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Static leaching of actinides and fission products from
fully radioactive waste glass of HLLW generated in
Tokai Reprocessing Plant

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POWER REACTOR AND NUCLEAR FUEL DEVELOPMENT CORPORATION

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STATIC LEACHING OF ACTINIDES AND FISSION PRODUCTS
FROM FULLY RADIOACTIVE WASTE GLASS OF HLLW
GENERATED IN TOKAI REPROCESSING PLANT

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要 旨

東海再処理工場で発生した高レベル廃液を用いて作成した実高レベルガラス固化体の浸出試験を CPF (Chemical Processing Facility) において実施した。試験の結果、種々の放射性核種の浸出挙動が把握でき以下の結論が得られた。

- (1) 模擬ガラス固化体の浸出挙動と比較して、ガラス主成分の浸出量はほぼ同じであり、放射線分解生成物による浸出量の増加は本試験条件においてはみられなかった。
- (2) 浸出の指標となる B の浸出量と比較することで Cs についてはコングルエントな浸出, Co, Sb, Ce, Eu, Pu, Am, Cm についてはインコングルエントな浸出となっていると考えられた。
- (3) 測定されたすべてのアクチニドについて、浸出容器壁面への吸着が認められた。それぞれのアクチニドの吸着量は、浸出容器壁面の硝酸洗浄により求めることができた。
- (4) 規格化浸出量で比べた場合、核種移行に寄与すると考えられる溶液中の割合は、Pu, Am, Cm については、Cs に比べ 1~2 桁小さいことがわかった。

尚、本論文は 1988 年 10 月にベルリンで開催された MRS 会議での発表をまとめたものである。

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ABSTRACT

Fully radioactive waste glass of HLLW generated in Tokai Reprocessing Plant was produced by using a small Joule-heated ceramic melter at the Chemical Processing Facility (CPF), Tokai Works, PNC, Japan. Static leach tests using the glass were carried out in doubly distilled water for a period of up to three months at 30°C and 90°C. Gamma spectrometry was performed to measure ^{134}Cs , ^{137}Cs and ^{60}Co in the leachates. After the chemical separation of Cs isotopes in the leachates, it was newly possible to measure ^{125}Sb , ^{144}Ce , ^{154}Eu and ^{155}Eu . Alpha spectrometry was performed to measure $^{239}\text{Pu}+^{240}\text{Pu}$, ^{241}Am and ^{244}Cm in the leachates. Adsorption of the actinides on the wall of the leach vessel was recognized in all cases. Leaching behavior of the measured radionuclides were evaluated by considering mass balance of the radionuclides which were leached.

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INTRODUCTION

Leaching of radionuclides from high-level waste glass represents a major concern to the performance assessment of the geologic repository. In most previous studies, the glass specimens doped with radionuclides have been used for leach tests to determine the release rates of radionuclides [1-4]. However, the application of fully radioactive waste glass for the leach test is scarce [5,6]. The important significances of the leach test using fully radioactive waste glass are to :

- determine leach rates of several important radionuclides simultaneously by the leach test.
- investigate the effect of radiolysis on leaching behavior caused by numerous radionuclides.
- compare the behavior of radioactive and non-radioactive glass.

PNC has advantages to study leaching of fully radioactive waste glass as follows.

- Actual HLLW is available from Tokai Reprocessing Plant, PNC.
- PNC has hot cells for vitrification of the HLLW and for characterization of the glass in the Chemical Processing Facility (CPF), so it is convenient to get specimens of fully radioactive waste glass which composition are analyzed.

The objectives of the present work are to :

- a) measure leach rates of important radionuclides, as many as possible, by using alpha, gamma spectrometry and chemical separation method.
- b) investigate mass balance of radionuclides released from the glass.
- c) investigate the effect of radiolysis on leaching.
- d) test a method by which adsorbed actinides are stripped from the walls of the leach vessels.

