 45 and 70°C. From the initial positive slopes of the curves in Fig.4, which are uninfluenced by the saturation effect, the rate constant k' at each temperature can be determined for the leaching process. The normalized elemental mass losses of the other elements in the initial stages of leaching are also represented by the equation (4) as shown in Fig. 5 and Fig. 6. Therefore, the rate constant of the initial release of each element at each temperature can be determined in a similar manner as above.

Figure 7 shows the rate constants k' of Si, Na, Sr, Cs and Pu as a function of reciprocal temperature. The rate constants of four elements except Pu, can be adequately approximated by one straight line, so that an activation energy can be determined according to the Arrhenius relation: $k' = A \cdot \exp(-E_a/RT)$, where A is the frequency factor, E_a represents the activation energy [kJ/mol], R represents the gas constant [8.318 J/

(mole·K)], and T is the temperature [K]. Its value was 78±9 kJ/mol, which agreed with the activation energies of 60 to 80 kJ/mol previously observed in the nonsaturating case [8]. This result implies that Na, Sr and Cs are released from the waste glass with the same mechanisms as the dissolution of the glass matrix in the initial stages of leaching, and that the effect of the leached surface layer on the initial leach rate of these elements can be neglected.

On the other hand, an activation energy obtained for Pu is 22±10 kJ/mol, which is much lower than the above activation energy of dissolution of glass matrix. This means that the release of Pu is not controlled by the glass matrix dissolution even in the initial stages of leaching. Based on the comparison between Pu concentration in solution and solubility of hydrous plutonium dioxide, $PuO_2 \cdot xH_2O$, Apted et al. have predicted that the amount of Pu released from the glass is controlled by the formation of amorphous $PuO_2 \cdot xH_2O$ on the glass surface during the leach test [9]. If the amorphous $PuO_2 \cdot xH_2O$ is formed in the leached surface layer, and its formation rate is much faster than the dissolution rate, the release of Pu should be controlled by the following reaction.

$$PuO_2 \cdot xH_2O \rightarrow Pu^{4+} + 4OH^- + (x-2)H_2O \qquad (5)$$

This reaction is also supported by the results reported by Rees and coworkers. That is, at 25°C and 90°C, a significant Pu^{4+} concentration of the leachates in the initial stages of leaching was measured [10]. Therefore, the activation energy obtained in the present experiments is suggested to be the activation energy of the reaction (5). Up to date, no experimental data on the temperature dependence of rate constants for this reaction can be found.

5. Release of Neptunium from a ^{237}Np-doped Borosilicate Waste Glass [11]

The MCC-1 static leach tests were performed for a ^{237}Np-doped borosilicate waste glass at 90°C with deionized water and silicate water leachants. We determined the concentrations of dissolved Np in the solutions contacting the ^{237}Np-doped glass in 3-day to 91-day leach tests. An attempt was made to speculate the release mechanism of Np from waste glasses.

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Experimental

The composition of the Np-doped glass is shown in Table 2. Standard MCC-1 leach tests were performed at 90°C. Teflon vessels were used as leach containers, which were cleaned enough to remove hydrofluoric acid to a negligibly low level. About 30 ml of leachant were added into a container, resulting in the SA/V ratio of 0.1 cm^{-1}. Deionized water and silicate water were used as leachants. At the desired leach durations, the Np concentrations in the leachates were determined by gamma-counting with a high-purity germanium detector.

Results and Discussion

1) The release of neptunium

The amounts of Np released from the glass are plotted as a function of time in Fig. 8 in terms of the normalized elemental mass loss $(NL)_{Np}$. Although the release behaviors as a function of time are appreciably different between the deionized water and silicate water, the $(NL)_{Np}$ values of about 5 g/m^2 are similar for the two leachates after 91-day leaching.

In Figure 9 comparison was made of the release behavior of Np obtained in this study with those of other elements from Ref. [12]. A linear relation between log(NL) and log(time) is observed for Na, B and Cs within the studied leaching durations. As time proceeds, NL's for Np and Sr approach to constant values.

According to our previous study [13], Na, B and Cs were found in the leachates but not found in the surface layer; they are released from the bulk glass by decomposition of the glass and diffuse through the surface layer without being trapped. Strontium was detected both in the surface layer and in the leachates. Probably Np, representing a similar time-dependent release behavior to that for Sr, is also present in surface layers.

