JAERI-M
6749

SAFETY EVALUATION OF THE RADIOACTIVE WASTE-CEMENT COMPOSITES

(4. LEACHING BEHAVIOR OF ^{137}Cs IN THE CRUSHED SAMPLES)

October 1976

H. MATSUZURU, Y. WADACHI, A. ITO

日本原子力研究所
Japan Atomic Energy Research Institute

JAERI-M 6749

Safety Evaluation of the Radioactive Waste-Cement Composites

(4. Leaching behavior of ^{137}Cs in crushed samples

Hideo MATSUZURU, Yoshiki WADACHI and Akihiko ITO

Environmental Safety Research Laboratory, Reactor Safety Research Center

Tokai, JAERI

(Received September 24 1976)

The leaching behavior of ^{137}Cs has been studied to evaluate safety of sea and ground disposal of the cement composites. The rate depends on flow rate of the external solution, particle radius and composition of the cement composite. The rate-determining step of the leaching in the dynamic condition is the internal diffusion through the matrix cement composite. The rate in the static condition, on the other hand is controlled by extrenal diffusion through the interface layer between solid and liquid.

The cement composites containing mineral zeolite(25%) give very low leachabiity; the leaching fraction is 0.001 - 0.02 for the portland cement and 0.001 - 0.002 for the slag cement.

JAERI－M 6749

放射性廃棄物のセメント固化体の安全評価
(4. 破砕試体からの^{137}Csの浸出)

日本原子力研究所東海研究所安全性試験研究センター
環境安全研究室
松鶴秀夫・和達嘉樹・伊藤彰彦

(1976年9月24日受理)

セメント固化体の海洋および陸地処分における安全性を確めるため，破砕試料からの^{137}Csの浸出挙動について研究を行った。浸出速度は浸出液の流速，粒子径および固化体の組成に依存する。動的条件における浸出の律速段階は固化体マトリックス中の内部拡散であり，他方，静的条件において測定された浸出速度は，固体と液体間の境膜中での外部拡散によって律せられることがわかった。

天然ゼオライトを含有（25wt－%）する試料では非常に低い浸出性を示し，ポルトランドセメントを用いた固化体では0.01～0.02，高炉セメントを用いた固化体では0.001～0.002の浸出比を与えた。

目 次 な し

1. INTRODUCTION

Preventing widespread dispersion of radionuclides into the human environment, the radioactive wastes produced in a nuclear facility have been incorporated in several matrixes. Low- and intermediate-level wastes such as evaporator concentrates have been routinely solidified with cement in a power reactor plant. In the final disposal of a solidified waste, it is natural to assume that the waste composite come into contact with natural water. Through this, radionuclides contained in a composite might be leached and enter into human environment. The leaching behavior is therefore one of the most important criterion for safety evaluation for a waste composite in the final disposal. In the previous paper,[(1)-(3)] leaching of ^{137}Cs and ^{60}Co from the cement composite (cylinder shape; 4.5cm in diameter and 4.4cm high)[(4)] has been systematically and extensively studied. From this, the leaching behavior of cement composite in a cylinder shape without any crack or defect was obtained in order to estimate the amount leached from a composite of 200 l drum size in the longer leaching times. In the case of actual cement composite produced in a nuclear facility, the craks or defects may be occured in the composite and further it may be crushed into fine fragments in the course of storage, transportation and disposal. By far the informations about the leaching behavior of the crushed state of specimen were not obtained.

In this paper, therefore, the study on the leaching of ^{137}Cs from the crushed state of cement composite was made to ascertain the effect of a drastic increase in the surface area of specimen on the leachability. The leaching rate was measured under both the static and dynamic conditions so as to obtain the effect on the leaching kinetics of agitation of liquid phase.

2. EXPERIMENTAL

2.1 Materials

The simulated evaporator concentrates produced in BWR was prepared by dissolving sodium sulfate into deionized water to 10 -20 wt%, and by adding ^{137}Cs to ca. 1 - 2.5 uCi/g of sample, and finally by adjusting pH to 9 - 10.

