

An Experimental Study on Factors Affecting the Leachability of Cs-137 in Cement Matrix and Leaching Model with Backfill

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시멘트 고화체내 Cs-137의 침출능에 영향을 미치는 인자에 대한 실험적 연구와 뒷채움재를 고려한 침출 모델

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Abstract

Various factors affecting the leachability of Cs-137 in cement matrix have been investigated. Factors investigated include such as pressure curing, vibration curing, pressure leaching, the effect of the clay addition, ion-exchange resin (IRN-77) addition, and CO₂ or air injection. Leaching experiments were conducted by the method recommended by IAEA. To analyze the experimental results, pore structure analysis of cement matrices was carried out by BET method.

Cement matrices may not contact directly with underground water in real repository, since the surroundings of disposed drums are filled with backfill. Thus, the effect of backfill to the leachability has been investigated. The well-known diffusion theory was utilized to predict long term leach rate and cumulative fraction leached of Cs-137 or non-radioactive species.

요 약

시멘트 고화체내 Cs-137의 침출에 영향을 미치는 여러 새로운 인자들에 대해 조사하였다. 조사된 인자들은 가압 상태 및 진동 상태에서의 시멘트 경화, 압력하에서의 침출, 여러 종류의 점토 첨가, 이온 교환 수지 (IRN-77)의 첨가, 그리고 CO₂ 또는 공기 주입의 영향이다. 침출실험은 IAEA가 제시한 방법에 의해 수행되었고, 실험 결과를 해석하기 위해 시멘트 고화체에 대한 기공 구조를 BET 방법으로 분석했다.

처분장에 처분된 고화 드럼 주위에는 뒷채움재가 채워져 있기 때문에 시멘트 고화체가 직접 지하수와 접촉할 가능성은 매우 희박하다. 그래서 뒷채움재가 침출능에 미치는 영향을 예측하였다. 잘 알려진 확산 이론을 이용하여 뒷채움재를 고려했을 때 Cs-137 또는 비방사능 물질의 장기 침출율과 누적 침출량을 예측하였다.

1. Introduction

Low-level radioactive liquid wastes(LLW) is generated by the operation and maintenance activities at light water reactors(LWR). These are disposed of in final disposal site after several treatment processes. If underground water permeates into the disposal site, the drums will be corroded and the solid matrix will come into contact with water. Then the leaching process begins and radioactive nuclides move along with the water into the environment. Therefore the study of leaching phenomena is very important for the safety analysis of LLW disposal. It is the initial objective of this paper to search for system factors and solid factors reducing the leach rate.

In the leaching experiment, following factors have been classified as follows[1] :

—system factors ;

time, temperature, radiation environment, ratio of solid surface to the volume of leachate.

—leachate factors ;

composition, pH, EH(oxidation–reduction potential), flow rate(or replacement frequency).

—solid factors ;

composition alteration by addition of vermiculite, surface condition.

In this paper new factors such as pressure curing, pressure leaching, vibration curing, addition of ion–exchange resin or various clay, porosity, and CO₂ or air injection will be considered.

Leaching experiments will be carried out by the method recommended by IAEA[2]. To analyze the experimental results following analyses will be conducted ; 1) pore structure analysis of cement pastes by the BET method, 2) survey of chemical composition of cement and additives, 3) the chemical reaction of Cs-137 with various additives.

Many experiments have been performed under the assumption that cement matrices might be in direct contact with underground water. However,

this assumption may not describe the true situation since the environment around the drums is expected to be filled with backfill. Therefore it is the second objective of this paper to predict long-term leach rate including the backfill. A well-known diffusion model[3, 4] will be utilized to find analytical solutions of leach rate and the cumulative fraction leached. Then these will be applied to 55 gal drum filled with various backfill thickness to predict long-term leach rate.

2. Experiment

2-1 Leaching Experiment

The specimens used in this experiment were prepared by combining the desired volume of wastes solution with predetermined weight of cement and their necessary various additives. The liquid wastes, which simulated the evaporator bottom concentrate generated at PWR plants, was prepared by dissolving boric acid into deionized water to make the solution concentration of 12 percent by weight as boric acid. It contained no radioactive material other than the tracer, Cs-137(CsCl type) manufactured by Du Pont. Prior to the addition of the tracer appropriate quantity of saturated sodium hydroxide solution was added to the wastes to adjust the pH of about 12. After the addition of Cs-137(about 1 ml), liquid wastes was left alone for 10 minutes to provide the homogeneous distribution of tracer. Samples of the prepared solution were taken and used as the feed material in the all subsequent experiment for activity determination.

The paste of cement was prepared by mixing the simulated wastes and the matrix material in one liter beaker. All specimens were prepared at the wastes to cement ratio(w/c) of 0.362 by weight. After sufficient mixing the resulting paste was poured into poly ethylene container A, which

was made to simulate the one dimensional system. In most cases the specimens were cured for 2 weeks at room temperature in closed vessel where shallow water exist to maintain about 100 percent relative humidity. After the curing the specimens in the container A was placed inside container B (see Figure 1), which was made of poly methyl meta acrylate (PMMA), and then the leach test was conducted following the IAEA method. Samples of all feed and solutions containing Cs-137 were analyzed using the AUTO-GAMMA 5110 manufactured by Hewlett Packard Instrument Company, INC..

The 13 specimens for leach tests were briefly described in Table 1.