EXPERIMENTAL PROCEDURE

Investigation of the HLLW

The HLLW for vitrification was generated from reprocessing of light-

water reactor fuel with the uranium burn-up range of 11,100~26,500Mwd/tU at Tokai Reprocessing Plant. Composition of the HLLW was measured by direct coupled plasma spectrometry (DCP), alpha and gamma spectrometry. The insoluble sediments in the HLLW were filtered, then measured by DCP, electron probe micro analysis (EPMA) and X-ray diffraction analysis.

Preparation of the glass specimens

All sample preparations were carried out in hot cells at CPF using remote controls. The HLLW was mixed with glass frit to make slurry and fed into a ceramic melter with glass melt surface of 0.03m^2 . The slurry was dried, calcined then melted at 1150°C for two hours in the melter. Molten glass was poured into a canister about 6cm diameter and 70cm long. The glass block was gradually cooled from 550°C to room temperature preventing formation of cracks. The glass block was gamma-scanned, then cut perpendicular to the cylindrical axis, drilled axially and sliced to produce pellets with $10\text{mm}\phi\times 10\text{mm}$ height, weighing approximately 2g, and containing approximately 100 GBq of radioactivity per specimen. Prior to leaching, all specimens for the leach tests were weighed and their dimensions were measured to calculate surface areas. In addition, several glass samples were taken from various positions in the glass block to evaluate the composition of the glass. EPMA and X-ray diffraction analysis were carried out on these samples. After the glass samples were dissolved with Na_2O_2 at 900°C , the solutions were analyzed by DCP, alpha and gamma spectrometry.

Static leaching of the glass

Static MCC-1 type experiments were carried out for 28 and 91 days in doubly distilled water at 30°C and 90°C . SA/V ratio was 0.1cm^{-1} . The standard MCC-1 Teflon vessel as used for the leach test of the glass doped with radionuclides has the risk of radiation damage in the case of using fully radioactive waste glass. So the present experiments were carried out in gilded stainless steel vessels during leaching. All inner surfaces of the leaching vessel are covered with a gold layer, $45\mu\text{m}$ thick. A measured and weighed glass sample was placed into the leaching vessel. The vessel was then kept for the specified leaching time at 90°C in an oven or at 30°C , the ambient temperature in the hot cell. At the end of a leaching experiment, the specimen was removed, rinsed in water, dried and weighed. The leachate was sampled for pH measurement, DCP, alpha and

gamma spectrometry.

Nitric acid was added to adjust the concentration of the remaining solution to 1N-HNO₃. The solution was placed in an oven at 90°C for one day to dissolve any adsorbed material. The acid cleaning was repeated two times. Adsorbed amounts of actinides on the wall of the leach vessels after the acid cleaning were accounted for by taking samples (thin plates stripped from the gold layers) and by measuring their alpha activity.

It has been difficult to measure radionuclides except ¹³⁴Cs and ¹³⁷Cs from the leachate of fully radioactive waste glass by gamma spectroscopy in previous work [6], because of the Compton plateaux of the Cs-isotopes. In the present work the radionuclides except the Cs-isotopes were separated from the leachates by a co-precipitation method using Fe(OH)₃ [7]; A volume of 10ml of the solution from the acid cleaning was transferred to a separate container. 2ml of 0.5M-Fe(NO₃)₃ were added and kept at 70°C for half an hour. Then 5ml of 1N-NH₄OH were added and the precipitate was filtered. The solution obtained by dissolving the precipitate with 1N-HNO₃ was analyzed by gamma spectrometry.

