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ANALYTICAL EVALUATION ON THE LEACHING OF RADIONUCLIDES FROM WASTE SOLIDS

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Analytical ~~Study~~ Evaluation on the Leaching of Radionuclides from Waste Solids

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The leaching data are applied to several theoretical and empirical formulas to evaluate the amount of radionuclides leaching out after disposal of the solidified radioactive waste. Diffusion equation, equation for diffusion with other simultaneous first-order reaction, and polynomial expressions were examined as to whether they agree with the leaching data to find the mechanism taking place in the leaching process. From these study, the followings were revealed.

(1) The polynomial expressions give the best approximation to the leaching data, even though each term has no physical significance, and the leaching mechanism is not clarified.

(2) Equation for diffusion with other simultaneous first-order reaction provides a good approximation and the leaching mechanism is largely clarified. This method, however, requires a laborious numerical calculation.

(3) The diffusion equation does not always express a leaching process accurately, though the treatment is both easy and simple.

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固化体からの放射性核種の浸出現象についての解析

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固形化した放射性廃棄物の処分後の放射性核種の浸出過程で起る機構を明らかにするために，拡散方程式，他の一次反応を伴なう拡散方程式および多項式を取り上げ，これらの式が浸出データに合うかどうかを調べた。

本研究から次のような結果が得られた。(1)多項式は各項に物理的意味を与えず，また浸出機構も明らかにしないが，浸出データに最も一致する。(2)他の一次反応を伴なう拡散方程式は，かなり良い近似を与え，反応機構も相当明確にする。しかしながらこの方程式を解くには非常厄介な数値計算が必要である。(3)拡散方程式はその取扱いが簡単で容易ではあるが，必らずしも浸出過程を正確に表わすものでない。

Contents

1. Introduction

It is desirable that radioactive wastes are solidified with suitable solidifying substances in order to immobilize the radionuclides contained therein and disposed out of human environment in such states that the radionuclides are not going to reenter into human environment. Sea and ground disposal, and surface storage seem to be possible means for final waste disposal.

In final disposal, to say nothing of sea damping, it is not unusual that the solidified radioactive waste products come into contact with surrounding water which might enter into human environment. Therefore, low leaching rate of radionuclides from solidified products is one of the most important properties required for the products.

In view of the foregoing, estimation of the quantities of radionuclides that are removed from the waste solids is essential in waste management. In order to evaluate them, several theoretical equations or empirical formulas have been proposed, but the radioactive wastes incorporated in cements, asphalts, plastics, glasses or ceramics are such complex compounds or heterogeneous mixtures that the leaching behaviors of the nuclides from the solids could not have been explained by single mathematical treatment. This makes it extremely difficult to permit intercomparison of leachability of various products from different processes or installations.

It seems however to be possible to find which mechanism of the leaching is predominant of all the mechanisms occurring in the leaching process, if the leaching of the radionuclides are observed for a long time. This is considered to be important so as to have a right understanding of the fundamental mass transport processes taking place in waste solids and to express them in mathematical forms.

In this report, various theoretical equations and empirical formulas hitherto proposed are summarized and tried to examine their applicability to various waste solids. In addition, a new evaluation formula was proposed for the waste products, to which conventional formulas could not be applied. This trial might make it possible to permit intercomparison of the leachability of various waste solids and would contribute to the development of improved waste solids.

2.1 Method with Diffusion Equation

In general, the leaching process is one of the physico-chemical transport phenomena, in which diffusion is considered to play an important role. Therefore, it has been proposed by IAEA that diffusion coefficient (leaching factor) might as well be used for intercomparison of leaching data of all the solidified products.

We will discuss here about mathematical expression of diffusion process of radioactive substances from solidified products of various shapes.

2.1.1 The diffusion equation based on a plane source model

In this section, a plane source model is used to simulate the system in which a radioactive substance is leached from the matrix into a sorrounding fluid. The system considered here consists of the matrix of waste solid in which a radioactive substance disperses uniformly on the macroscopic scale, and a sorrounding fluid which is taken as to have a homogeneous composition. The rate of loss of diffusing substance from the unit surface of a plane sheet is represented by the Fick's second law

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \qquad (1)$$

where C is the concentration of the radioactive substance, D is the diffusion coefficient, with initial and boundary conditions,

$$t = 0, \quad \infty > x > 0, \quad C = C_0 \qquad (2)$$

$$t = 0, \qquad x < 0, \qquad C = 0 \tag{3}$$

$$t > 0, \qquad x = 0, \qquad C = 0 \tag{4}$$

where C_o is the initial concentration of a radioactive substance. The solution of Eq. 1 under the above conditions is$^{(1)}$

$$C = C_o \ \mathrm{erf} \left(\frac{x}{2\sqrt{D\,t}} \right), \tag{5}$$

then the quantity of a diffusing substance, Q, which diffuses through the unit surface in time t is given by

$$Q = \int_o^t -D \left(\frac{\partial C}{\partial x} \right)_{x=o} dt = \frac{2\,C_o \sqrt{D\,t}}{\sqrt{\pi}}. \tag{6}$$

If the quantity of a radioactive substance a(Ci) is leached in time t(day) from the specimen having the surface area of S(cm^2), the volume of V(cm^3) and the initial quantity of radioactive substance A(Ci), the fraction leached is

$$f = \frac{a}{A} = \frac{2\,S\sqrt{D\,t}}{V\sqrt{\pi}}. \tag{7}$$

Using this equation, it can be predicted whether a diffusion process is operating or not by confirming the linearity exsisted between the terms, $t^{\frac{1}{2}}$ and f. The diffusion coefficient D (cm^2/day) can be calculated from the slope m of this linear relation,

$$m = 2\,S\sqrt{D}\,/\,V\sqrt{\pi}\,, \tag{8}$$

from which

$$D = m^2 V^2 \pi / 4\,S^2. \tag{9}$$

The amount of a radioactive substance leached from the specimen over the given period can be predicted from Eq. 7 provided that the constant diffusion coefficient is obtained.