2) Solubility limits to the Np release

It is reasonable to assume that Np concentrations in leachates are controlled by the solubilities of Np solid phases formed in the surface layer. This assumption leads to that the solid phases formed in surface layers must be primarily identified in order to predict Np concentrations in glass leachates. Since none of present analytical techniques is applicable to wet surfaces, the Np species in the surface layers can not

be identified directly. Then an attempt was made to speculate it based on the predicted species in the bulk glass and that in leachates.

In bulk glasses either the tetravalent [14,15] or the pentavalent [16] species possibly exists. Neptunium species in aqueous solutions can be estimated by pH and Eh of the solutions. However, such redox parameters have not been studied for solutions contained in surface layers. Instead, we use pH and Eh values of the leachates. The measured pH and Eh of the leachates in the present experiments are plotted in Fig. 10. These values change with time, but they are similar for different leach durations except 3 days. Referring to available pH-Eh diagrams, the tetravalent and the pentavalent species are possibly present in comparable amounts in the present leachates, and the trivalent and the hexavalent species are probably absent. Since the tetravalent and/or pentavalant species are expected to exist in both the bulk glasses and leachates, the valence of Np in the surface layer is also likely to be tetravalent and/or pentavalent.

Considering the above estimation on the valence and OH^- as a predominant complexing anion present in the leachates, we take NpO_2xH_2O(am) and NpO_2OH(am) as Np solid phases in the surface layer, and assume the following three types of solubility equilibrium; (1) $NpO_2OH(am) = NpO_2^+$, $NpO_2OH(aq)$, and $NpO_2CO_3^-$, (2) $NpO_2 \cdot xH_2O(am) = NpO_2^+$, (3) $NpO_2 \cdot xH_2O(am) = Np(OH)_4(aq)$.

Apparent steady-state concentrations of Np from MCC-1 leach tests are plotted in Fig. 11. Solubilities of NpO_2OH(am) and $NpO_2 \cdot xH_2O$(am) calculated from equilibrium constants at 25°C are also shown in the same figure by dotted and hatched regions, respectively. These regions include the predicted solubilities for different ionic strengths of aqueous solutions. As seen in Fig. 11, Np concentrations in the leachates are apparently limited by the solubilities of NpO_2xH_2O(am); the above-mentioned equilibria (2) and (3) are expected. Neptunium concentrations obtained from the leachates are distinguishably lower than the solubilities of NpO_2OH(am). If Np in the surface layers had been NpO_2OH(am), the Np concentrations in the leachates should have been higher, approaching to the NpO_2OH(am) solubilities. These facts imply that Np exists as the tetravalent solid phase $NpO_2 \cdot xH_2O$(am) rather than the pentavalent solid phase NpO_2OH(am) in the surface layers of leached waste glasses.

6. Leaching Behavior of Simulated High-Level Waste Glass in Groundwater [17,18,19]

The purpose of the work is to examine the leaching behavior of simulated high-level waste glass in actual groundwater in Japan. In-situ burial tests were carried out by immersing the sample in groundwater coming through schalstein-type rock in southwestern Japan. The results were compared with the ones of laboratory test obtained using synthesized groundwater and deionized water.

Figure 12 [17] shows the scanning electron microphotographs of the surface before and after leaching. In the case of actual groundwater (Fig. 12(b)) and synthesized groundwater (Fig. 12(c)), many grooves occur on the specimen along with the surrounding flat surface, indicating that some parts of simulated high-level waste glass dissolve more easily than others. On the other hand, in the case of deionized water (Fig. 12(d)), such grooves are not clearly observed, which means that leaching is progressing more uniformly than in the case of groundwater.

We assume that the leaching behavior of the simulated high-level waste glass is divided into two categories; one is leaching from the flat surface and the other is that from the grooves. The extent of leaching from the flat surface can be measured by SEM-EDX [18]. Here we define the C/C_0-values as the ratio of the concentration of Na on the flat surface of a leached specimen (C) to the initial concentration of Na before leaching (C_0).

We pave the way for estimating the order of normalized elemental mass loss of Na (NL_{Na}) of the glass leached in groundwater by measuring the C/C_0-value and measuring the size and the number of grooves without leachate examinations. For instance, in the case of the specimen leached in actual groundwater for one year and seven months, the C/C_0-value is about 0.86 which corresponds to NL_{Na} of 6.5×10^{-5} g/cm^2 for the flat surface. On the other hand, by measuring the size and the number of the grooves, we obtain NL_{Na} of 3.9×10^{-4} g/cm^2 which corresponds to the amount of Na leached from the grooves. The sum of 6.5×10^{-5} g/cm^2 for the flat surface and 3.9×10^{-4} g/cm^2 for the grooves is 4.6×10^{-4} g/cm^2, resulting in a leach rate of about 8×10^{-7} g/(cm^{2}day) [19].