RESULTS AND DISCUSSION

The HLLW

The HLLW contained approximately 1×10^4 GBq/l. The composition of HLLW is shown in Table I. It is not possible to measure ²⁴¹Am alone by alpha spectrometry because ²³⁸Pu has a peak at the same alpha energy as that of ²⁴¹Am. However, the calculated radioactivity of ²³⁸Pu in the HLLW was less than 1/1000 of the value of ²⁴¹Am. So the peak at the alpha energy of ²³⁸Pu+²⁴¹Am was regarded as that of ²⁴¹Am alone. Small amount of the insoluble sediments were observed in the HLLW. These were mainly composed of Mo(36%), Zr(30%) and Fe(9%), and content of noble metals such as Ru, Rh and Pd was less than 10% of the total mass. Needle shaped crystals about 10µm long were observed in the insoluble sediments by SEM. X-ray diffraction analysis showed that these were mainly composed of zirconium molybdate (ZrMo₂O₇(OH)₂(H₂O)₂) [8].

Composition of the glass

Table II shows the composition of the glass. Gamma scanning, alpha and gamma spectrometry of the glass shows that the actinides and fission products in the glass were distributed homogeneously (see Figs. 1 and 2).

Small amounts of noble metal precipitates such as Ru, Rh and Pd in the glass were recognized by EPMA, but no yellow phase was detected.

Radiolysis effect on leaching

The normalized elemental mass loss value (N_{Li}) is calculated using the following equation:

$$N_{Li} = \frac{C_i \cdot V}{f_i \cdot SA}$$

where

V = volume of the leachate (ml)

C_i = concentration of element i in the solution (g/ml)
 (or radioactivity concentration of nuclide i in the solution
 (Bq/ml))

SA = surface area of the glass leached (m²)

f_i = mass fraction of element i in the glass, dimensionless
 (or radioactivity concentration of nuclide i in the glass
 (Bq/g))

All N_{Li} in the present study are averages of two values from separate specimens. Table III shows pH of leachates, total mass losses, and N_{Li} of glass network-former elements B, Si, Al and of Li.

McVay and Pederson have shown that, in the presence of air, radiolysis can reduce the solution pH resulting in a significant increase in the leaching rate [9]. However, in the present case, the pH values were in the range of 6-8 where the leaching rate is usually minimal. In the case of a simulated waste glass of essentially the same composition as the glass in the present work, the total mass losses were 6.4 and 10.0, and pH values were 8.9 and 7.6 at 90°C for 28 and 91 days respectively [10]. Thus, the effect of radiolysis was not significant for the total mass losses in the present case as well as in previous work [4,6,11].

Release of fission products and ⁶⁰Co

The noise-level of gamma spectra from radionuclides in the leachates was reduced up to 1/50 by the chemical separation of Cs isotopes. So it was possible to measure ¹²⁵Sb, ¹⁴⁴Ce, ¹⁵⁴Eu and ¹⁵⁵Eu in addition to ¹³⁴Cs, ¹³⁷Cs and ⁶⁰Co (see Table IV). N_{Li} of these radionuclides increased with leaching time and temperature (see Fig. 3).

The dependence of incongruent leaching has been studied using the parameter N_{Li}/NL_B, which is the ratio of the normalized mass loss of

element *i* to the normalized mass loss of the non-solubility-limited network-former element boron [12]. $N_{Li}/N_{LB} = 1$ indicates congruent leaching, whereas $N_{Li}/N_{LB} < 1$ is assumed to indicate selective retention of the element *i* in a layer on the glass surface or elsewhere in the leaching vessel (incongruent leaching), because of low solubility of the element *i* in certain pH range. N_{Li}/N_{LB} was close to unity for ^{134}Cs and ^{137}Cs . No measured fission product was leached significantly more than the network-former element boron. N_{Li}/N_{LB} was less than unity for ^{125}Sb , ^{144}Ce , ^{154}Eu and ^{155}Eu . N_{Li}/N_{LB} of these radionuclides indicates not only the fraction in leachate but include the amount adsorbed on the walls of leach vessels. The difference in N_{Li} between these radionuclides with boron revealed that these radionuclides were retained in a layer on the glass surface.