Several studies(2)-(4) have been made on the analysis of the data for leaching from the various waste solids such as asphalts, cements, glasses, ceramics, plastics and cement coated with asphalt, and have shown that Eq.2 could be used to analyze the leaching data while in some cases it predicts only approximately. In the data for leaching of ^{137}Cs from the waste-cement-zeolite(natural) system, the linearity between $t^{\frac{1}{2}}$ and f is observable as seen in Fig. 1. In the case of the waste-cement system, however, this linearity is not always obtained throughout the period tested as shown in Figs. 2 and 3. The reason why the experimental data deviate from the calculated values may be considered as follows:

(i) In this plane source model, it is assumed that the part of a specimen which takes part in the leaching process is limited to the extremely thin layer of the surface. The amount of ^{137}Cs leached from the specimen is so much that this assumption can not be valid.

(ii) The leaching process is really complicated, and in some cases it consists of several physicochemical processes. This makes it difficult to describe only with the single diffusion coefficient.

(III) The specimen used in the leaching test is not ideal, and has the factors which can not be introduced into the leaching model, for example, the difference in the state of a radioactive substance which exsists whether at the surface or in the interior of a specimen.

In spite of the insufficiency of Eq.7, this equation is frequently used in the analysis of leaching data because of its simplicity.

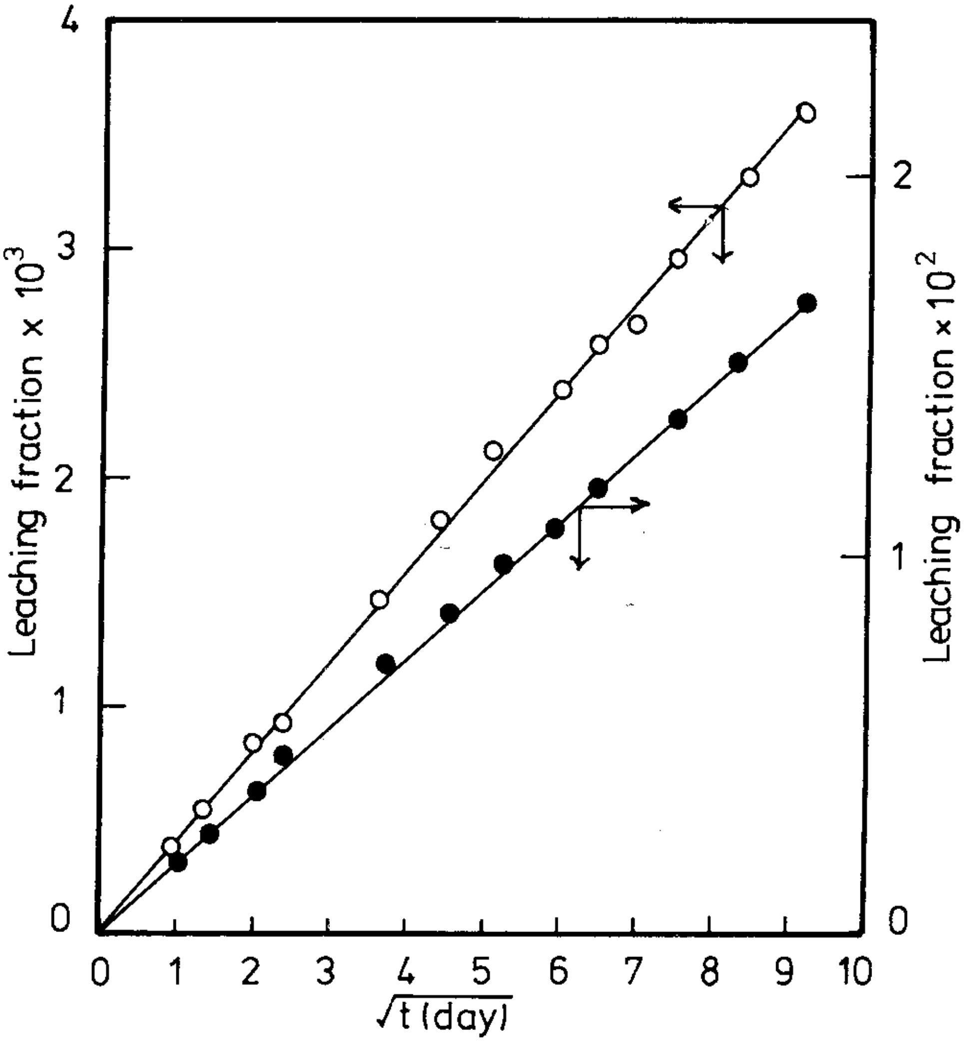

Fig.1 Variation of the leaching fraction as a function of $\sqrt{t}$, 25°C. ○: sample no.1, ●: sample no. 2

Controlling coefficient for leaching process

Sample no	Cement	m(day^{-1})	D(cm^2/day)
1	Portland	1.78×10^{-3}	1.38×10^{-6}
2	Slag	4.08×10^{-4}	7.24×10^{-8}

