Method for Evaluating Leaching From LSA-III Material

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INTRODUCTION

The IAEA transport regulations (1985 edition) are scheduled to be introduced in Japan. New regulations are supposed to be set forth for low specific activity (LSA) material and industrial packaging (IP) as solidified concentrated waste water should correspond to the LSA material. Solidified concentrated waste water should be transported in accordance with the new transport regulations which reflect the IAEA transport regulations. As one of the regulations for LSA material, the "leaching test" for LSA−Ⅲ materials states that the radioactive loss due to leaching without the packaging should not exceed $0.1A_2$ when left in the water for 7 days. This test method is called "Transport regulations" hereafter. Since the test had not been conducted in Japan be fore now, there was no available data. Consequently, it is necessary to make an assessment on whether the current solidified concentrated waste water can satisfy the leaching amount of radioactive nuclide specified in the IAEA transport regulations. If the test is performed in accordance with the IAEA transport regulations, however, it is necessary to measure the amount of radioactive nuclide actually leached from the solidified concentrated waste water. Since the solidified concentrated waste water is put in a drum cam, it is necessary to prepare large−scale hot test equipment. Terefore it is difficult to perform such a measurement by using ordinary equipment.

In this study, therefore, the leaching test was conducted on the solidified concentrated waste water to propose the means of a leaching assessment which can be conducted with ordinary equipment to evaluate the leaching for assessment of the a daptability to IAEA transport regulations. In addition, the leaching test was performed in accordance with the IAEA method (test method concerned with leaching at the time of ocean or burial disposal) to examine the co−relation between the transport regulations and the IAEA method. Many test results have been reported for the IAEA method in Japan, which will be detailed later on.

LEACHING TEST

The "Leaching" test was conducted by using solidified cement material, solidified asphalt material and solidified plastic material in order to examine the relation between dimension, tracer density and other conditions in accordance with the flow shown in Fig. 1.

- Non-radioactive
  - o Large specimen (Transport regulations method)
  - o Small specimen (Transport regulations method)
- Radioactive
  - o Small specimen (Transport regulations method)
  - o Small specimen (IAEA method)

The comparison was made on the result of leaching for radioactive small specimen between the transport regulations and the IAEA method, each of which test method is described further on.

(1) Cold leaching test

The cold leaching test was made by using both large and small specimens.
The test was performed in accordance with the transport regulations described in S.S. No. 6 article−603 of the IAEA transport regulations, of which details will be described in the following.
The test conditions are as shown in Table−1.

o Specimen .... Solidified material having a volume equivalent to the total contents of the package is immersed in ambient temperature water for 7 days.

o Leaching water ...... Volume of water to be used for the test must be sufficient so that the volume of water left without being absorbed or reacted at the end of 7−day test is at least more than 10% of the solidified specimen volume itself.
Water must provide pH of 6~8 and a maximum