2-2 Pore Structure Analysis

Pore analyses were used to analyze the results of the leach tests and these were performed by the

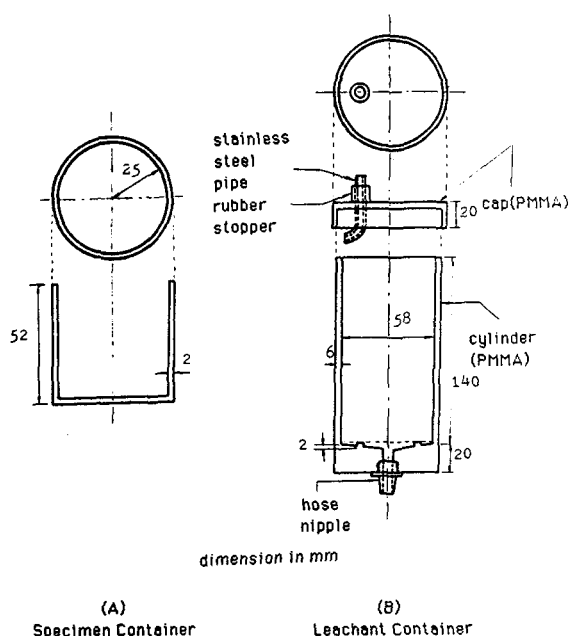


Fig. 1. Leaching Experiment Containers

Table 1. Description of Specimens Used for Leaching Experiment

sample name	curing condition	initial activity(μ Ci)	sample name	curing condition	initial activity(μ Ci)
A-1	a	4.82	B-6(g)	c	2.41
A-2	b	4.93	B-8(h)	c	2.32
A-5	c	4.88	B-10(h)	c	2.32
A-6(e)	c	4.90	B-12(h)	c	2.26
A-9(e)	c	1.60	D-1	c	4.90
B-1(f)	c	4.57	D-2	c	4.95
B-3(f)	c	2.86			

a : Cured for 17 hours at 25 psia and then until 2 weeks under about 100% relative humidity(RH)

b : Cured for 1 hours under vibration and then until 2 weeks under about 100% RH

c : Cured for 2 weeks under about 100% RH

d : Cured for 2 weeks under about 100% RH

e : pressure leaching

f, g, h : Addition of Ion-exchange resin(IRN-77), Pottery clay, and Koline respectively

BET method[5]. Adsorption isotherm was used to find the pore size distribution in this analysis because certain hardened Portland cement pastes with large fraction of pores have wide bodies with very narrow entrance like ink bottle[6].

Specimens for this test were made by the same method as specimens for leaching experiments, but no tracer addition. Experiments were conducted as following procedures(see Figure 2) :

1) Break specimens as sizable as granule and dry

these granule at 300°C for 20 minutes.

- 2) Take a few granule and determine their weight with maximum precision.
- 3) Placed the sample into sample system, and then connect to manifold system.
- 4) Open all valves except valve 2, and then degas for 20 minutes at 300°C by heating mantles.
- 5) After a removal of the mantles, allow sample tubes down to room temperature and allow liquid nitrogen to settle down at least 45 minutes.
- 6) Close valve 3 and 4, then check liquid nitrogen levels on sample system.
- 7) Open appropriately adsorbate valve until the predetermined pressures are attained, and then close valve 2.
- 8) Record pressure as P_1 , and then open valve 4 and wait until equilibrium state is reached.
- 9) Record pressure as P_2 and close valve 4.
- 10) Repeat procedures from 7) to 9).

New P_1 must have greater value than previous one. From pressure data the amount of adsorbed nitrogen gas was calculated by using equation 1.

$$\frac{V_a}{W_s} = \frac{273}{760 W_s} \left[\frac{V_d}{T_d} (P_1 - P_2) - \left(\frac{V_s}{T_s} + \frac{V_i}{T_i} \right) (P_2 - P_e) - \frac{V_s}{T_s} (P_2^2 - P_e^2) \right] \quad (1)$$

Here P_e is the same to P_2 of previous procedure. Pore surface of each sample is given by equations 2 and 3.

$$\frac{P}{V_a (P_s - P)} = \frac{1}{V_m C'} + \left(\frac{C' - 1}{V_m C'} \right) \frac{P}{P_s} \quad (2)$$

$$S_w = \frac{4.35}{\text{slope} + \text{intercept}} \quad (3)$$

Slope and intercept in equation 3 can be obtained by plotting of equation 2 for $P/V_a(P_s - P)$ versus P/P_s . Equation 4 was used to find pore size distribution.

$$V_p - V_c = \int_{r_c}^{\infty} \pi (r_c - t)^2 L(r) dr \quad (4)$$

A more detailed calculational procedure was described in reference [7].

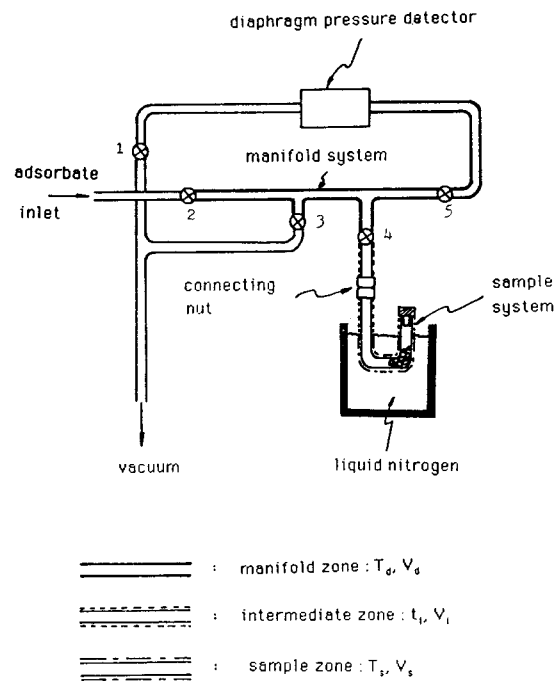


Fig. 2. Schematic Diagram of BET Experiment Apparatus

3. Result and Discussion

Thirteen tests were made to evaluate the leaching of Cs-137 from the cement matrices with deionized water. The results are presented in this section as plots of the cumulative fraction leached ($\Sigma a_n/A_o$) versus square root of time.