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Table 1 Composition of Simulated High-Level Waste Glasses

Component	Content (wt%) Non-doped Glass*	Content (wt%) ^{238}Pu-doped Glass	Component	Content (wt%) Non-doped Glass*	Content (wt%) ^{238}Pu-doped Glass
Additive			Waste		
SiO_2	45.15	45.15	TeO_2	0.23	0.23
B_2O_3	13.90	13.90	Cs_2O	0.98	0.98
Al_2O_3	4.89	4.89	BaO	0.62	0.62
CaO	4.00	4.00	La_2O_3	0.50	0.45
Na_2O	9.79	9.79	CeO_2	1.91**	0.90
ZnO	2.47	2.47	Pr_6O_{11}	0.49	0.44
Li_2O	2.00	2.00	Nd_2O_3	1.65	1.48
			Sm_2O_3	0.32	0.29
Waste			Eu_2O_3	0.06	0.05
Rb_2O	0.12	0.12	Gd_2O_3	0.04	0.03
SrO	0.34	0.34	SeO_2	0.02	0.02
Y_2O_3	0.20	0.18	RuO_2	0.80	0.80
ZrO_2	2.64	2.64	Fe_2O_3	2.90	2.90
MoO_3	1.73	1.73	NiO	0.40	0.40
MnO_2	0.26	0.26	Cr_2O_3	0.50	0.50
Ag_2O	0.03	0.03	P_2O_5	0.30	0.30
CdO	0.03	0.03	Ru	0.12	0.12
SnO_2	0.02	0.02	Rh	0.15	0.15
Sb_2O_3	0.01	0.01	Pd	0.43	0.43
			PuO_2	-	1.35

* : This represents the non-radioactive simulated waste glass.
**: This value includes the total content of actinide oxides (0.9 wt%) simulated by CeO_2.

Table 2 Composition of ^{237}Np-doped JAERI glass

Component	Content (wt %)	Component	Content (wt %)
Additive		Waste	
SiO_2	45.15	TeO_2	0.23
B_2O_3	13.90	Cs_2O	0.97
Al_2O_3	4.89	BaO	0.62
CaO	4.01	La_2O_3	0.48
Na_2O	9.79 *	CeO_2	0.95
ZnO	2.47	Pr_6O_{11}	0.46
Li_2O	2.00	Nd_2O_3	1.55
		Sm_2O_3	0.31
Waste		Eu_2O_3	0.06
Rb_2O	0.12	Gd_2O_3	0.03
SrO	0.34	SeO_2	0.02
Y_2O_3	0.19	RuO_2	0.80
ZrO_2	2.64	Fe_2O_3	2.90
MoO_3	1.73	NiO	0.40
MnO_2	0.26	Cr_2O_3	0.50
Ag_2O	0.03	P_2O_5	0.30
CdO	0.03	Ru	0.12
SnO_2	0.02	Rh	0.15
Sb_2O_3	0.004	Pd	0.43
		$^{237}NpO_2$	1.15

* : Component contains both additive and waste.

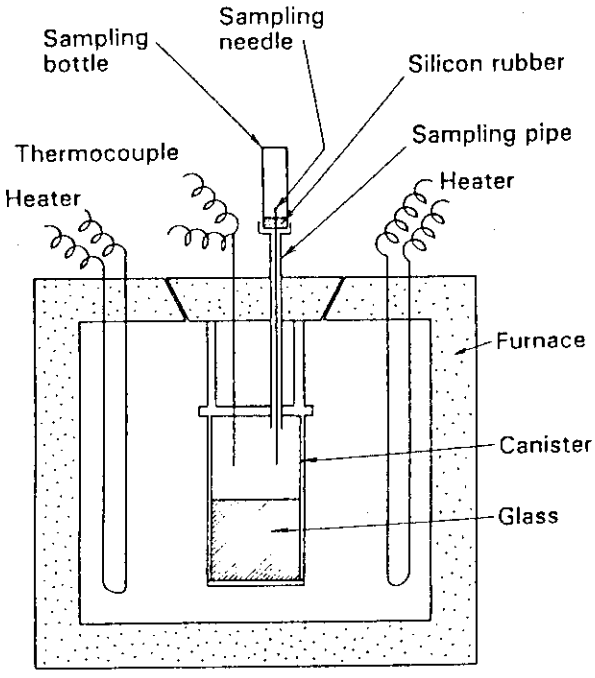

Fig. 1 Schematic drawing of the apparatus.