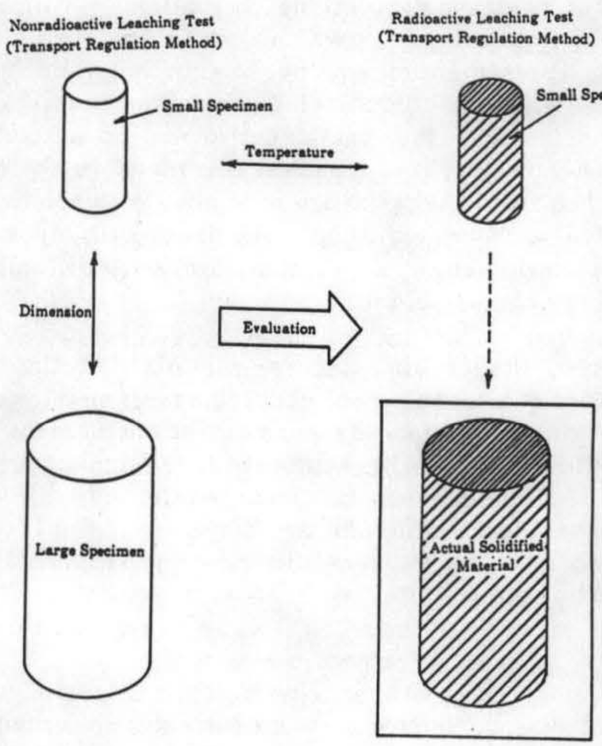

Fig. 1 Evaluation Method of Leaching Test

	electrical conductivity of 1 ms/m (10μmho/cm) at the tempera ture of 20℃ at the initial stage.
o Test method …………	Measure total radioactivity of remaining water after immersing test specimen for 7 days.

Since the solidified concentrated waste water which is generated at the nuclear power plant contains a lot of radioactive nuclides, it is difficult to perfectly simulate the radioactive nuclide due to restrictions such as adaptability of tracer, detection limit of tracer, etc. when performing the cold leaching test.
Besides, there may exist such nuclide which will not affect the limit value ($0.1A_2$) of leaching even if the total content, is leached because there is limited nuclide contained in the solidified concentrated waste water.
It is also necessary to add chemical material in a volume greatly exceeding the volume of the solidified concentrated waste water. Depending on the type of nuclide, the sensitivity of the chemical tracer is inferior to that of the RI tracer. Thereby the properties of the specimen may become different from those of the solidified concentrated waste water.
In this regard, CsCl was selected as a chemical tracer, taking the adjustability with solidified concenrated waste water into consideration in this cold leaching test.

(2) Hot leaching test

The radioactive nuclide was measured for leaching by using the small specimen in the hot leaching test in accordance with the transport regulations.
The amount of leaching of the radioactive nuclide of the solidified concentrated waste water was deduced from the subsequent result.
The relationship of leaching between the small specimen and large specimen obtained in the cold leaching test (1) was used for the deduction.
The radioactive nuclide of the small specimen was measured for leaching in accordance with the IAEA method to examine the relation between the IAEA method and transport regulations.
The testing condition is shown in Table−2, and the details of the IAEA method in the following.

o Specimen ……………	Cylindrical specimen with height of 44mm and diameter of 45mm
o Leaching water ……	Underground water or composite water at disposal point, or seawater or composite seawater at disposal sea area
o Temperature ………	± 3 ℃ of temperature at disposal point, or 25℃ ± 3 ℃ where it is not applicable
o Test method ………	Leaching water of 750mℓ was prepared, and the specimen was held at a height of 2 cm above the bottom of the holding container, so that the leaching water with a thickness of 2 cm could exist at the clearancy the container wall surface. Leaching water was replaced with new leaching water for sampling in accordance with the following schedule. The leaching water was subjected to analysis/measurement. o Once every day for the initial one week o Once every week for eight weeks thereafter o Once every month for six months thereafter o Once every six months thereafter

Since the test is intended to examine the relation of radioactive nuclide leaching between the transport regulations and IAEA method, the period of the test for the IAEA method was set at 7 days in accordance with the transport regulatios.
Since the measuring instrument for RI tracer provides a high detection sensitivity, making it possible to measure RI tracer even when an extremely limited amount of RI tracer is mixed in the specimen, it is possible to execute the leaching test by using the specimen which simulates the properties of solidified concentrated waste water.
In selecting the RI tracer, it is necessary to consider the content and leaching behaivior of the radioactive nuclide contained in the solidified concentrated waste water.