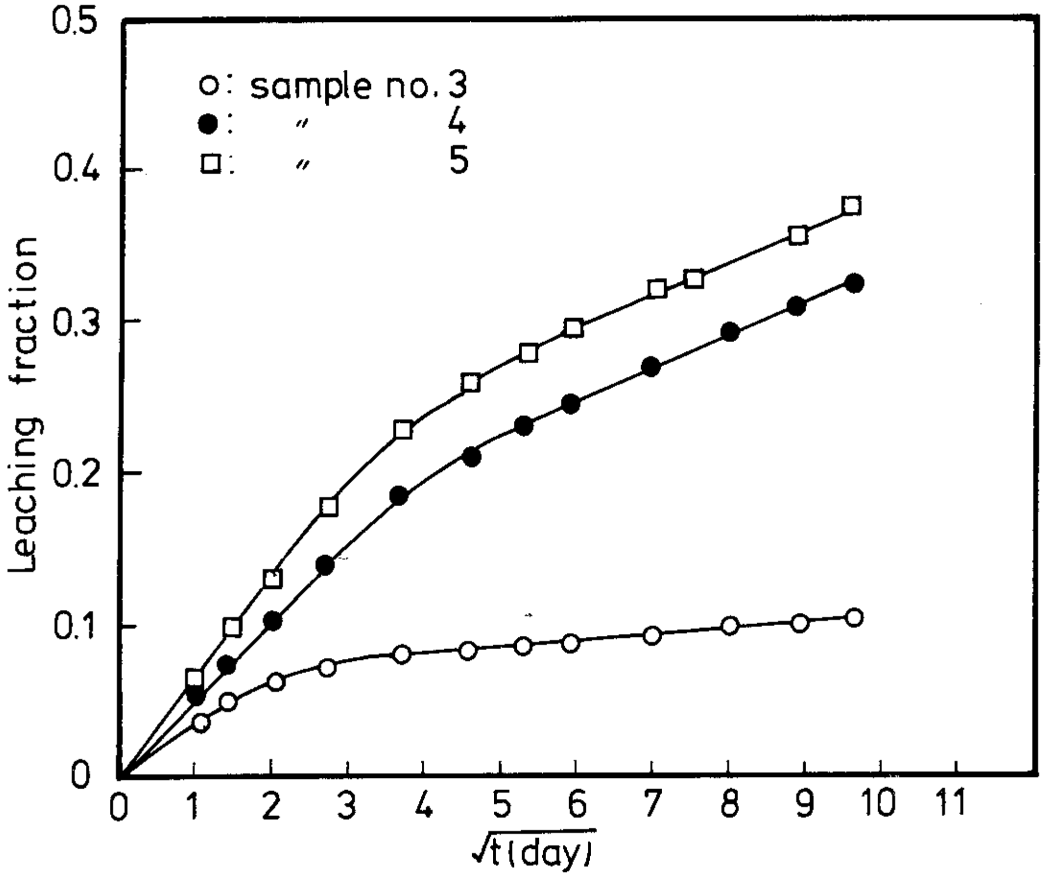

Fig. 2 Plots of leaching fraction vs. $\sqrt{t}$ for the leaching of Cs-137 from the cement composite, 25 °C.

Controlling coefficient for leaching process

sample no.	D_i (cm^2/day)	D_l (cm^2/day)	α	m_i (day^{-1})	m_l (day^{-1})
3	2.17×10^{-3}	2.09×10^{-4}	0.164	6.93×10^{-2}	2.19×10^{-2}
4	1.19×10^{-3}	2.06×10^{-4}	0.118	5.23×10^{-2}	2.18×10^{-2}
5	6.91×10^{-4}	5.96×10^{-6}	0.0699	3.44×10^{-2}	3.33×10^{-3}