Two types of cement were used; portland ("normal" type by JIS) and slag ("C" type by JIS). The chemical composition of cement is summarized in Table 1. The radionuclide ^{137}Cs was used.

The specimen was prepared by mixing cement with the simulated waste at one of the various waste-cement ratios (Wa/C). After sufficient mixing,the paste was poured in a polyethylene bag. This bag was then tightly sealed tp prevent the evaporation of water from the cement paste. The curing time of the paste was 28 days. The dried hardened cement paste was crushed into fine particles, and then screened and sized to obtain the fractions; 3.26 - 0.99 mm, 0.99 - 0.70 mm and 0.70 - 0.42 mm.

The natural zeolite (consists of mainly mordenite and clinoptilolite) mined at Oshamanbe, Hokkaido was used.

2.2 Procedures

All of the leaching measurements at the static condition were made by the batch method. Ten grams of the crushed sample and 750 ml of the leachant (deionized water or synthetic sea water) were weighted into a 1000 ml polyethylene bottle. This was submerged in a thermostat kept at 25°C. At preset time intervals, the leachant was removed by decantation method for measuring radioactivity leached with a conventional low background gas flow counter.

A modification of the limited bath technique was used for the leaching measurement at the dynamic condition. A three necked flask containing

Table 1 Chemical Composition of Cement (wt%)

Component	Portlan cement	Slag cement
SiO_2	21.8	28.7
Al_2O_3	5.3	11.5
Fe_2O_3	3.2	2.3
CaO	64.8	50.9
MgO	1.6	3.2
SO_3	1.7	1.9
insoluble residue	0.5	0.8
ignition loss	0.8	0.6

Table 2 Composition of Synthetic Sea Water

Component	Concentration(wt%)
NaCl	2.72
$MgCl_2$	0.381
$CaSO_4$	0.126
$MgSO_4$	0.166
K_2SO_4	0.0863
$CaCO_3$	0.0123
$MgBr_2$	0.0076

Table 3 Chemical Composition of Natural Zeolite

Component	Content(wt%)
SiO_2	82.4
Al_2O_3	9.02
Fe_2O_3	5.22
CaO	0.83
K_2O	0.78
MgO	0.31
MnO	0.55

Table 4 List of Samples Tested

No	Cement	Wa/C	Content of zeolite
1	Portland	39	—
2	Portland	42	—
3	Portland	45	—
4	Slag	39	—
5	Slag	42	—
6	Slag	45	—
7	Portland	60	25 wt%
8	Slag	60	25 wt%

10.0 g of the sample and 750 ml of the leachant was immersed in a thermostat. From a requirement in a heterogeneous reaction, the reaction system was stirred at a constant rate (ca. 400 rpm). At each preset time interval, 100 ul of the leachant was taken out for the radioactivity measurement.

3. ANALYTICAL METHOD FOR EXPRESSING THE LEACHING DATA

In general, the leaching process is one of the physicochemical transport phenomena, in which diffusion plays an important role. Therefore it has been assumed that the leaching of ^{137}Cs was controlled by diffusion process. In this paper, a spherical source model is used to simulate the leaching process. The system considered here consists of the matrix of cement composite in which a radioactive substance disperses uniformly, and a surrounding fluid which is taken as to have a homogeneous composition. The rate of loss of diffusing substance from the spherical specimen is[5]

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right]. \tag{1}$$

If we replace the concentration of the substance in a matrix C by the expression, C = u/r, Eq.(1) is converted to the form

$$\frac{\partial u}{\partial t} = D\,\partial^2 u/\partial r^2, \tag{2}$$

with the initial and boundary conditions,

$$u = 0, \qquad r = 0, \qquad t > 0,$$

$$u = 0, \qquad r = r_o, \qquad t > 0,$$

$$u = uC_o, \qquad 0 < r < r_o, \qquad t = 0,$$

where r_o is the radius of a spherical body, r the radial space coordinate, C_o the initial concentration of a radioactive substance in a spherical body. The solution of Eq.(2) under the above initial and boundary conditions is[6]