Table 1 Test Condition

Items		Test Condition	
Test Method		Transport Regulation	
Specimen		Large Specimen	Small Specimen
Leaching Time		7 days	
Specimen	Dimension(mm)	$\phi 570\times 840^H$ (Inside Dimersion of Packaing)	$\phi 45\times 44^H$
Specimen	Volume	$0.21m^3$ $(2.01m^2)$	$70.0cm^3$ $(94.0cm^2)$
Specimen	Solidifying Material	Cement, Asphalt, Plastic	
Ambient Liquid	Physical・Chemical Property	Distilled Water or Ion Exchange Water ph=7 Electrical Conductibity 1mS/m lower	
Ambient Liquid	Volume	$0.21m^3$	$750cm^3$
Ambient Liquid	Replacement Frequency	No Replacement	
Ambient Liquid	Temperature	25±3℃	
thers	Packaging for Leaching Test	Steel $(\phi 725\times 1200^H)$	Beaker
thers	Liquid Contact Method	All-surface liquid contact for cement solidifying material and plastic material, and upper-surface contact for asphalt solidifying material	

For the nuclide which will not affect the limit value ($0.1A_2$) of LSA−Ⅲ leaching even if the total content is leached, it is thought not necessary to use as RI tracer.
By comparing each nuclide with an A_2 value to the radioactive nuclides contained in the solidified concentrated waste water, it was proved that the proportion with an A_2 value was very large and the nuclides essential in assessing the leaching were ^{60}Co, ^{90}Sr, ^{137}Cs, and ^{239}Pu. In assessing the leaching behavior, the points considered were the properties of the leaching liquid such as pH value the ease of leaching the radioactive nuclide.
The radioractive nuclide to be mixed in the specimen used for the hot leaching test was selected as follows in accordance with the above approarch.

(i) To select ^{137}Cs for nuclide existing as ions within a wide range of pH
(ii) To select ^{60}Co for nuclide which rarely exist as irons on the alkali side of pH
(iii) To select ^{85}Sr as nuclide which shows a medium property between (i) and (ii) above
(iv) To simulate ^{127}Pu, actinides, by using ^{152}Eu, lanthanoid element having similar chemical features. Since the movement due to deffusion of ^{239}Pu occurs in ^{125}Eu or less, it is possible to evaluate the leaching behavior of ^{239}Pu safety by using the leaching behavior of ^{10}Eu.

TEST RESULT

Table-2 Hot Leaching Test Conditions

Item	Test Conditions	
Regulations	IAEA Method	Transport Regulations Method
Solidifying Material	Cement, Asphalt, Plastic	
Size of Specimen	45mm ϕ ×44mm or equivalent	
Amount of Water Leached	750ml	
Leaching Temperature	25℃±3℃	
Liquid Contact Method	All-surface liquid contact for cement solidifying material and plastic material, and upper-surface contact for asphalt soldifying material	
Replacement Frequency of Leaching Water	Everyday for upto 7 days	No Replacement for 7 days
Leaching Liquid	Puer Water	

Table-3 Result of Cold Leaching Test by Large Specimen

Type of Solidified Material	Cement		Asphalt	Plastic
Dimension of Specimen				
Diameter(cm)	56.6	56.6	56.6	56.2
Hight (cm)	75.8	75.8	68.4	76.3
Weight of Specimen				
Before Test(kg)	397.7	381.8	254.5	333.6
Afer Test (kg)	380.6	381.8	254.6	333.4
Ambient Liquid after Test				
PH	12.1	12.3	7.5	5.3
Electrical Conductivity (μS/cm)	470	3540	1.6	4430
Weight (kg)	207.7	208.0	209.3	209.7
Amount of Tracer Mixed (g)	79.0	79.0	758.0	1579.6
Amount of Tracer Leached (g)	0.77	0.67	0.0036	21
Leaching Ratio	9.7×10^{-3}	8.5×10^{-3}	4.75×10^{-6}	1.3×10^{-2}

(1) Cold leaching test

The result of the cold leaching test using a large specimen is shown in Table-3, and that using a small specimen in Table-4.

(2) Hot leaching test

The result of the hot leaching test in accordance with the transport regulations and IAEA method is shown in Table-5.

PRESUMPTION OF LEACHING AMOUNT

The amount of radioactive nuclide leached from the solidified concentrated waste water is deduced by using the test result in accordance with the assessment method shown in Fig.1.

The amount of radioactive nuclide leached must be determined by some parameters such as surface area or nuclide density.

In this study, the leaching amount was evaluated by setting the following five parameters.