To compute the pore surface area, plotting of relative pressure (P_2/P_s) versus $P_2/V_a(P_s - P_2)$ was made as Figure 3. Slope and intercept of all samples were found from this figure, and were utilized for the calculation of pore surface area like Table 2.

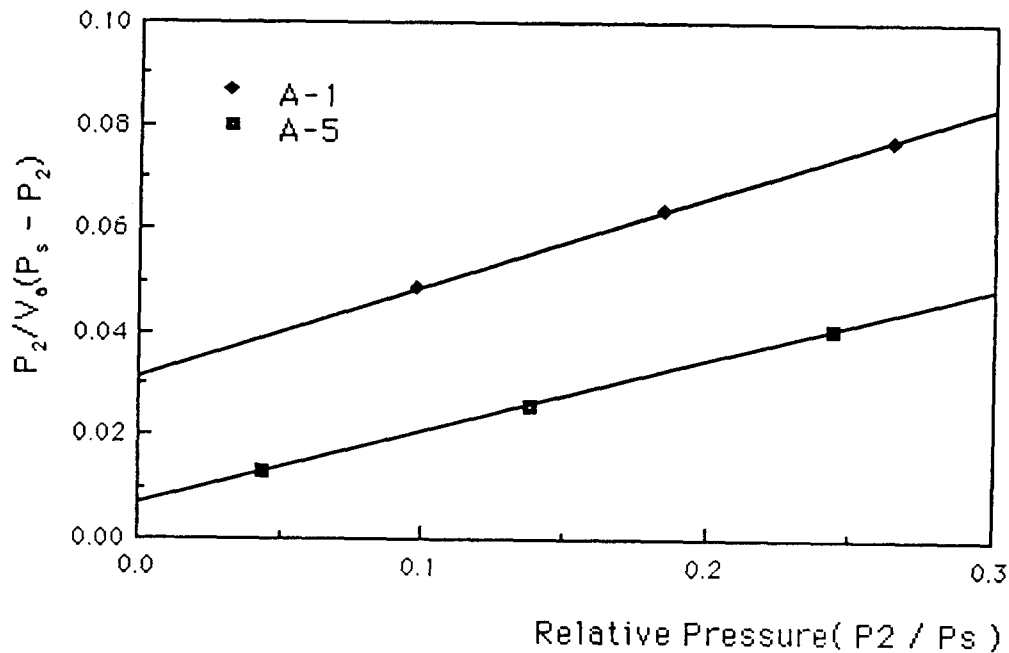


Fig. 3. Plot of BET Equation

(A-1 : Curing under Pressurized Condition, A-5 : Reference Sample)

Table 2. BET Surface Area

sample name	intercept	slope	surface area (m ² /g)	note
A-1	3.149×10^{-2}	0.1718	21.400	pressure
A-5	7.025×10^{-3}	0.1392	29.745	reference

3-1 Effect of Pressure and Vibration Curing

In figure 4, A-5 is reference sample which is cured for 2 weeks under about 100% relative humidity. A-2 is sample cured for 1 hour under vibration with potable sieve shaker and then cured under the same condition and period as A-5 sample. A-1 sample was cured for 17 hours under 25 psi and then cured under the same condition and period as A-5 sample. Specimens of A-2 and A-5

have similar cumulative fraction of Cs-137 leached for 49 days(CF49). But CF49 of A-1 sample is reduced by 45% compared with A-5.

These results are considered due to small porosity of cement matrix caused by pressure. Pore analysis shows that matrix of pressure curing has less pore surface area as Table 2 and more micropores than the reference sample as Figure 5. In small pores, the hydration products have not enough space to grow into crystals[8].

3-2 Effect of Pressure leaching

Figure 6 shows the effect of pressure leaching. Here, for the case of the specimens A-5, A-6, and A-9, the leach test was carried through at atmospheric pressure, 30 psia, and 40 psia, respectively. Experimental results show that CF49 of A-6 is increased by 72% compared with A-5. For the case of specimen A-9, it results in 106% increase.

It is known that there is no general relationship between pressure and leach rate and few data available on the effect of pressure on leachability of the cement matrix. However, the overall results indicate that cumulative fractional increase exists with increasing pressure. It is suspected that the above results are caused by the increase of water intrusion into the pores of the concrete and the effect of desorption isotherm on the matrix.