Table 5 Relation of B t and t[8]

f	B t	f	B t	f	B t	f	B t
0.01	0.00009	0.25	0.0623	0.50	0.301	0.75	0.905
0.02	0.00036	0.26	0.0678	0.51	0.316	0.76	0.944
0.03	0.00076	0.27	0.0736	0.52	0.332	0.77	0.985
0.04	0.00141	0.28	0.0797	0.53	0.348	0.78	1.028
0.05	0.00219	0.29	0.0861	0.54	0.365	0.79	1.073
0.06	0.0032	0.30	0.0928	0.55	0.382	0.80	1.120
0.07	0.0044	0.31	0.0998	0.56	o.4oo	0.81	1.171
0.08	0.0057	0.32	0.1070	0.57	0.419	0.82	1.224
0.09	0.0073	0.33	0.1147	0.58	0.438	0.83	1.280
0.10	0.0091	0.34	0.1226	0.59	0.458	0.84	1.340
0.11	0.0111	0.35	0.1308	0.60	0.479	0.85	1.404
0.12	0.0132	0.36	0.1391	0.61	0.500	0.86	1.468
0.13	0.0156	0.37	o.1485	0.62	0.522	0.87	1.543
0.14	0.0184	0.38	0.1577	0.63	0.545	0.88	1.623
0.15	0.0210	0.39	0.167	0.64	0.569	0.89	1.710
0.16	0.0241	0.40	0.177	0.65	0.594	0.90	1.80
0.17	0.0274	0.41	0.188	0.66	0.620	0.91	1.91
0.18	0.0309	0.42	0.199	0.67	0.647	0.92	2.03
0.19	0.0346	0.43	0.210	0.68	0.675	0.93	2.16
0.20	0.0386	0.44	0.222	0.69	0.703	0.94	2.32
0.21	0.0428	0.45	0.234	0.70	0.734	0.95	2.50
0.22	0.0473	0.46	0.246	0.71	0.765	0.96	2.72
0.23	0.0520	0.47	0.259	0.72	0.798	0.97	3.01
0.24	0.00570	0.48	0.273	0.73	0.832	0.98	3.41
		0.49	0.287	0.74	0.868	0.99	4.11

$$\frac{C_o - C}{C_o} = 1 + \frac{2\, r_o}{r\, \pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin\frac{\pi n r}{r_o} \exp(-n^2 B\, t)\ , \qquad (3)$$

where $B = D\pi^2/r_o^2$.

The total amounts of diffusing substance leaving from a sphere at time t is

$$Q = \frac{4}{3}\pi r_o^2 \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 B\, t)\right]. \qquad (4)$$

From this, the expression for the leaching fraction, f, may be written as

$$f = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 B\, t)\ . \qquad (5)$$

In this relation, the leaching fraction depends on the demensionless parameter $B\,t$.

4. RESULTS AND DISCUSSION

4.1 Kinetics

4.1.1 Leaching at the dynamic condition

The leaching data obtained at the dynamic condition were analyzed using above method. When the leaching rate is controlled by internal diffusion as assumed in Eq.(5), the relation $B\,t$ and t is linear, and the value of B is inversely proportional to the square of the particle radius. To ascertain the confirmity of the leaching data with Eq.(5), $B\,t - t$ relation was tabulated in Table 6. As seen from the table, in both portland and slag cement composites, the value of B is almost constant and independent of the leaching time tested. The leaching process at the dynamic condition thus controlled by internal diffusion.