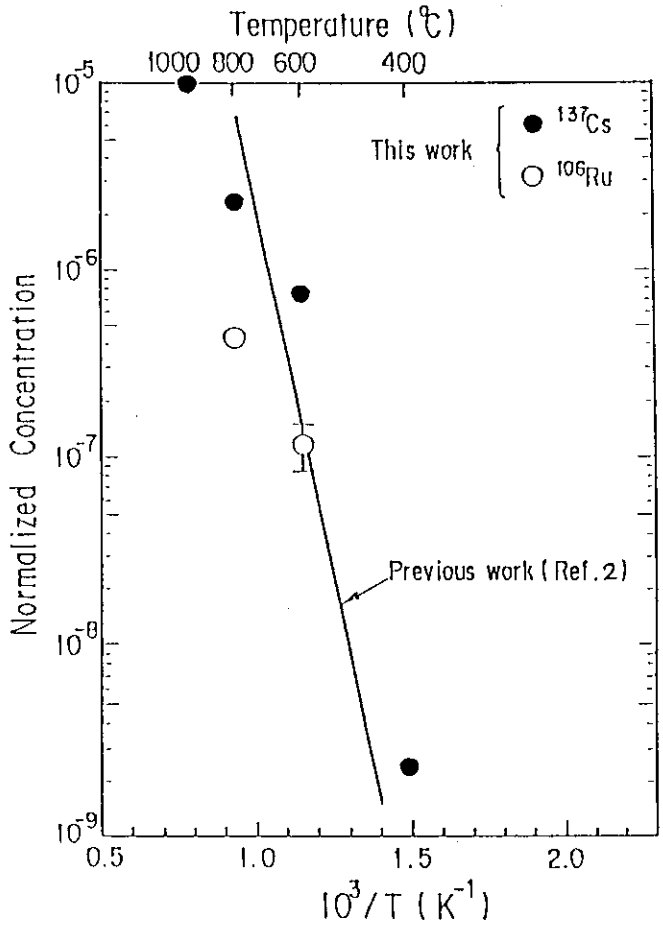

Fig. 2 Temperature-dependence of the volatility of ^{137}Cs and ^{106}Ru.

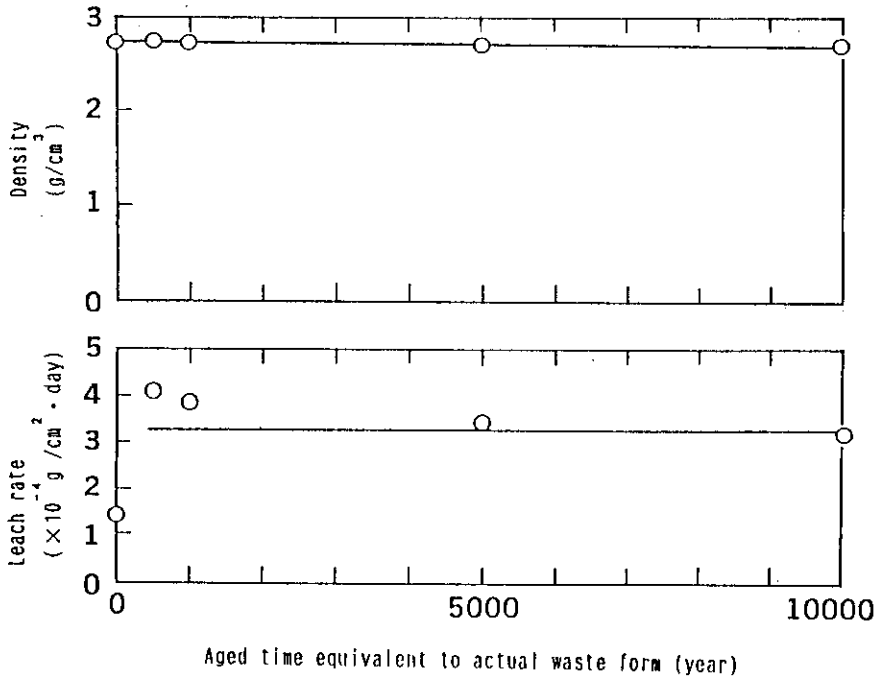

Fig. 3 Results of accelerated alpha radiation stability test for the waste glass.