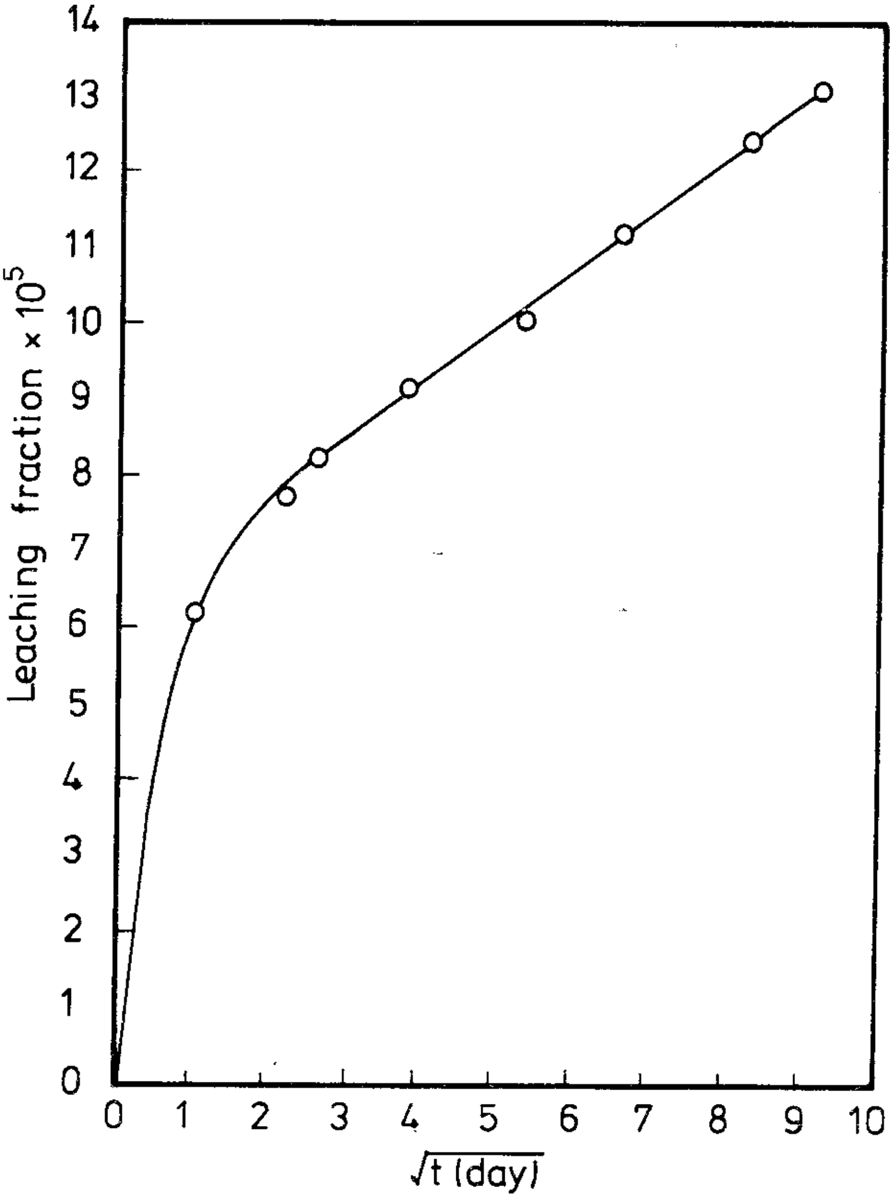

Fig. 3 Plots of leaching fraction vs. $\sqrt{t}$ for the leaching of Co-60 from the cement composite, 25 °C, sample no. 6

2.1.2 The diffusion equation based on a cylindrical source model

In this section, a long circular cylinder model is used to analyze the amount of radioactive substance leached out from the cylindrical matrix as a function of time t. The concentration of radioactive substance is then the functions of radius r and time t only, and the diffusion equation becomes

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\, D\frac{\partial C}{\partial r}\right). \qquad (10)$$

If the concentration of substance C is replaced by the expression u exp(-D α^2 t), the Eq.10 is converted into the equation

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} + \alpha^2 u = 0, \qquad (11)$$

where u and α are parameters. This equation is Bessel's equation of order zero, and the solution of which can be presented in terms of the corresponding Bessel functions, the selection of which is established by the initial and boundary conditions. Thus if the initial concentration distribution is $C_o(r)$ and the surface $r = r_o$ is maintained at zero concentration, the solution of Eq.10 is required to satisfy

$$C = 0, \qquad r = r_o, \qquad t > 0, \qquad (12)$$

$$C = C_o(r), \qquad 0 < r < r_o, \qquad t = 0. \qquad (13)$$

The solution of Eq.10 satisfying the above conditions is(5)

$$\frac{C}{C_o} = \frac{2}{r_o}\sum_{n=1}^{\infty}\frac{J_o(r\,\alpha_n)}{J_1(r_o\,\alpha_n)\alpha_n}\exp(-D\,\alpha_n^2\,t), \qquad (14)$$

where α_n is the n-th root of the Bessel function of the kind of order zero

$$J_o(r_o\ \alpha_n) = 0. \tag{15}$$

Here, in order to simlify the numerical treatment, the dimensionless parameter $\beta_n = r_o\ \alpha_n$ is introduced, where β_n is the n-th root of the Bessel function

$$J_o(\beta_n) = 0. \tag{16}$$

Then Eq.14 becomes

$$\frac{C}{C_o} = \sum_{n=1}^{\infty} \frac{2\ J_o(r/r_o\ \beta_n)}{\beta_n J_1(\beta_n)} \exp(-\beta_n^2 D\, t/r_o^2). \tag{17}$$

From this equation, the leaching ratio, f, in unit height of the cylinder at time t can be obtained as follows

$$f = \frac{2\pi\, r_o}{r_o^2\ C_o \pi} \int_0^t \left(-D \left| \frac{\partial C}{\partial r} \right|_{r=r_o}\right) dt \tag{18}$$

$$= \sum_{n=1}^{\infty} \frac{4}{\beta_n^2} \left[1 - \exp(-\beta_n^2\ B\, t)\right], \tag{19}$$

where $B = D/r_o^2$.

The values of Bt for the corresponding f are calculated for 40 roots of the Bessel functions, and the results are given in Table 1.