The effect of increasing the mean radius of specimen on the leaching rate is shown in Table 7. With increasing the mean radius by factors of 1.55 and 3.45, the value of B is reduced by factors of 2.18 and 10.8, respectively. Now $(1.55)^2 = 2.40$ and $(3.45)^2 = 11.9$, so that to within ca. 10% (which is considered to be about the over-all experimental error),

Table 6 Dependence of the value of B t on time (Sample No.5 and 2, radius: 0.19 cm, temp.: 25°C, leachant: deionized water)

Time(hr)	f	B t	B(hr^{-1})
	Sample No. 5		
1	0.16	0.0241	0.024
2	0.21	0.0428	0.021
3	0.25	0.0623	0.021
4	0.28	0.0861	0.022
5	0.31	0.0998	0.020
6	0.33	0.1147	0.019
	Sample No. 2		
1	0.27	0.0736	0.074
2	0.38	0.1577	0.079
3	0.45	0.234	0.078
4	0.51	0.316	0.079
5	0.55	0.382	0.076
6	0.57	0.419	0.070

Table 7 Dependence of the value of B on the radius at the dynamic condition(Sample No. 5)

Radius(cm)	B(hr^{-1})
0.055	0.0019
0.085	0.0041
0.19	0.021

the value of B is inversely proportional to the square of the partocle radius, in agreement with Eq.(5). The diffusion coefficient of ^{137}Cs calculated from the relation $D = B\ r_0^2/\pi^2$, is 7.7×10^{-4} cm^2/hr (1.8×10^{-3} cm^2/day) for slag cement specimen(sample No. 5), and 2.8×10^{-4} cm^2/hr (6.7×10^{-3} cm^2/day) for portland cement composite(sample No. 2), respectively.

The initial diffusion coefficient of ^{137}Cs obtaine from the leaching study with a specimen of cylinder shape (4.5 cm in diameter and 4.4 cm high) is 1.02×10^{-3} cm^2/day for slag cement specimen having the same composition as sample No.5, and 2.83×10^{-3} cm^2/day for portalnd cement one having the same composition as sample No. 2, respectively.[3]
The initial diffusion coefficients(leach coefficient) are about 1/2 times that obtained with the crushed sample at the dynamic condition.

4.1.2 Leaching at the static condition

Applying Eq.(5) with the leaching data obtained at the static condition, it revealed that the calculated value of B was not constant over the period tested. It can be said that the leaching rate of ^{137}Cs at the static condition is not controlled by internal diffusion alone.

If the reaction rate is controlled by the diffusion through a liquid film formed at the interface of specimen and leachant, the leaching rate obeys the following relation,[9]

$$-\ln(1 - f) = Rt\ , \qquad (6)$$

where $R = 3\ D/r_0 \delta\ K$, δ is the film thickness (cm), K the volume ratio of leachant and specimen. From Eq.(6), if the external diffusion controles the leaching rate, the relation of $-\ln(1 - f)$ and leaching time is linear. As seen from Table 8, the relationship between $-\ln(1 - f)$ and t is linear corresponding Eq.(6) except for the initial leaching stage. This derivation from the theoretical relation may be ascribed to release of

Table 8 Dependence of the value of $-\ln(1 - f)$ on time (Sample No. 5 and 2, radius: 0.19 cm, temp.: 25°C, leachant: deionized water)

Time(hr)	f	-ln(1 - f)
	Sample No. 5	
1	0.041	0.042
2	0.066	0.068
3	0.092	0.096
4	0.115	0.122
5	0.138	0.148
6	0.159	0.173
	Sample No. 2	
1	0.032	0.033
2	0.044	0.045
3	0.056	0.058
4	0.068	0.070
5	0.080	0.083
6	0.091	0.095

Table 9 Dependence of the value of R on the radius at the static condition

Radius(cm)	R(hr^{-1})
Sample No. 5	
0.055	0.083
0.085	0.055
0.19	0.025

of the very fine particles contaminated with ^{137}Cs from the surface of samples by rinsing with leachant.

The effect of varying the mean radius of sample on the leaching rate (Table 9) shows that the value of R increases with decreasing the radius satisfying the requirement of Eq.(6), i.e., the value of R is inversely proportional to r_o.

From these results, the leaching behavior of ^{137}Cs at the static condition is governed by external diffusion rather than internal diffusion.