Release of actinides

$^{239}\text{Pu}+^{240}\text{Pu}$, ^{241}Am and ^{244}Cm were measured by alpha spectrometry of leachates and acid cleaning solutions. Adsorption of the actinides on the walls of the leach vessels was recognized in all cases. Fig. 4 shows the effect of the acid cleanings to strip the actinides which were adsorbed on the walls of the leach vessels. Since the 1st acid cleaning solution included small amount of leachate, the amounts of actinides stripped by the 1st acid cleaning were corrected. The amounts of the desorbed actinides in the 2nd acid cleaning solution were negligible, compared with the values in the 1st acid cleaning solution. The amounts of actinides on the walls of leach vessels, after the acid cleanings, were determined by alpha spectrometry of thin plates stripped from the gold layer on the walls of the leach vessels to confirm the efficiency of the acid cleanings. These values were less than 0.1% of the amounts of the actinides in the 1st acid cleaning solution. So the total amounts of the adsorbed actinides were determined from the alpha spectrometry of the 1st acid cleaning solution.

Table V shows N_{Li} and N_{Li}/N_{LB} calculated from alpha spectrometry of leachates and acid cleaning solutions. N_{Li} of the actinides from analyses of leachates increased with leaching time and temperature (see Fig. 5), whereas N_{Li} of the actinides from analyses of the 1st acid cleaning solutions were nearly constant at 90°C from 28 to 91 days.

The leached actinides were assumed to be distributed in a layer on the glass surface, on the walls of the leach vessels and in leachates.

Significant decrease of actinides concentration in leachates, after filtration of leachates by using 0.2 μ m filter, shows colloids containing actinides appeared to exist in leachates. The ratios N_{Li}/N_{L_B} show mass balance of the leached actinides (see Table VI). The mass balance explains the leaching behavior of the actinides at 90°C from 28 to 91 days as follows.

$^{239}\text{Pu}+^{240}\text{Pu}$ were distributed between a layer on the glass surface, 52 to 62%, on the wall of the leach vessels, 34 to 35%, and in leachates, 3 to 14%. Note that the percentages on the wall of the leach vessels are considerably higher than those in the leachates.

^{241}Am were distributed between a layer on the glass surface, 82 to 93%, on the wall of the leach vessels, 4 to 5%, and in leachates, 2 to 14%. ^{241}Am was highly retained in a layer on the glass surface.

^{244}Cm were distributed between a layer on the glass surface, 83 to 94%, on the walls of the leach vessels, 3 to 4%, and in leachates, 2 to 14%. Leaching behavior of Cm was quite similar to that of Am. ^{244}Cm was also highly retained in a layer on the glass surface.

Pu, Am and Cm show quite similarly low release values in the leachates, only 2 to 14% that of boron. N_{Li} of these actinides are one to two orders of magnitude lower than that of Cs isotopes. This effect may be important in an evaluation of the relative concentrations of radionuclides released from the glass into solution.

CONCLUSIONS

- The effect of radiolysis on glass leaching was negligible.
- Leaching behavior of ^{134}Cs and ^{137}Cs indicates congruent leaching, whereas that of ^{60}Co , ^{125}Sb , ^{144}Ce , ^{154}Eu , ^{155}Eu , $^{239}\text{Pu}+^{240}\text{Pu}$, ^{241}Am and ^{244}Cm indicates selective retention in a layer on the glass surface.
- Adsorption of the actinides on the walls of the leach vessels was recognized in all cases. The total amounts of the adsorbed actinides were determined by acid cleaning.
- N_{Li} of Pu, Am and Cm, i.e., the mobile fraction of these elements, is one to two orders of magnitude lower than that of congruent leached radionuclides, e.g. ^{134}Cs and ^{137}Cs .