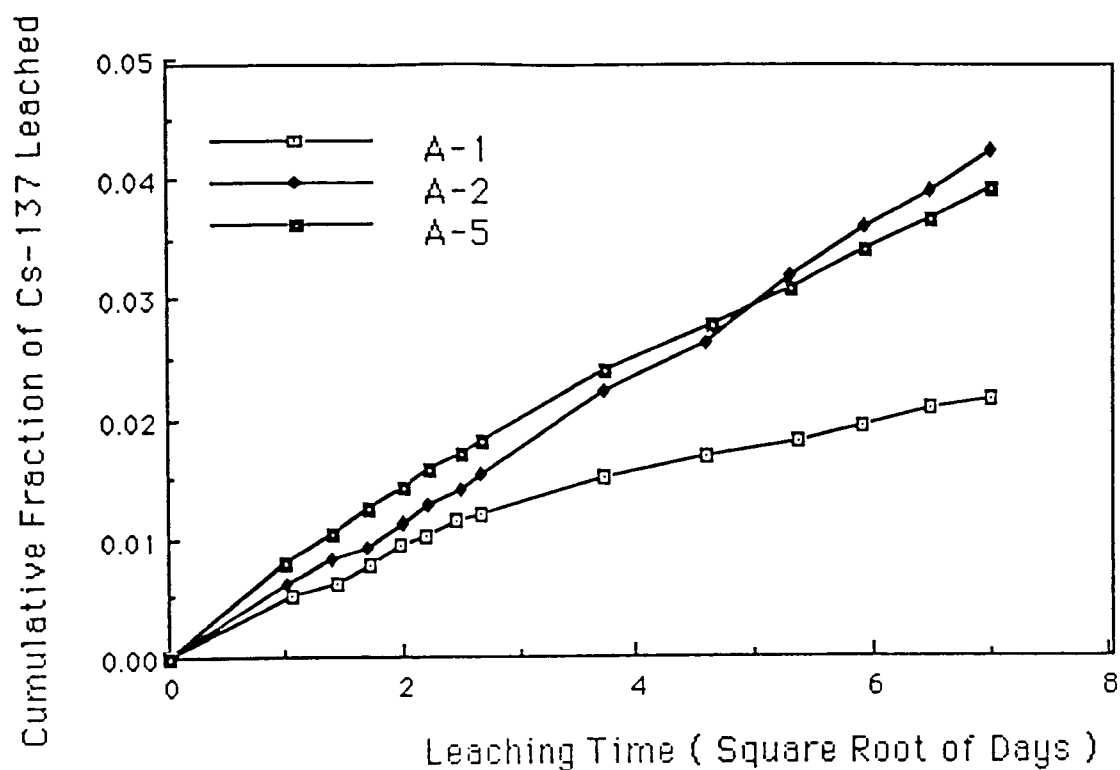


Fig. 4. Effect of Pressure Curing and Vibration Curing

(A-1 : Pressure Curing, A-2 : Vibration Curing, A-5 : Reference)

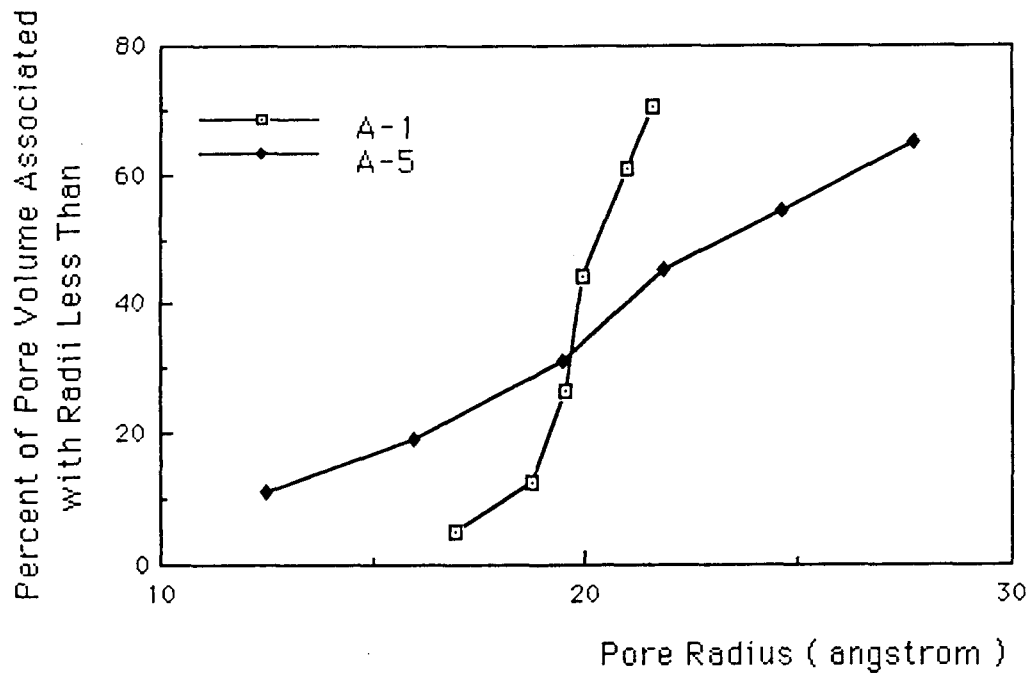


Fig. 5. Pore Volume Distribution

(A-1 : Pressure Curing, A-5 : Reference Sample)