4.2 Leaching behavior

Previous discussion on the kinetic behavior of leaching indicates that the dynamic condition gives a higher leaching rate than that at the static conditon. In a case of natural hydrosphere, a water current flows at a certain rate which results in that the leaching system in nature has the intermediate condition between dynamic and static. From this, we choose the dynamic condition in the leaching test in order to make the conservative safety assessment.

Fig. 1 shows the effects on the leachability of varying Wa/C ratio for both portland and slag cement samples. The leaching fraction given in the figure was measured at the duration of 72 hr. A preliminary kinetic examination suggests that this leaching period gives an apparent equilibrium.

The leaching fraction increases with increasing Wa/C, and this tendency prevails in the case of samples with larger radius, for both portland and slag cement specimens.

Fig. 2 shows the relation between the particle radius and the leaching fraction. For both slag and portland cement specimens without zeolite, the leaching fraction decreases with increasing radius, whereas

Table 10 Comparison of leachants with resppect to the leachability (radius: 0.19 cm, temp.: 25°C)

Sample No.	Leachant	Leaching fraction
1	DW	0.563
1	SW	0.537
2	DW	0.602
2	SW	0.598
3	DW	0.672
3	SW	0.651
4	DW	0.316
4	SW	0.301
5	DW	0.362
5	SW	0.342
6	DW	0.391
6	SW	0.378
7	DW	0.0124
7	SW	0.0125
8	DW	0.00187
8	SW	0.00174