For each experimentally observed value of f, a value of Bt is read from Table 1 and divided by the time. If the leaching process obeys the above diffusion equation, the graphical dependence of Bt upon t should be expressed by a straight line and the value of B should be constant; knowing the radius of cylinder , r_o, an average value of the diffusion coefficient can be obtained. Clearly Eq.19 is not so useful in predicting the leaching process as the corresponding equation

Table 1

Bt	f	Bt	f	Bt	f	Bt	f
0.001	0.0703	0.026	0.3370	0.051	0.4560	0.076	0.5401
0.002	0.0989	0.027	0.3428	0.052	0.4599	0.077	0.5441
0.003	0.1205	0.028	0.3486	0.053	0.4638	0.078	0.5471
0.004	0.1387	0.029	0.3542	0.054	0.4675	0.079	0.5500
0.005	0.1545	0.030	0.3596	0.055	0.4713	0.080	0.5529
0.006	0.1687	0.031	0.3651	0.056	0.4750	0.081	0.5558
0.007	0.1817	0.032	0.3704	0.057	0.4787	0.082	0.5586
0.008	0.1937	0.033	0.3756	0.058	0.4823	0.083	0.5614
0.009	0.2049	0.034	0.3807	0.059	0.4859	0.084	0.5642
0.010	0.2154	0.035	0.3857	0.060	0.4894	0.085	0.5670
0.011	0.2254	0.036	0.3906	0.061	0.4923	0.086	0.5697
0.012	0.2349	0.037	0.3955	0.062	0.4964	0.087	0.5724
0.013	0.2440	0.038	0.4003	0.063	0.4998	0.088	0.5751
0.014	0.2527	0.039	0.4049	0.064	0.5031	0.089	0.5768
0.015	0.2610	0.040	0.4096	0.065	0.5065	0.090	0.5804
0.016	0.2690	0.041	0.4141	0.066	0.5088	0.091	0.5830
0.017	0.2768	0.042	0.4186	0.067	0.5131	0.092	0.5856
0.018	0.2848	0.043	0.4230	0.068	0.5163	0.093	0.5883
0.019	0.2915	0.044	0.4273	0.069	0.5196	0.094	0.5908
0.020	0.2985	0.045	0.4316	0.070	0.5227	0.095	0.5934
0.021	0.3053	0.046	0.4358	0.071	0.5259	0.096	0.5959
0.022	0.3120	0.047	0.4399	0.072	0.5290	0.097	0.5984
0.023	0.3185	0.048	0.4440	0.073	0.5321	0.098	0.6009
0.024	0.3248	0.049	0.4481	0.074	0.5351	0.099	0.6034
0.025	0.3309	0.050	0.4521	0.075	0.5382	0.100	0.6058

Table 2 Diffusion coefficients of ^{137}Cs in cement pastes*

Leachant	W/C (%)	Diffusion coefficient (cm^2/sec)						
		Time of leaching (day)						
		2	5	10	20	50	100	Average
Tap water	35	3.5×10^{-8}	3.4×10^{-8}	2.9×10^{-8}	2.6×10^{-8}	2.1×10^{-8}	1.9×10^{-8}	2.7×10^{-8}
	40	4.5×10^{-8}	4.2×10^{-8}	3.6×10^{-8}	3.2×10^{-8}	2.6×10^{-8}	2.3×10^{-8}	3.4×10^{-8}
	50	7.1×10^{-8}	6.0×10^{-8}	5.4×10^{-8}	$5.o\times10^{-8}$	3.8×10^{-8}	3.3×10^{-8}	5.1×10^{-8}
	60	9.0×10^{-8}	8.5×10^{-8}	7.4×10^{-8}	6.8×10^{-8}	5.2×10^{-8}	4.6×10^{-8}	6.9×10^{-8}
Sea water	35	2.8×10^{-8}	4.0×10^{-8}	2.9×10^{-8}	2.4×10^{-8}	1.5×10^{-8}	1.0×10^{-8}	2.4×10^{-8}
	40	6.0×10^{-8}	4.7×10^{-8}	4.2×10^{-8}	3.3×10^{-8}	2.0×10^{-8}	1.4×10^{-8}	3.6×10^{-8}
	50	5.5×10^{-8}	5.5×10^{-8}	4.7×10^{-8}	3.6×10^{-8}	2.4×10^{-8}	1.7×10^{-8}	3.9×10^{-8}
	60	7.0×10^{-8}	7.5×10^{-8}	6.2×10^{-8}	5.3×10^{-8}	4.0×10^{-8}	3.0×10^{-8}	5.5×10^{-8}

* This table was cited from Y. Terashima et al., Doboku Gakkai Ronbunhokokushu, (in Japanese) 201, 51 (1972).

(Eq.7) for the plane source; in practice it is not an easy matter to calculate the leaching fraction at any given time without using Table 1.

To explain the data for leaching of ^{137}Cs, ^{90}Sr and ^{60}Co from cement composites, Terashima et al(6),(7) used Eq.19 and found that this equation could be employed for this purpose while the diffusion coefficient was not necessarily constant, but was slightly dependent on the leaching period, as seen in Table 2.

2.1.3 The diffusion equation based on a spherical source model

In this section it is assumed that the radioactive substance is leached from a spherical body. In this case, we begin by writing the diffusion equation for spherical body in the form

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2\partial C}{r\partial r} \right). \tag{20}$$

If we make the substitution u = C r, Eq.20 may be written alternatively as

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial r^2}, \tag{21}$$

with the initial and boundary conditions,

$$u = 0, \qquad r = 0, \qquad t > 0, \tag{22}$$

$$u = 0, \qquad r = r_0, \qquad t > 0, \tag{23}$$

$$u = uC_0, \qquad 0 < r < r_0, \qquad t = 0, \tag{24}$$

where r_0 is the radius of a spherical body, r is the radial space coordinate, C_0 is the initial concentration of a radioactive substance in a spherical body which distributed uniformly in it.