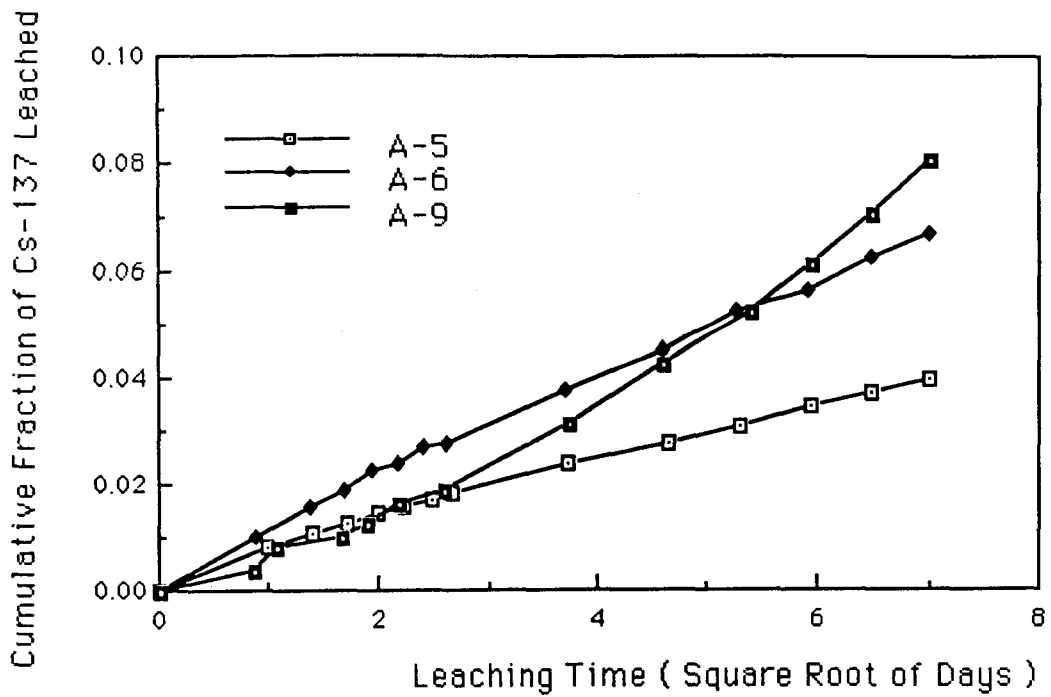


Fig. 6. Effect of Pressure Leaching

(A-5 : Reference Sample, A-6 : Leaching under 30 psia A-9 : Leaching under 40 psia)

3-3. Effect of Ion-exchange Resin (IRN-77) Addition

The following experiment was performed to examine the effect of ion-exchange resin (IRN-77) on leachability. To prepare the specimens, cesium chloride (CsCl) and IRN-77 was added to the waste solution, and the solution was left to react for about 10 minutes. Then the prepared solution was mixed the cement in one liter beaker.

Figure 7 represents that cumulative fraction of Cs-137 leached for 49 days (CF49). This is increased by 46% for the the case of specimen B-1 (resin/cement ratio 9.7 w/o as dry resin basis). Specimen B-3 (r/c ratio 19.4 w/o) was still remained soft after curing for 2 weeks. So after leaving it untouched for 1 day at room conditions, the leach test was conducted. In this case the

surface specimen swelled up in a few hours after contact with leachate. After all, CF49 of B-3 results in 613% increase over that of A-5.

The above results indicate that IRN-77 has retarding effect on cement hydration like boric acid. IRN-77 is cation type ion-exchange, and phenomena of swelling and cracking of ion-exchange resin waste forms can be directly attributed to the presence of the cation form of resin. According to the SEM analysis of cation resin beads in cement paste, they interact with the components of the cement and the resin appears to adsorb not only calcium and alumina (Al_2O_3), which are the important elements for cement curing, preferentially but also some silicon. Moreover, because sulfur is enriched in cement sampled close to resin beads, resin beads may be giving up sulfur to the cement [12].

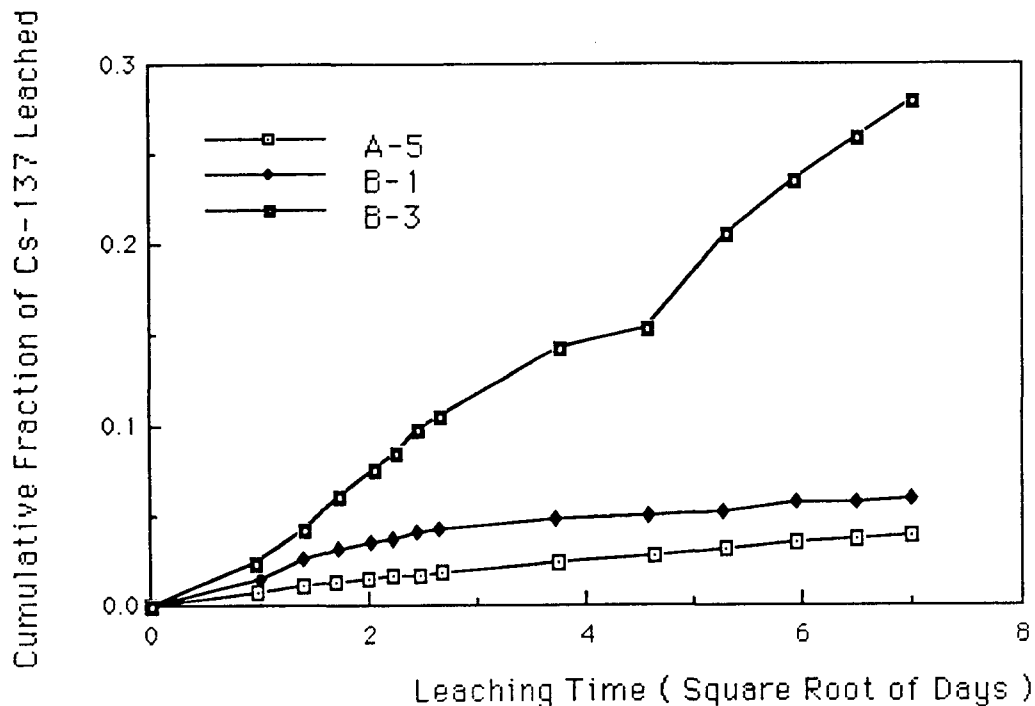


Fig. 7. Effect of Ion-exchange Resin (IRN-77) Addition

(A-5 : Reference Sample, B-1 : R/C Ratio of 9.7 w/o B-3 : R/C Ratio of 19.4 w/o)