DW: deionized water

SW: synthetic sea water

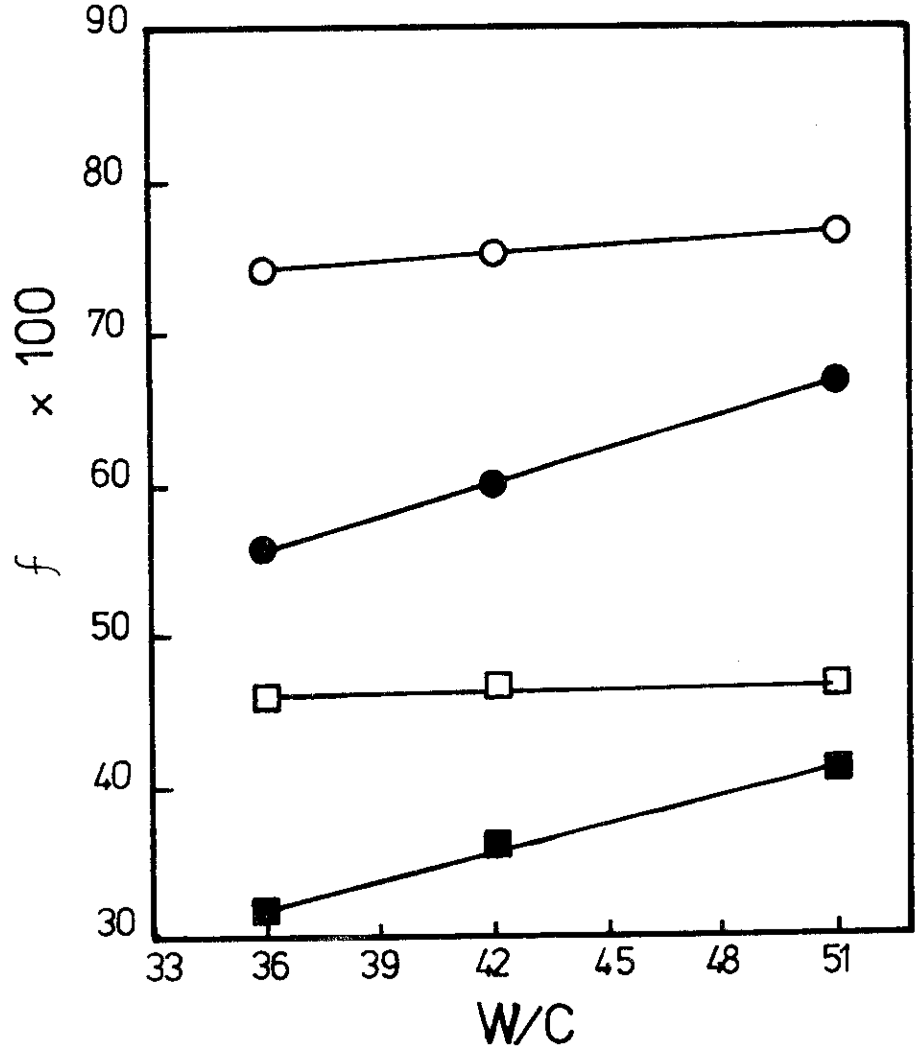

Fig. 1 Effect of W/C

○: Portland cement, r: 0.055 cm
●: 〃 , r: 0.19 cm
□: Slag cement, r: 0.055 cm
■: 〃 , r: 0.19 cm