The solution of Eq. 2-21 under the above initial and boundary conditions is given by (8)

$$\frac{C_o - C}{C_o} = 1 + \frac{2\,r_o}{\pi\,r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin\frac{\pi n r}{r_o} \exp(-n^2 B\,t), \qquad (25)$$

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

The total amount of diffusing substance leaving from the sphere at time t is given by

$$Q = 4\pi r_o^2 \int_o^t - D(\partial\bar{C}/\partial r)_{r=r_o}\,dt \qquad (26)$$

$$= 4\pi r_o^3 C_o \left[1 - \frac{6}{\;^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 B\,t)\right]. \qquad (27)$$

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

$$f = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 B\,t). \qquad (28)$$

In this relation, the leaching ratio depends on the dimensionless parameter, B t.

When f is considerably high, only first term of the series represented by Eq. 28 is needed to be used. Thus

$$f = 1 - \frac{6}{\pi^2} \exp(-B\,t). \qquad (29)$$

For the lower range of values of f , Eq. 28 may be transformed by the Poisson's formula,(9)

$$\sum_{n=1}^{\infty} \exp(-Bt\,n^2) = -\tfrac{1}{2} + \sqrt{\frac{\pi}{Bt}}\left[\tfrac{1}{2} + \sum_{n=1}^{\infty} \exp(-\pi^2 n^2/Bt)\right]. \qquad (30)$$

Integrating with respect to Bt,

Table 3

f	Bt	f	Bt	f	Bt	f	Bt
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	0.0861	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	0.400	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	0.1485	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	0.0570	0.48	0.273	0.73	0.832	0.98	3.41
		0.49	0.287	0.74	0.868	0.99	4.11

$$f = \frac{1}{3/2} - \frac{3}{\pi^2}(Bt) + \frac{6}{3/2}\int_0^{Bt} \frac{\sum_{n=1}^{\infty} \exp(-\pi^2 n^2/Bt)}{Bt}, \qquad (31)$$

the approximation is

$$f = \frac{6}{3/2} \, B\,t - \frac{3}{\pi^2} \, B\,t. \qquad (32)$$

The value of $B\,t$ for the corresponding value of leaching fraction was calculated by Reichenberg(10) using Eq. 29 for the higher value of f, and Eq. 32 for the lower range of f. The result is given in Table 3. The data for the leaching of ^{137}Cs from the crushed sample of cement-waste composite were analyzed using Eq. 28, and the results are given in Table 4. As seen in this table, in both cases, portland and slag cement composites, the value of B is almost constant and almost independent of the leaching time. Therefore, Eq. 28 can be used for analyzing the leaching data given in Fig. 4.

Thus far the rate equation for the reaction which is controlled by internal diffusion has been developed. In the case that the reaction is controlled by external boundary film (Nernst film), the corresponding equation is given by(21)

$$f = 1 - \exp(-3D\,C\,t/r\,\delta\,\underline{C}) \qquad (32')$$

where $C/\underline{C}$ is distribution coefficient, δ is the thickness of boundary film, r is the radius of the sample.