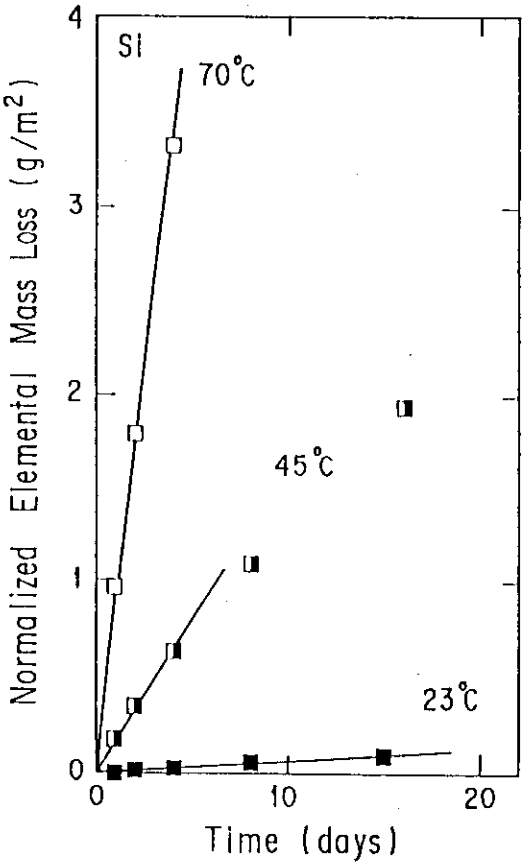

Fig. 4 The normalized elemental mass loss of Si in the initial stages of the ISO-test as a function of time at 23C, 45°C and 70°C.

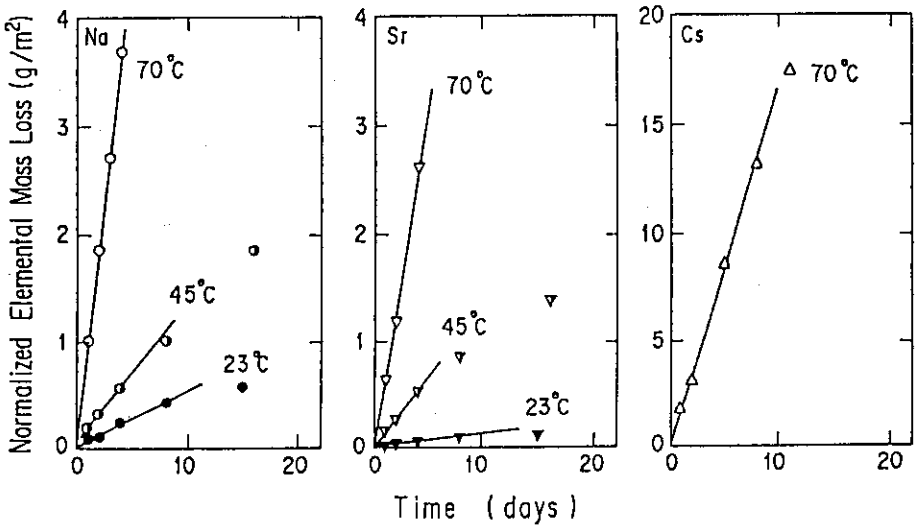

Fig. 5 The normalized elemental mass loss of Na, Sr and Cs in the initial stage of the ISO-test as a function of time at 23°C, 45°C and 70°C.

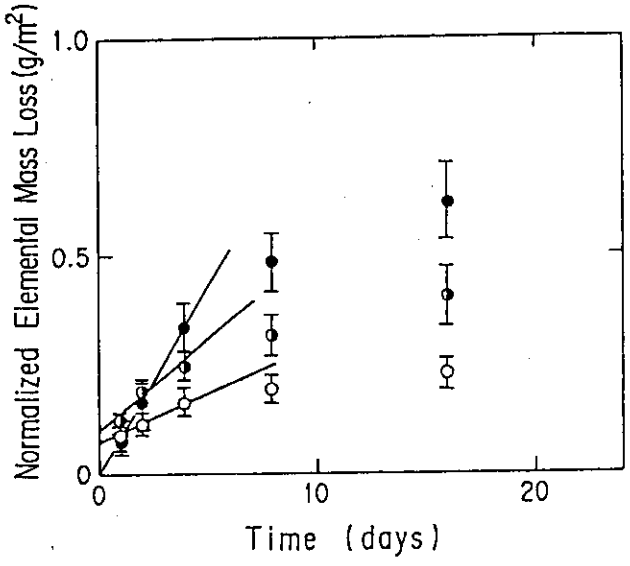

Fig. 6 The normalized elemental mass loss of ^{238}Pu in the initial stages of the ISO-test as a function of time at 25°C (○), 60°C (◑) and 90°C (●). Error bars show the standard deviation of each plot.