S ……… Surface area

C ……… Nuclide density

Table-4　Result of Cold Leaching Test by Small Specimen

Type of Solidified Material	Cement		Asphalt		Plastic	
Dimension of Specimen Diameter(cm) Hight (cm)	4.5 4.4	4.5 4.4	4.5 4.4	4.5 4.4	4.5 4.4	4.5 4.4
Weight of Specimen Before Test(kg) Afer Test (kg)	137.95	138.15	90.74	87.09	118.93	119.38
Ambient Liquid after Test PH Electrical Conductivity (μS/cm) Weight (kg)	12.3 2700 747	12.0 2600 750	8.3 19 738	8.3 14 742	7.4 480 748	7.6 970 748
Amount of Tracer Mixed (g)	0.0237	0.0237	0.316	0.303	0.527	0.529
Amount of Tracer Leached (g)	1.40×10^{-3}	1.15×10^{-3}	4.25×10^{-6}	4.55×10^{-6}	6.21×10^{-3}	3.59×10^{-3}
Leaching Ratio	5.91×10^{-2}	4.85×10^{-2}	1.34×10^{-5}	1.50×10^{-5}	1.18×10^{-2}	6.79×10^{-3}

Table-5　Result of Leaching Test by Small Specimen

Item	Trpe of Nuclide	Co-60	Sr-85	Cs-137	Eu-152
Specimen	Test Method	Integrated Leaching Ratio(-)	Integrated Leaching Ratio(-)	Integrated Leaching Ratio(-)	Integrated Leaching Ratio(-)
Solidified Cememt	IAEA Method	2.0×10^{-3}	4.8×10^{-4}	5.6×10^{-3}	1.7×10^{-4}
	Transport Regulation Method	1.8×10^{-6}	4.2×10^{-4}	4.0×10^{-3}	9.8×10^{-7}
	IARA/Transport Regulations	1.1×10^{3}	1.1	1.4	1.7×10^{3}
Solidified Asphalt	IARA Method	2.6×10^{-4}	5.4×10^{-5}	5.2×10^{-5}	4.8×10^{-5}
	Transport Regulation Method	2.7×10^{-4}	4.3×10^{-5}	4.2×10^{-5}	6.5×10^{-6}
	IAEA/Transport Regulations	1.0	1.30	1.2	7.4
Solidified Plastic	IAEA Method	1.0×10^{-3}	1.2×10^{-3}	3.4×10^{-4}	8.5×10^{-4}
	Trnsport Regulation Method	1.2×10^{-3}	1.5×10^{-3}	3.4×10^{-4}	4.7×10^{-4}
	IAEA/Transport Regulations	0.8	0.8	1.0	1.8

* 1) Each sample was used for IAEA method and transport regulation method respectively ,however, the average value was found and entered.

T ········ Thickness contributing to leaching
t ········ Immersion time
H ········ Easiness of diffusion within solidified material

The relasionship between each parameter and leaching amount (A) is described further on.

The surface area (S) and nuclide density (C) must be in proportion to the leaching amount if the size of the solidified material is greater than some fixed value determined by the other parameter.
The thickness (T) contributing to leaching will not affect the leaching amount as long as the size of solidified material remains greater than some fixed value determined by the other parameter.
The immersion time (t) will not affect the leaching amount as it remains constant for 7 days.
The ease of diffusion (H) within the solidified material of the nuclide is determined by the properties of the solidified material and will not affect the leaching amount as long as the solidifying material is the same.
Accordingly, the calculation for leaching amount (A) was set as follows;

$$A = K \times S \times C$$

In this case, "K" is a scale factor which expresses the effect of solidified material size. The scale factor (K) of large specimens and small specimens was obtained from the cold leaching test result, which is shown in Table−6.