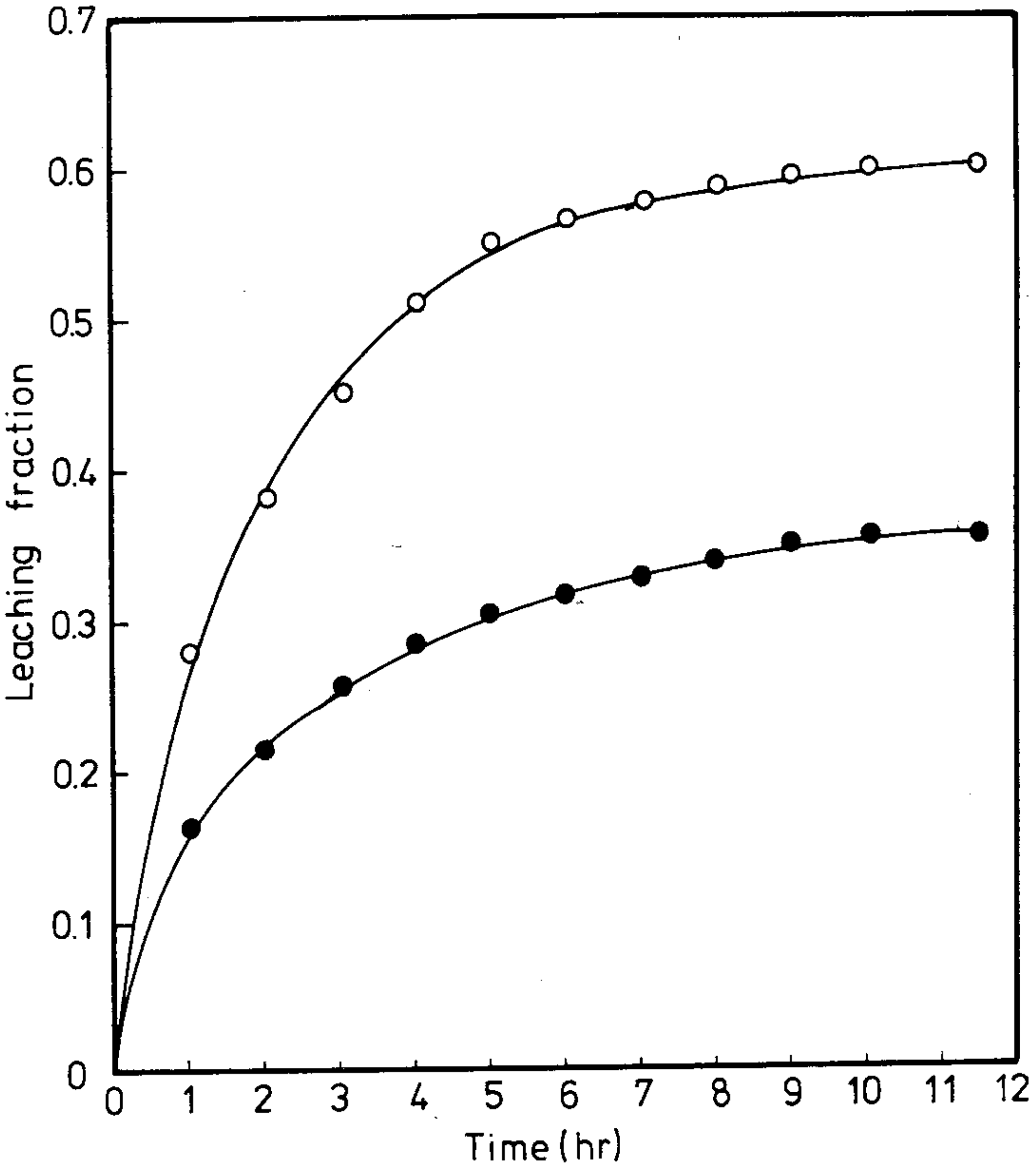

Fig. 4 Plot of leaching fraction vs. t for the leaching of Cs-137 from the crushed cement composites, 25 °C, radius of sample: 1.9 mm

●: sample no. 7
○: 〃 8

Table 4 Numerical evaluation of the diffusion coefficient

Time(hr)	f	Bt	B
	Portland cement composite(sample no. 8)		
1	0.27	0.0736	0.074
2	0.38	0.158	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
			mean 0.076
	$D = \frac{B\ r^2}{\pi^2} = 6.7 \times 10^{-3}\ \mathrm{cm}^2/\mathrm{day}$		
	Slag cement composite(sample no. 7)		
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
			mean 0.021
	$D = \frac{B\ r^2}{\pi^2} = 1.8 \times 10^{-3}\ \mathrm{cm}^2/\mathrm{day}$		

2.2 Model for Leaching Process Due to Diffusion with Other Simultaneous Reactions

The simple diffusion equations described above sections are still imperfect, because of their limited applicability to the complicated real leaching system in which the diffusing substance is initially present in an immobilized form. According to the model, it must be at first mobilized by such physicochemical processes as dissolution of diffusing substance and/ or matrix of waste solid, and ion-exchange, before diffusing out into a sorrounding fluid. If the rate of mobilization is sufficiently rapid compared with that of diffusing out, the diffusing substance is essentially regarded as freely movable one. In this case, the simple diffusion equation may be applicable. However, if the rate of mobilization is comparable or less comparable to that of diffusing out, the ideal diffusion model can no longer simulate the leaching process. That is to say, in the early stage of leaching process, only diffusing substance present in the surface layer contributes to this process. Therefore, the concentration of mobilizable species is gradually decreased because the rate of supply of mobilized species to this layer from the interior part is slow owing to the slow mobilization rate. In this case, the leaching rate must be corrected for this mobilization rate.

To describe the sorption process in which the diffusing substance is immobilized by a simultaneous irreversible first-order or pseudo first-order reaction, a general concept of diffusion-immobilization was proposed by Danckwerts.(10,11)

This model seems applicable to describe the leaching process which is the entirely reverse phenomenon of the sorption process.

The system considered here is the same as that of a plane source model. When the rate of diffusion is comparable to that of mobilization process, the mechanism of leaching process is

$$S_1 \xrightarrow{k} S_2 \xrightarrow{D} S_3 \qquad (33)$$

where S_1, S_2 and S_3 denote immobile, mobilized and diffusing species, respectively, k is the first-order rate constant for mobilization step, and D is the diffusion coefficient of mobilized species. The rate equation for this system is

$$\frac{\partial C}{\partial t} = \frac{D\,\partial^2 C}{\partial x^2} - kC \qquad (34)$$

with the initial and boundary conditions,

$$t = 0, \quad \infty > x > 0, \quad C = C_o, \qquad (35)$$

$$t = 0, \quad x < 0. \quad C = 0, \qquad (36)$$

$$t > 0, \quad x = 0, \quad C = 0, \qquad (37)$$

$$t > 0, \quad x = \infty, \quad C = C_o. \qquad (38)$$

The solution of Eq. 34 is

$$\frac{C}{C_o} = \frac{1}{2} \exp\left(-x\sqrt{\frac{k}{D}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} - kt\right) + \frac{1}{2} \exp\left(x\sqrt{\frac{k}{D}}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + kt\right). \qquad (39)$$

The rate of leaching per unit surface area is

$$\frac{\partial Q}{\partial t} = -D\left(\frac{\partial C}{\partial x}\right)_{x=o} = C_o\sqrt{Dk}\left(\operatorname{erf}\sqrt{kt} + \frac{e^{-kt}}{\sqrt{kt\pi}}\right), \qquad (40)$$

from this the amount of substance leached through the unit surface in time t is given by

$$Q = C_0\sqrt{\frac{D}{k}}\left[\left(kt + \tfrac{1}{2}\right) \operatorname{erf}\sqrt{kt} + \sqrt{kt/\pi}\cdot e^{-kt}\right]. \qquad (41)$$