REFERENCES

1. M.J. Apted, G.L. Mcvay and J.W. Wald, Nucl. Technol. 73, 165 (1986).
2. R.D. Peters and H. Diamond, PNL-3971 (1981).
3. H.C. Weed, D.G. Coles, D.J. Bradley, R.W. Mensing and J.S. Schweiger, in Scientific Basis for Nuclear Waste Management I, edited by G.L. McCarthy (Plenum Press, 1979) pp. 141-147.
4. S. Fillet, J.L. Nagues, E. Vernas and N. Jacquet-Francillon, in Scientific Basis for Nuclear Waste Management IV, edited by L.O. Werme (Elsevier Science Publishers, New York, 1985) pp. 211-218.
5. D.J. Bradley, PNL-2664 (1978).
6. JSS-Project Phase IV, JSS Technical Report 87-01, SKB (1987).
7. K. Muta, Y. Kojima, M. Sato, H. Huruya and T. Tamai, Atomic Energy Society of Japan, RWM-87009, 53 (1987).
8. A. Clearfield and R.H. Blessing, J. Inorg. Nucl. Chem., 34, 2643 (1972).
9. G.L. Mcvay and L.R. Pederson, J. Am. Ceram. Soc., 64(3), 154 (1981).
10. H. Sonobe (unpublished data).
11. H. Hermansson, H. Christensen, D.E. Clark, I. Bjorner, H. Yokoyama and L. Werme, in Scientific Basis for Nuclear Waste Management VII, edited by G.L. McVay (North-Holland, 1984) pp. 671-679.
12. B. Grambow, in Scientific Basis for Nuclear Waste Management V, edited by W. Lutze, (North-Holland, 1982) pp. 93-102.

Table I The composition of the HLLW

(µg/ml)		(MBq/ml)	
Na 9.3×10^3	La 1.1×10^3	$^{239}\text{Pu} + ^{240}\text{Pu}$ 3.3×10^{-1}	^{106}Ru 4.8×10^2
Fe 3.5×10^3	Ce 1.8×10^3	^{241}Am 1.9×10	^{134}Cs 4.8×10^2
Cr 2.8×10^2	Nd 3.1×10^3	^{242}Cm 1.5	^{137}Cs 2.0×10^3
Ni 4.2×10^2	Mo 9.0×10^2	^{244}Cm 1.9×10	^{144}Ce 9.3×10^2
Sr 5.7×10^2	Tc 4.3×10^2		^{154}Eu 7.0×10
Ba 1.4×10^3	Ru 1.1×10^3		

Table II(a) Composition of the glass (Wt%)

Frit	SiO ₂	B ₂ O ₃	Li ₂ O	CaO	ZnO	Al ₂ O ₃	Other	Na ₂ O	Fe ₂ O ₃	NiO	Cr ₂ O ₃
	49.0	17.4	2.9	2.2	2.8	5.0*	Oxides	10.0*	2.0	0.2	0.2
Fission Products	SrO	MoO ₃	RuO ₂	Rh ₂ O ₃	PdO	Y ₂ O ₃	La ₂ O ₃	Nd ₂ O ₃	CeO ₂	Pr ₆ O ₁₁	Sm ₂ O ₃
	0.2	0.3	0.1	0.2	0.2	0.1	0.5	1.1	1.1	0.3	0.2

* Calculated values from initially additive amounts.

Table II(b) Radioactivity of radionuclides in the glass (MBq/g)

Fission Products	^{125}Sb	^{134}Cs	^{137}Cs	^{144}Ce	^{154}Eu	^{155}Eu	^{60}Co
	3.7×10	6.3×10^2	3.6×10^3	9.3×10^2	7.8×10	8.1×10	7.0
Actinides	$^{239}\text{Pu} + ^{240}\text{Pu}$		^{241}Am	^{242}Cm	^{244}Cm		
	1.0		7.4×10	6.0	6.7×10		