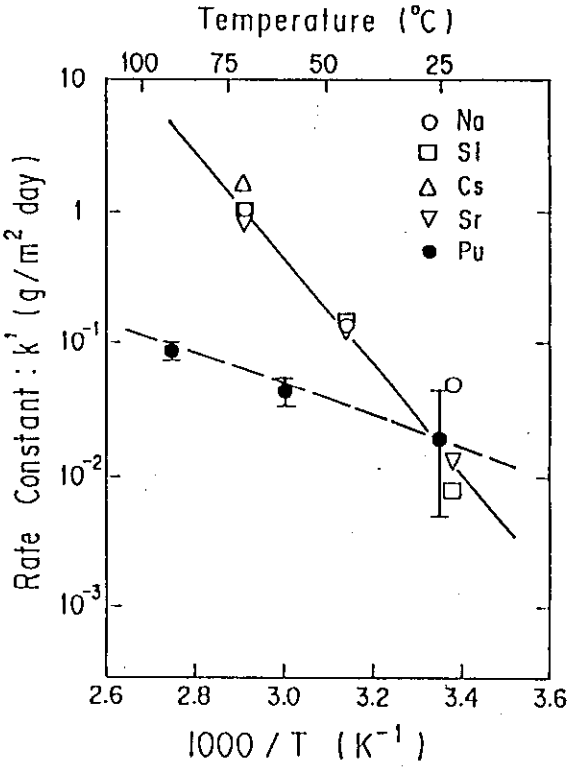

Fig. 7 The rate constants k' for the leaching process of the waste glass as a function of reciplocal temperature.

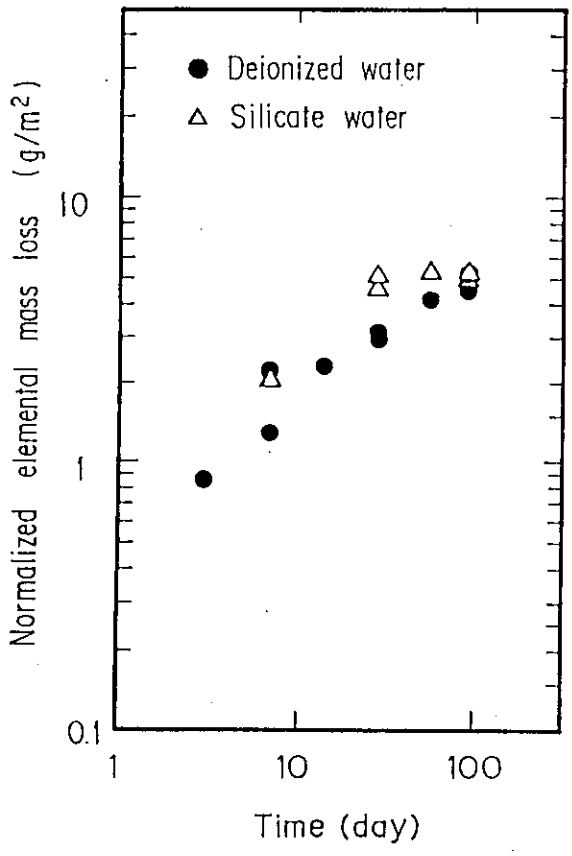

Fig. 8 The normalized elemental mass losses as a function of time for Np released from the ^{237}Np-doped borosilicate waste glass in the MCC-1 static leach tests at 90°C.

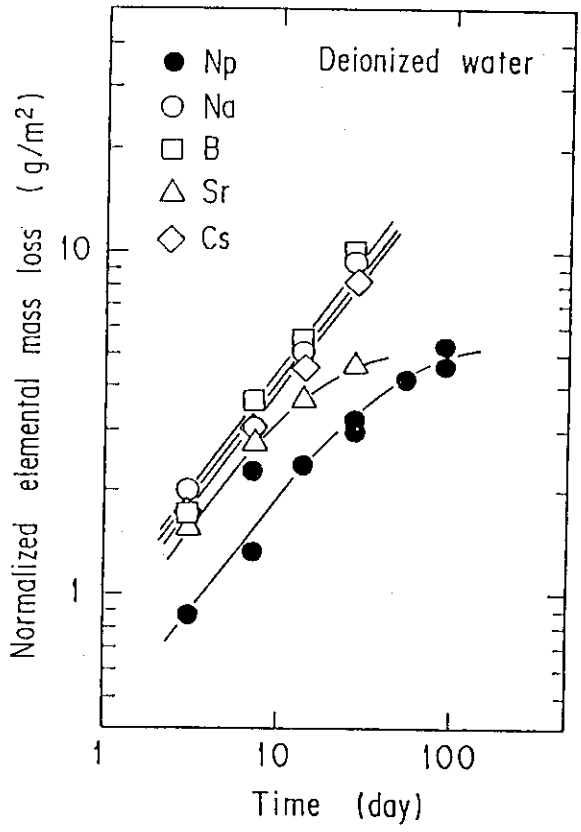

Fig. 9 The normalized elemental mass losses as a function of time for Na, B, Sr, Cs and Np-released from JAERI glasses in the MCC-1 static leach tests. Data on neptunium in Fig. 8 for deionized water were replotted. Data on Na, B, Sr and Cs were cited from Ref.(12).