3-4 Effect of CO₂ or air Injection

It is well-known that the CO₂ forms insoluble carbonate by reacting with soluble Cs-137. Also it is expected that air has blocking effect on the porous surface. In order to examine the phenomena, the following experiments have been conducted.

The experiment is as follows: Cement was mixed with liquid wastes. Specimen D-1 was prepared by injecting CO₂ for 5 minutes, and D-2 was made by injecting air for 10 minutes. According to experimental results as shown in Figure 8, CF49 of D-1 is reduced by 36% compared with A-5. However, that of D-2 is somewhat increased.

It is suspected that the increased leach rate of

specimen D-2 was caused by the increase of porosity due to the air injection. For the case of D-1, experimental results were interpreted from following two viewpoints;

The first is due to the relationship between leachate pH and leach rate, and the other is due to the formation of insoluble carbonate by reaction between CO₂ and Cs-137 in cement matrix. Generally leach rate increases with the increase of pH of leachate for the case of the cement matrix. CO₂ has reducing effect on the pH of leachant. The experiment shows that the pH value of leachant of D-1 is lower one than the others. The mechanism for Cs-137 immobilization with cement materials comes from the carbonation reaction [9].

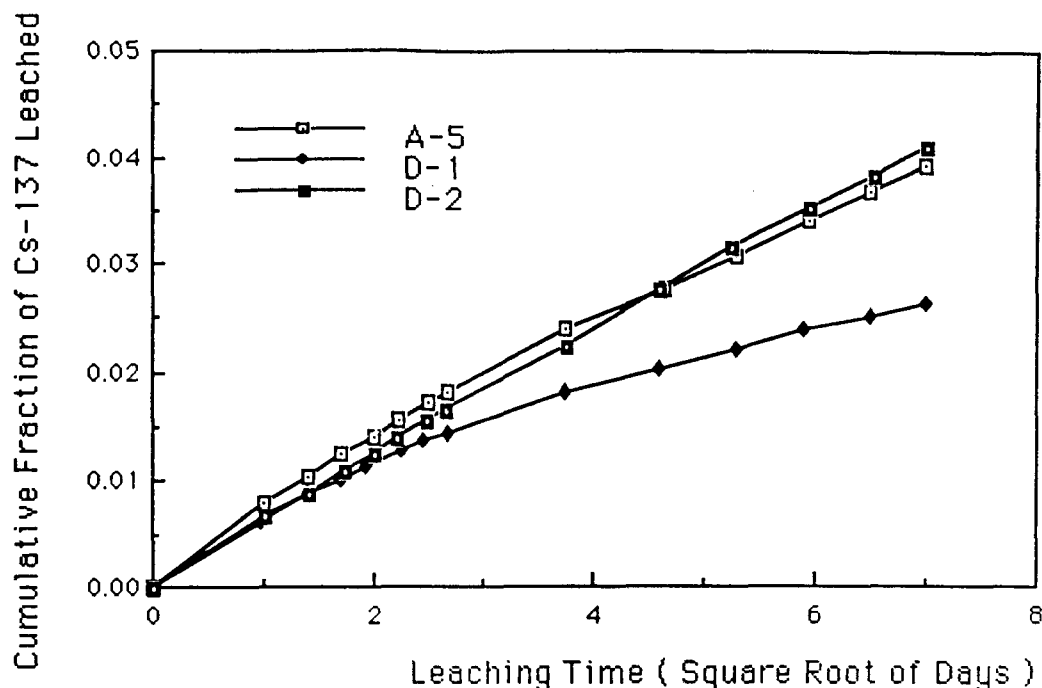


Fig. 8. Effect of CO₂ and Air Injection

(A-5: Reference Sample, D-1: CO₂ Injection, D-2: Air Injection)

3-5 Effect of Various Clay Addition

Specimens were made with various clay(with or without calcination)/cement ratios. According to the test, CF49 has turned out to be independent of clay/cement ratio and CF49 of all the specimens(without calcination) are reduced by 84% compared A-5. In Figure 9, specimens B-6, B-8, B-10, and B-12 were made by the addition of pottery clay, kaoline(white), kaoline(pink A), and koline(pink C), respectively. All specimens have clay/cement ratio of 16.2 w/o. All added materials calcined at 120°C for 16 hours. Figure 9 shows that pottery clay has the best capability for the immobilization of Cs-137. CF49 of B-6 shows 92% reduction.