Table III The total mass losses, NLi of elements and the pH values of leachates

	Leaching time (days)	pH	Total mass loss (g/m ²)	B	NLi (g/m ²)		
					Si	Al	Li
30°C	28	6.8	-	-	-	-	-
	91	6.9	-	-	-	-	-
90°C	28	7.1	7.0	10.0	7.2	-	-
	91	7.9	9.1	13.2	8.9	6.6	11.6

Table IV(a) NLi and NLi/NL_B for fission products and ⁶⁰Co

Analyzed solution	Leaching time (days)		¹³⁴ Cs		¹³⁷ Cs		⁶⁰ Co	
			NLi (g/m ²)	NLi/NL _B	NLi (g/m ²)	NLi/NL _B	NLi (g/m ²)	NLi/NL _B
Leachate	30°C	28	0.29	-	0.28	-	-	-
		91	0.54	-	0.57	-	-	-
	90°C	28	8.53	0.85	8.48	0.85	2.55	0.26
		91	11.3	0.86	11.9	0.90	2.78	0.21

Table IV(b) NLi and NLi/NL_B for fission products

Analyzed solution	Leaching time (days)		¹²⁵ Sb		¹⁴⁴ Ce		¹⁵⁴ Eu		¹⁵⁵ Eu	
			NLi (g/m ²)	NLi/NL _B	NLi (g/m ²)	NLi/NL _B	NLi (g/m ²)	NLi/NL _B	NLi (g/m ²)	NLi/NL _B
Cs-removed solution	30°C	28	-	-	-	-	-	-	-	-
		91	-	-	-	-	0.06	-	0.06	-
	90°C	28	3.90	0.39	0.86	0.09	1.70	0.17	2.00	0.20
		91	4.30	0.33	2.06	0.16	3.38	0.26	3.40	0.26

Table V NLi and NLi/NL_B for actinides

Analyzed solution	Leaching time (days)		²³⁹ Pu+ ²⁴⁰ Pu		²⁴¹ Am		²⁴⁴ Cm	
			NLi (g/m ²)	NLi/NL _B	NLi (g/m ²)	NLi/NL _B	NLi (g/m ²)	NLi/NL _B
Leachate	30°C	28	0.04	-	-	-	-	-
		91	0.07	-	0.03	-	-	-
	90°C	28	0.32	0.03	0.21	0.02	0.22	0.02
		91	1.89	0.14	1.81	0.14	1.81	0.14
The 1st acid cleaning* solution	30°C	28	0.50	-	0.04	-	-	-
		91	0.71	-	0.05	-	-	-
	90°C	28	3.45	0.35	0.53	0.05	0.37	0.04
		91	4.54	0.34	0.49	0.04	0.44	0.03

* These values mean the total amounts of the adsorbed actinides on the wall of the leach vessels calculated by subtracting the amounts of actinides in small amounts of the leachates which were contained in the 1st acid cleaning solution.