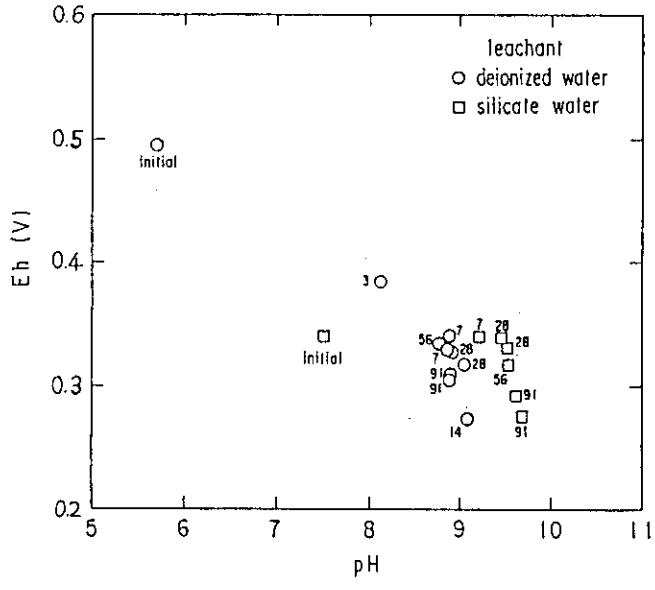

Fig. 10 Measured pH and Eh values of the glass leachates. Numbers next to the points denote the leach durations. The "initial"s denote the values for leachants.