Above result can attribute to the immobilizing ability of pottery clay on Cs-137. Pottery clay is known to be silica-alumina compound which ex-

ists as both Bronsted acid and Lewis acid[5]. These can react with cesium chloride(CsCl) differently to form an adsorbed cesium ion depending on the positions of acid[7]. Generally silica-alumina compound, which is amorphous, typically has maximum degree of acidity and activity at an Al/Si atomic ratio of less than unity. This can be explained by the concept that Al-O-Si-type of bonds are desired rather than the -Al-O-Al- type and that the formation of the former is enhanced by excess of silicagel[5]. It is known that Al/Si ratio of pottery clay produced in Korea is lower than the others [10].

According to the experimental results, calcined additives have better immobilizing ability on Cs-137 than natural ones. In other word, we can see that Cs-137 reacts with Lewis acid type better than Bronsted acid type.

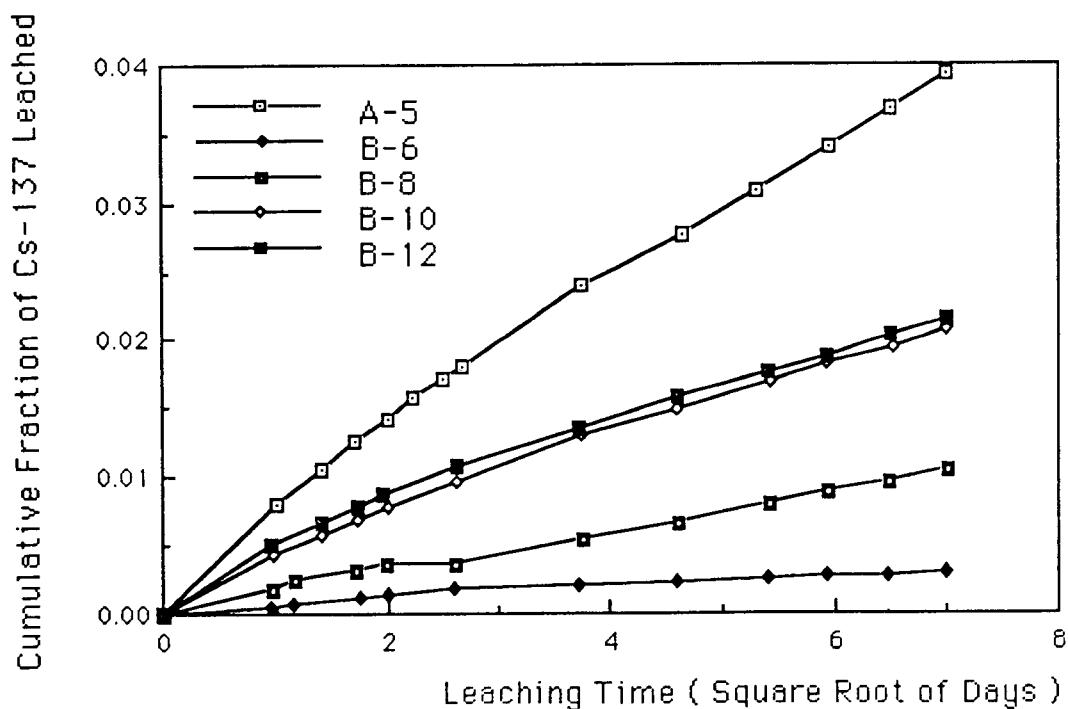


Fig. 9. Effect of Calcined Various Clay Addition

(A-5 : Reference Sample, B-6 : Pottery Clay, B-8 : Kaoline(white), B-10 : Kaoline(pink A), B-12 : Kaoline(pink C))

4. Long-Term Leach Rate Prediction by Model with Backfill

Many leaching models can be applied only when cement matrix contacts directly with ground water. But cement matrices in the disposal site rarely contact directly with underground water because backfill were supposed to be compacted at the surroundings of drums. Water will contact with matrix after passing through backfill and the radioactive nuclides will be leached in water through the reverse route. So nuclides in matrix go through two distinctive media by diffusion process.

We will consider the linear problem. Let us consider the backfill diffusion problem with the given geometry illustrated in Figure 10. If we denote the diffusion coefficients in the phases I and II by D_1 and D_2 respectively, we have the following solution for leach rate and cumulative fraction leached [7]. In other words, leach rate at $X=l_2$ is given by

$$J(t) = D_2 \left(\frac{\partial C_2}{\partial X} \right)_{X=l_2} = \frac{C_0 K \sqrt{D_1 D_2}}{(K \sqrt{D_2} + \sqrt{D_1}) \sqrt{\pi t}} \exp\left(-\frac{l_2^2}{4D_2 t}\right), \quad (5)$$

where C_0 = initial concentration of a species,

$$K = (C_2)_{X=0} / (C_1)_{X=0}$$

and, cumulative fraction leached is given by

$$CF = H \left[2 \sqrt{\frac{t}{\pi}} \exp\left(-\frac{1}{4\tau}\right) - \text{Berfc}\left(\frac{1}{2\sqrt{\tau}}\right) \right], \quad (6)$$

$$\text{where } H = \frac{AK \sqrt{D_1 D_2}}{V(K \sqrt{D_2} + \sqrt{D_1})}, \quad \tau = \frac{D_2 \cdot t}{l_2^2},$$

$$B = \frac{l_2}{\sqrt{D_2}}$$

where, A is the surface area contacting with leachant and V is the volume of a matrix.