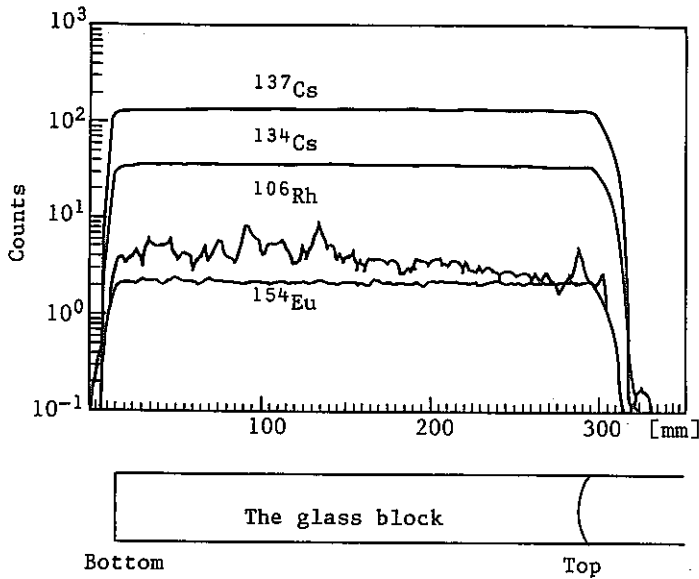


Fig. 1 Gamma scanning profile in the glass block

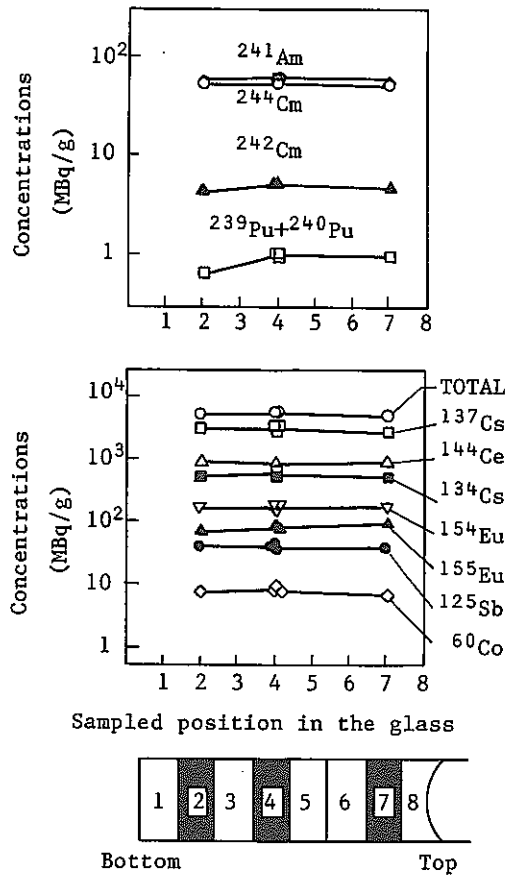


Fig. 2 Distribution of actinides and fission products in the glass block

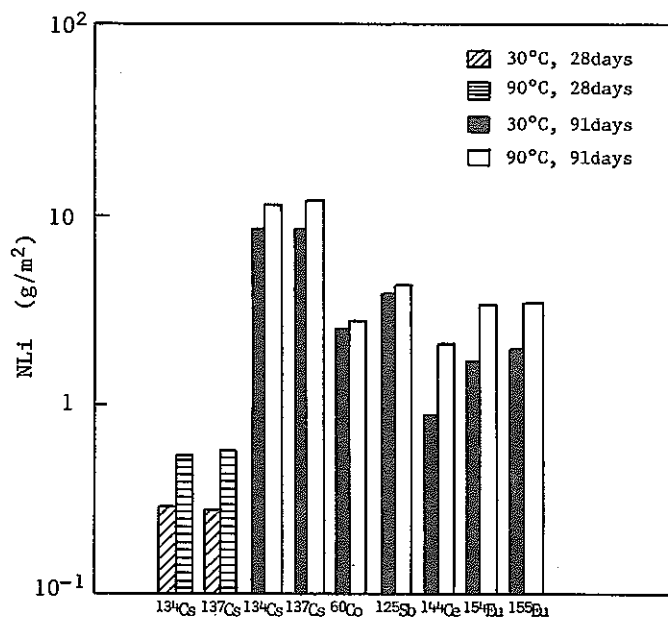