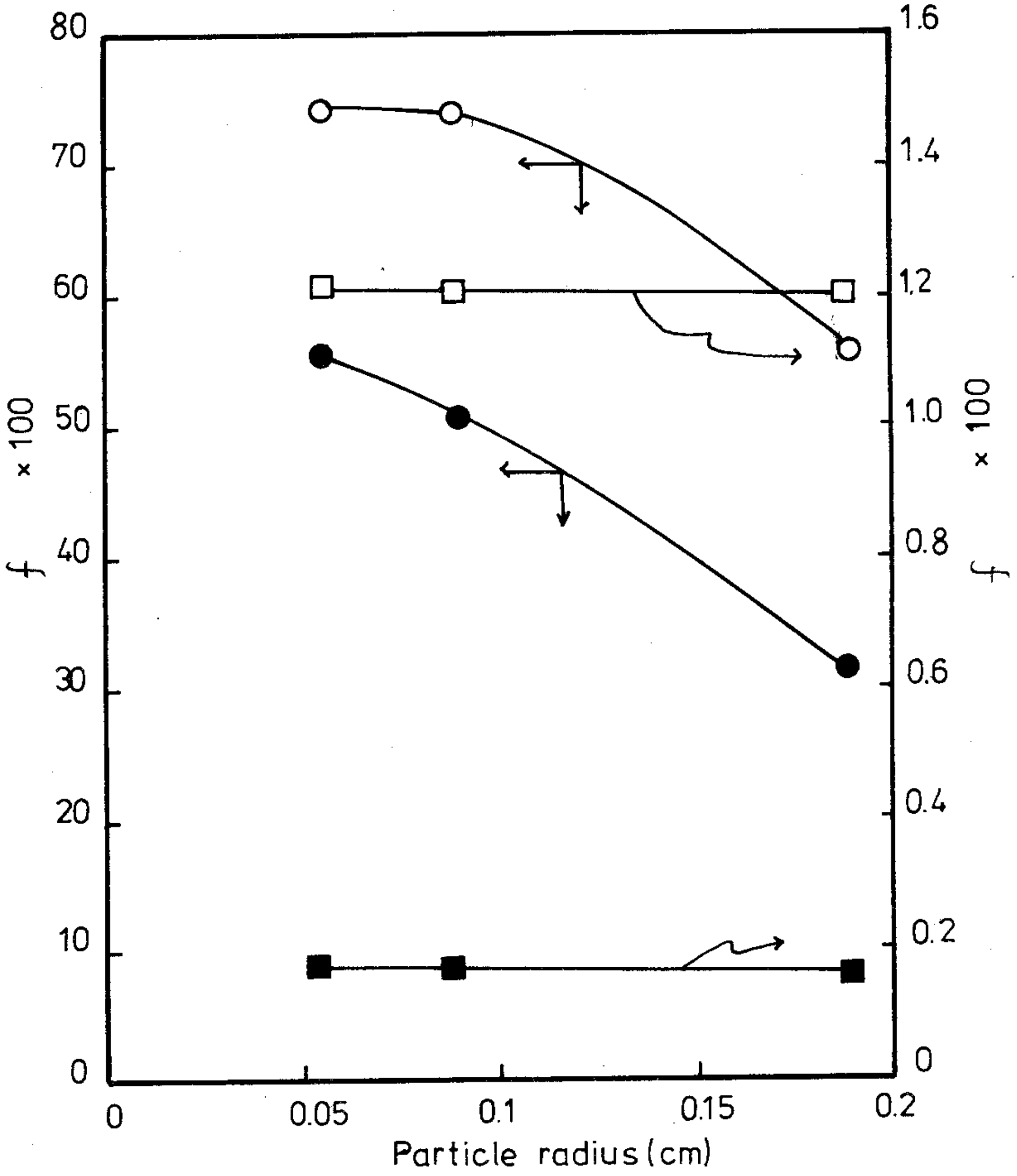

Fig. 2 Effect of Particle Size

○: Portland cement
●: Slag cement
□: Portland cement - Zeolite (25%)
■: Slag cement - Zeolite (25%)

the specimens containing mineral zeolite (25 wt%) gives almost constant leaching fractions independing on the radius over the range tested (0.19 - 0.055 cm).

The comparison of leachnats, deionized and synthetic sea water, with respect to the leaching fraction was given in Table 10. The leaching fraction in synthetic sea water is only slightly smaller than that in deionized water.

5. CONCLUDING REMARKS

The specimen without mineral zeolite gives a high leachability; the leaching fraction measured at the duration of 72 hr amounts to ca. 0.6 - 0.7 for portland cement, and ca. 0.3 - 0.4 for slag cement specimen. The sample contained mineral zeolite (25 wt%), however, gives a very low leachability independing on the radius over the range tested; i.e., 0.01 - 0.02 for portland cement and 0.0001 - 0.0002 for slag cement specimen. The cement composite containing natural zeolite thus holds safety even in the case of disruption of the composite during sea damping. Moreover, the presence of natural zeolite in the cement composite does not reduce the durability of cement composite[7], and does not affect the leachability of other nuclides such as ^{60}Co and ^{90}Sr. These also suggest that natural zeolite holds promise for immobolization of ^{137}Cs in cement composite resulting in the reduction of a high leachability of ^{137}Cs.

The rate-dertermining step for leaching varies with the leaching condition; at the dynamic condition the leaching obeys the rate equation for internal diffusion controlled kinetics, and at the static condition the corresponding step is external diffusion. Although the actual leaching system may have the intermediate condition between static and dynamic, the leaching test should be made at the dynamic condition in the case of the samples of fine particles, to permit the conservative safety analysis.

6. ACKNOWLEDGEMENT

The authors with to express their deep thanks to Dr. I. MIYANAGA for helpful suggestions and discussions.

7. REFERENCES

(1) MATUSZURU,H., HISA,I., OUCHI,K., MORIYAMA,N., WADACHI,Y. and ITO,A.: JAERI-M 6361 (in Japanese), 1976.

(2) MATSUZURU,H., HISA,I., OUCHI,K., MORIYAMA,N., WADACHI,Y. and ITO,A.: JAERI-M 6457 (in Japanese), 1976.

(3) MATSUZURU,H., MORIYAMA,N., WADCHI,Y. and ITO,A.:"Leaching Behavior of ^{137}Cs in Cement-Waste Composite" to be published in Health Physics.

(4) HESPE,E.D.: At. Energy Rev., 9(1), 195 (1971).

(5) SKELLAND,A.H.: "Diffusional Mass Transfer", p.23, John Wiley, New York (1974).

(6) p.27 of Ref. (5).

(7) HISA,I., OUCHI,K. et al.,: Private communication (1976).

(8) REICHENBERG,D.: J. Amer. Chem. Soc., 75,589 (1953).

(9) HELFERICH,F.: "Ion Exchange" p.264, McGrwa-Hill (1962).