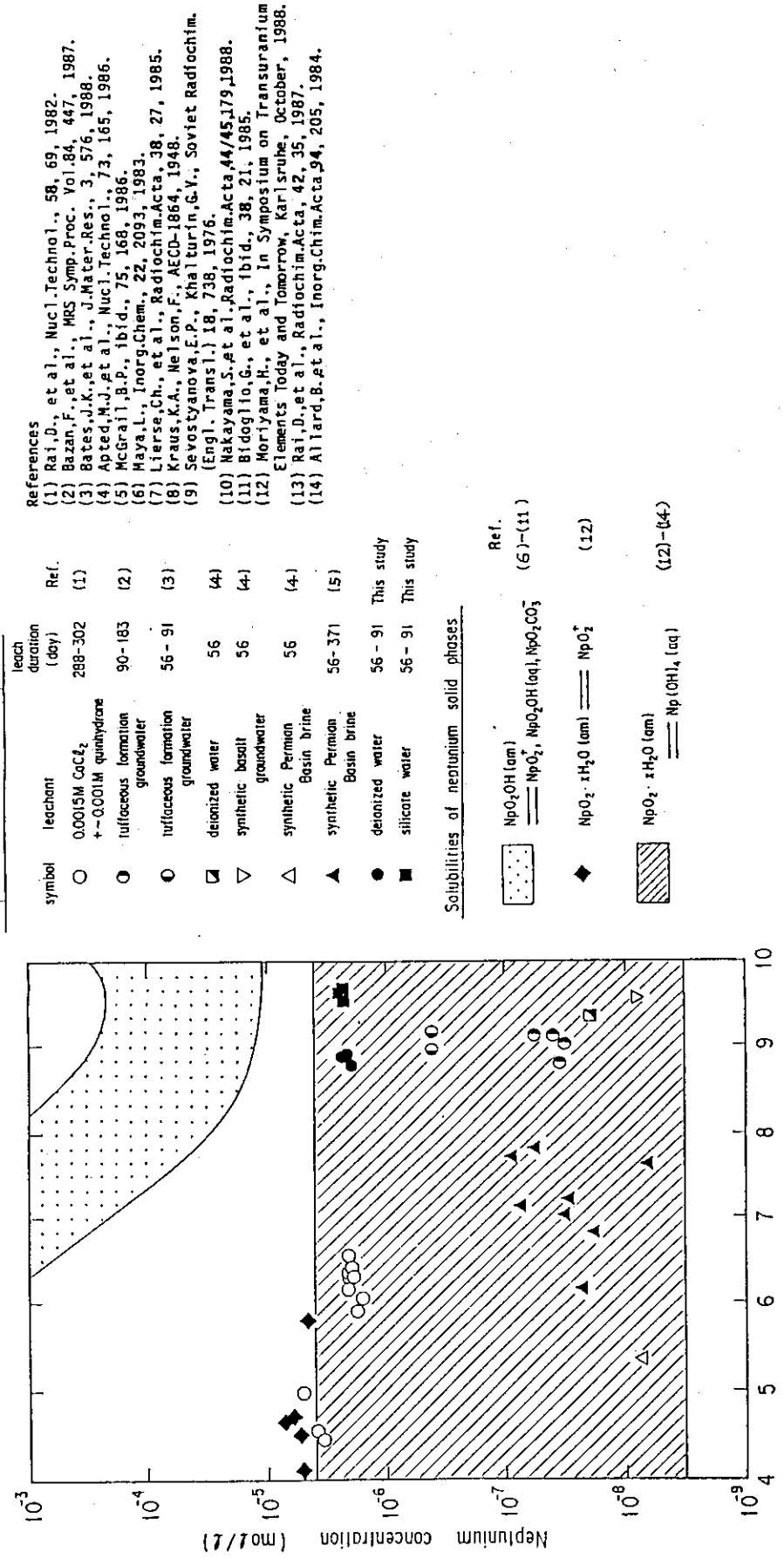

Fig. 11 Neptunium concentrations in glass leachates obtained from the MCC-1-type static leach tests for durations of 56 days or longer, and expected solubilities of $NpO_2 \cdot xH_2O$(am) and NpO_2OH(am) based on thermodynamic data.

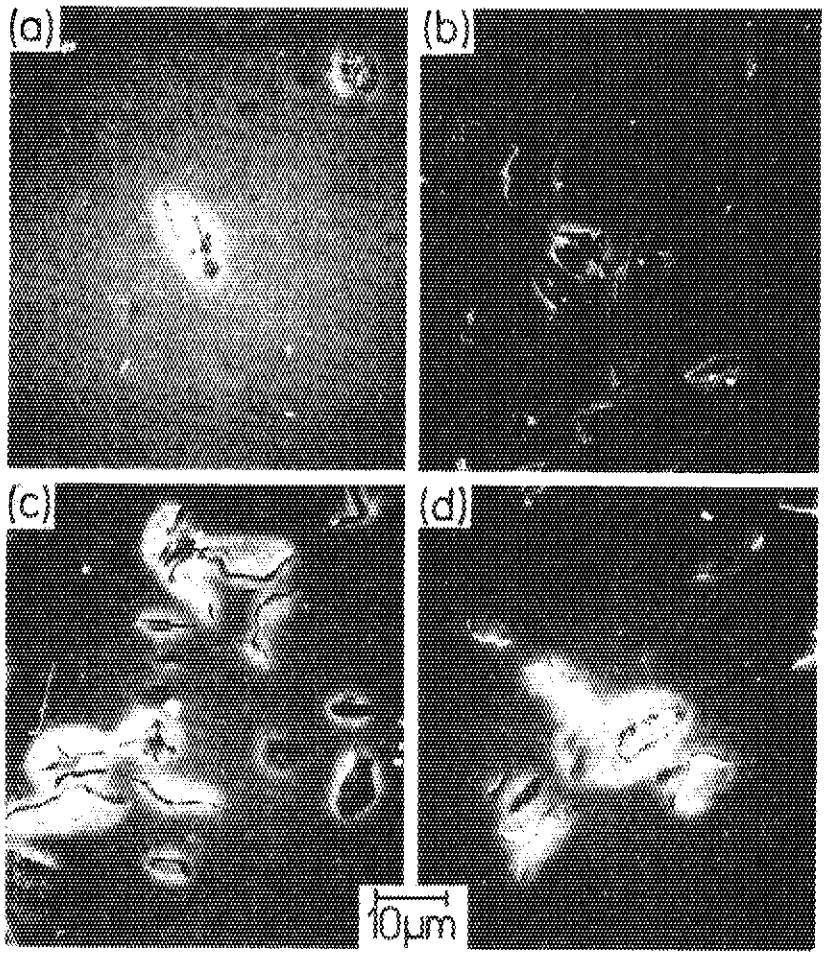

Fig. 12 Scanning electron micrographs of the surface of the unleached specimen (a) and the surface of the specimens leached in actual groundwater (b), in synthesized groundwater (c) and in deionized water (d) for 1 year.