Fig. 3 NLi of fission products

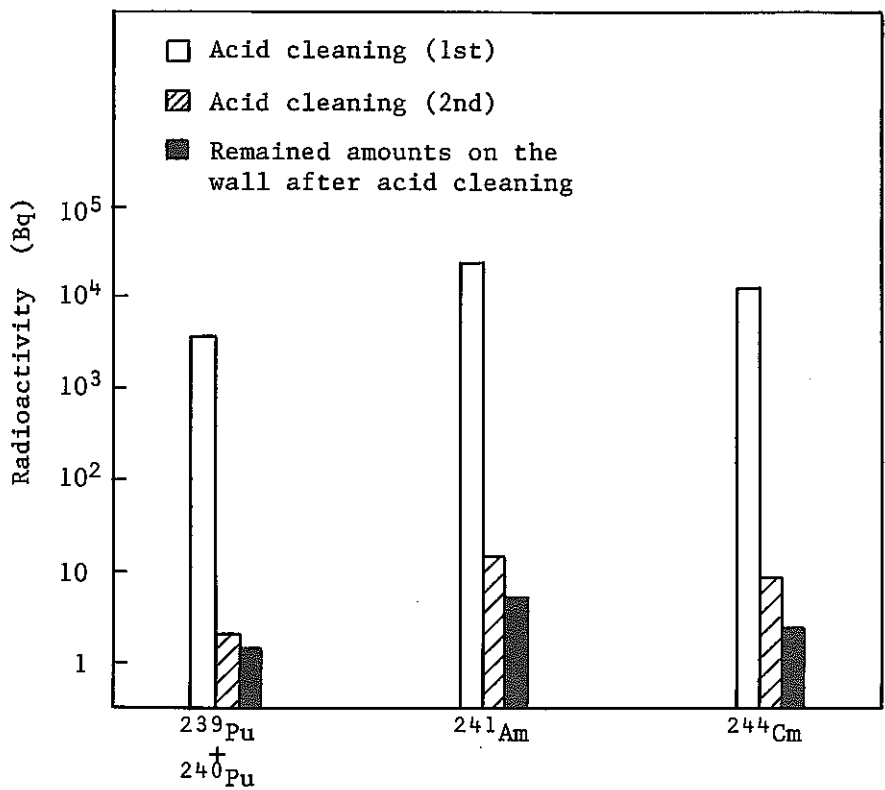


Fig. 4 The effect of acid cleaning on the wall of leach vessel

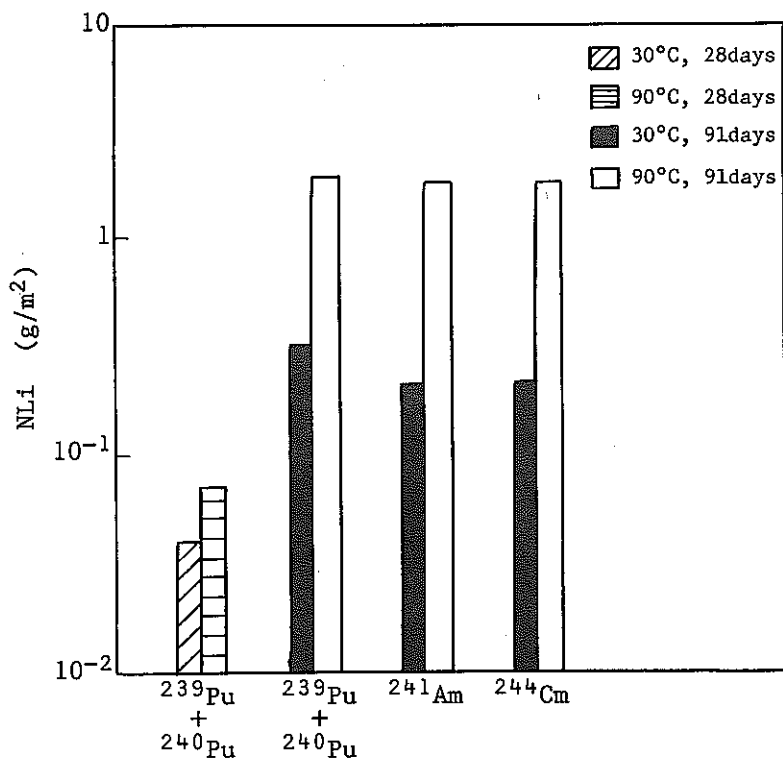


Fig. 5 NLI of actinides from leachates