Table−6 Scale Factor

Type of Solidified Material	Large Specimen	Small Specimen
Cement	9.4×10^{-2}	4.0×10^{-2}
Asphalt	4.8×10^{-5}	1.1×10^{-5}
Plastic	1.4×10^{-1}	6.9×10^{-3}

The amount of nuclide leached from the solidified concentrated waste water (A_2) can be expressed as follows;

$$A_2 = \frac{K_2 \times S_2 \times C_2}{K_1 \times S_1 \times C_1} A_1$$

where, the subscript "$_1$" shows the small specimen and "$_2$" the large specimen.
The formula was used to deduce the amount of nuclide leached from the solidified concentrated waste water.
The nuclide not used as RI tracer in the hot leaching test was evaluated, were assumed to be leached completely.
The resutl is shown in Table−7.

CONSIDERATIONS

(1) As shown in Table−4, each solidified material and two specimens were used for the cold leaching test by using the small specimen.
Observing the leaching ratio for two specimens of each solidified material that they were almost equal for the solidified cement and solidified asphalt materials and at most double for solidified plastic. This revealed satisfactory repeatability.

(2) As shown in Table−7, the result of radioactive nuclide leached from the solidified concentrated waste water is given as follows;
- o Solidified cement material .... 1.7×10^{-3}
- o Solidified asphalt material .... 1.1×10^{-3}
- o Solidified plastic .... 2.3×10^{-3}

Accordingly, it was proved that the limit value ($0.1A_2$) of LAS−Ⅲ could be fully satisfied in case of the solidified concentrated waste water having radioactive nuclide density equivalent to that estimated in this study.

(3) The leaching ratios of the following nuclides differ greatly between the transport regulations and IAEA method: $_{60}$Co and $_{152}$Eu for the solidified cement, and $_{152}$Ea for the solidified asphalt only.
All other nuclides provide less than double the ratios of the IAEA method and transport regulation, and leaching by the IAEA method is a greater then by the latter. The following can be considerable from this result.

(i) The density of radioactive nuclide tends to decrease, and the leaching ratio tends to increase as compared with the transport regulations because the leaching liquid is replaced every day in the case of the IAEA method.
However, the difference in the density double is at most in 7 days.

(ii) Since the leaching liquid pH level is increased to approx. 12 from 7 at the initial stage in the leaching test in accordance with transport regulations of solidified cement material, the amount of $_{60}$Co leached, which can hardly exist as an ion at the alkali side, decreases.
In the case of the IAEA method, however, such a tendency is not observed.
Since the leaching liquid is replaced every day in the IAEA method, the pH will not increase as much as in the transport regulation method. Consequently, $_{60}$Co is readily ionized in the IAEA method for solidified cement and thus is readily leached.
The defference in the leaching ratio between the IAEA method and the transport regulations is thought to be brought about due to a similar reason.

(iii) The leaching ratio of $_{152}$Eu for solidified asphalt reaches 7.4 times the ration obtained by the transport regulation method. The difference in the leaching ratio between the IAEA method and the transport regulation method is probably brought about due to a similar reason, as the pH of the leaching liquid reaches approx. 8.

(4) Scale factor "K" indicates the diffusion of nuclide from the inside (bulk) of the solidified material to the vicinity of the surface, movement of nuclide from the surface of the solidified material to the liquid, and the quality of the solidified material (especially the difference between the large specimen and the small specimen.)

CONCLUSION

The result of this study revealed the following :

According to the result of the leaching test conducted on the cold large specimen/small specimen and hot large specimen, it is possible to predict the amount of radioactive nuclide leached from the solidified concentrated waste water. The leaching amount deduced by using an example of nuclide composition in solidified concentrated waste water could satisfy the limit value of LAS− Ⅲ. In addition, since the co−relation for the leaching ratio between the IAEA method and the transport regulation method could be obtained for Co, Cr, Cs and Eu, it is possible to predict the leaching amount from the result of the IAEA method by the use of the transport regulation method.
If the relationship between the properties of nuclide and ease of leaching is known, it is also possible to evaluate the leaching amount for other nuclides from the result of the IAEA method. The co−relation between the IAEA method and the transport regulation method is expected to be further reviewed in the future.