Decay terms usually neglected for short-term leach test of radionuclide with long half life. But, for the case of the long-term leach rate prediction, decay term must be considered. For the case of semi-infinite slab model with backfill, solution of the mass transfer equations that include the radioactive decay phenomena from waste container are given as follows ;

* leach rate

$$J^*(t) = J(t) \exp(-\lambda t) \quad (7)$$

* cumulative fraction leached

$$CF^*(t) = \frac{A}{VC_0} \int_0^t J^*(t) dt \quad (8)$$

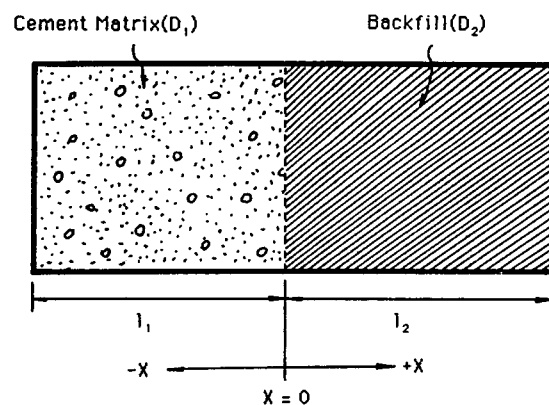


Fig. 10. Geometry for Analysis of System With Backfill

A number of figures were plotted from above equations for long-term prediction. The comparison of results of semi-infinite slab model, finite slab model, and semi-infinite slab model with backfill was performed by plotting cumulative fraction versus leaching time. All models were applied to 55 gal drum (84.5cm × 57.2cm) [11].

Figure 11 shows characteristic of each model with Cs-137 decay. And it shows that cumulative fraction leached decreases remarkably with increase of backfill thickness. For example, when

backfill thickness is 10cm, cumulative fraction of Cs-137 leached is about 0.01% after 100 years. This value is one-tenth of that of finite slab model.

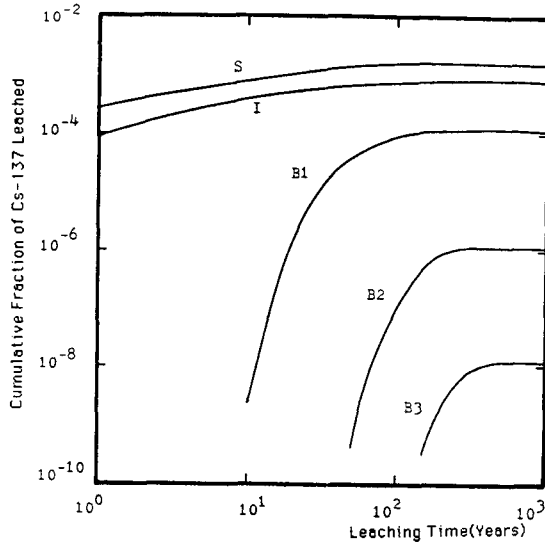


Fig. 11. Comparison of Various Model(log-log plot)

(S: semi-infinite model, I: finite slab model, B1, B2, B3: backfill model of backfill thickness 10cm, 30cm, 50cm respectively; calculation data: $D_1 = 1.27 \times 10^{-6} \text{cm}^2/\text{day}$, $\ell_1 = 84.5 \text{cm}$, $D_2 = 1.21 \times 10^{-3} \text{cm}^2/\text{day}$, $k=3$.)

5. Conclusion

The following conclusions have been drawn in this study.

- 1) It is proved that pressure curing shows reducing effect on leach rate and vibration curing make little contribution to the leachability.
- 2) For the case of pressure leaching, the leach rate increase with increasing pressure. It is impossible to find general relationship between pressure and leach rate in the case of cement matrix leaching because of data deficiency. More extensive study is necessary.
- 3) Ion-exchange resin(IRN-77) shows retarding effect on cement hydration. It is thought that

mechanism of retarding is caused by adsorption on cation resin beads of the important elements for cement curing.

- 4) CO_2 injection reduced the leach rate of Cs-137 by lowering the pH of leachant and formation of insoluble cesium carbonate. But, air injection results in the increase of leach rate.
- 5) Clay addition in cement matrix results in remarkable reduction of leach rate of Cs-137. Pottery clay shows better ability for immobilization of Cs-137 than the others, because of the least Al/Si ratio compared to the other clay.
- 6) Calcined clay reacts well with CsCl compared to the natural clay. That is, Lewis acid form of silica-alumina compound shows good reactivity with CsCl.
- 7) Leach rate of backfill model decrease remarkably with increasing backfill thickness. Therefore backfill must be considered to determine long-term leach rate for safety analysis of disposal site.

Nomenclature

C	constant
$CF^*(t)$	cumulative fraction of radioactive species
$J(t)$	leach rate of stable species($\text{mol}/\text{cm}^2.\text{day}$)
$J^*(t)$	leach rate of radioactive species($\text{mol}/\text{cm}^2.\text{day}$)
$L(r)$	pore size distribution function describing the total length of all pores of radius r per unit weight of adsorbent
P_s	saturation pressure(mm Hg)
r_c	pore radius(\AA)
S_w	pore surface area(m^2/g)
t	layer thickness of adsorbent wetted pore wall
T_d	temperature of manifold zone
T_i	temperature of intermediate zone

V_a	volume of gas adsorbed pressure $P(\text{cm}^3)$
V_c	volume of liquid remaining condensed(cm^3)
V_d	volume of manifold zone
V_i	Volume of interconnecting tubing(cm^3)
V_m	volume adsorbed when the entire adsorbing surface is covered by a monomolecular layer(cm^3)
V_p	total pore volume(cm^3)
W_s	weight of sample(g)

Acknowledgments

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