Then, if the quantity of the radionuclide a (Ci) is leached in time t (day) from the specimen having the surface area of S (cm^2), the volume of V (cm^3) and the initial quantity of radionuclide of A (Ci), the leaching fraction is given by

$$f = (S/V)\sqrt{D/k}\ \left(kt + \tfrac{1}{2}\right) \operatorname{erf}\sqrt{kt} + \sqrt{kt/\pi}\cdot \exp(-kt)\ . \qquad (42)$$

When kt is sufficiently large, $\operatorname{erf}\sqrt{kt}$ approaches unity, and then Eq. 42 becomes

$$f = (S/V)\sqrt{Dk}\left(t + \tfrac{1}{2}k\right), \qquad (43)$$

and if kt is very small, the powers of kt higher than the first term in expanding $\operatorname{erf}\sqrt{kt}$ and $\exp(-kt)$ can be neglected, thus Eq. 42 becomes

$$f = (S/V)\sqrt{4D/\pi}\left(1 + \tfrac{1}{2}kt\right)t^{\frac{1}{2}}. \qquad (44)$$

Further, if $kt \ll 1$, Eq. 42 becomes

$$f = (S/V)\sqrt{4Dt/\pi}\ . \qquad (45)$$

This equation is analogous to Eq. 7.

The leaching process is generally described with Eq. 42 and in such particular cases that kt is very small or large, Eq. 44 or 43 can be used for this purpose. To analyze the leaching data for the waste-bitumen product, Amarantos and Petropoulos(13) used Eqs. 43 and 45. It was found that the amount of Na^+ leached from the specimen of 0.5 cm thickness is directly proportional to the square root of the leaching time, and in the case of the sample having the thickness of 2.5 cm, the induction period is observed, though the above reationship is maintained after this period.

On the other hand, the amount of Ca^{2+}(in the form of $CaCO_3$, slightly soluble salt) leached from the specimen is directly proportional to the leaching time, except for the initial stage of leaching process.

Godbee and Joy(14) confirmed applicability of Eq. 43 to the leaching data of cement-sludge, asphalt-sludge, phosphate glass, and borosilicate glass products.

2.3 Polynomial Representation of Data

In order to obtain the maximum usefullness from a set of experimental data, it is frequently desirable to express the data by an emprical equation such as polynomial. If the mechanism of leaching process is known, the rate equation can be derived from the rate-determining steps. In many cases, however, the leaching mechanism is not always elucidated, therefore it is practically convenient to use a polynomial for representing data. An advantage of this method is that data are represented in a compact fashion and in a form which is convenient for extrapolation. In many cases, the form of the relation between the independent and dependent variables is unknown and must be determined, therefore it is best to use a power series of the type,

$$y = a + bx + cx^2 + dx^3 + \cdots\cdots \qquad (46)$$

with as many emprical constants as necessary to represent the data within the experimental uncertainty.

We will discuss here about polynomial representation of the leaching data.

2.3.1 Orthogonal polynomial

The orthogonal polynomial is one of the most useful equation for representing experimental data. The general form of the orthogonal polynomial is

$$y = \sum_{i=1}^{n} A_i g_i(x), \qquad (47)$$

where A_i is the parameter to be determined, $g_i(x)$ is the function of x. The method based on this polynomial is presented in this section to describe the leaching process. As seen in Figs. 2 and 3, the fraction leached from the specimen appears to be a function of the square root of the leaching time, $t^{\frac{1}{2}}$, thus $g_i(x)$ is taken as $t^{i/2}$. The fraction leached f is

$$f = \sum_{i=1}^{n} A_i t^{i/2}. \qquad (48)$$

To simplify the mathematical treatment for searching the unknown parameter, the equation of 3rd-degree polynomial was used,

$$f = A_1 t^{\frac{1}{2}} + A_2 t + A_3 t^{3/2}. \qquad (49)$$

The data for the cement-waste solid represented in Fig. 3 were applied to this analytical method to give

$$f = 6.12 \times 10^{-2} t^{\frac{1}{2}} - 3.74 \times 10^{-3} t + 8.64 \times 10^{-5} t^{3/2}. \qquad (50)$$

A comparison of the experimental values with those calculated from Eq. 50 is given in Table 6. A good agreement between the calculated leaching fraction and observed one indicates that this type of polynomial gives excellent applicability to the leaching data .

Studies on the reaction of various glasses with aqueous solutions by Douglas and El-Shamy(15) in which the amounts of alkali and silica leached were determined, indicated that there was a linear relation between the quantity of alkai leached and the square root of time in the very early stage of the process. In the latter stage, however,above-mentioned relation is not maintained, and the quantity of alkali leached Q is given by the purely empirical expression of the form

$$Q = A t^{\frac{1}{2}} + B t. \qquad (51)$$

Table 6 Comparison of polynomials representing the leaching data (sample no. 4)

Time	$f^{*}_{exp.}$	f^{**}_{1}	f^{***}_{2}
1	0.0552	0.0564	0.0552
2	0.0747	0.0764	0.0746
3	0.0925	0.0936	0.0924
5	0.121	0.119	0.121
7	0.143	0.146	0.143
14	0.187	0.187	0.183
21	0.212	0.210	0.213
35	0.246	0.248	0.244
49	0.270	0.274	0.271
98	0.324	0.322	0.326

* Experimentally determined leaching fraction.

** Predicted values by using Eq. 50 (Orthogonal polynomial)

*** Predicted values by using Eq. 55 (BIKO equation)

2.3.3 BIKO equation

The BIKO equation was derived by Brownell et al.(16)-(18) to analyze the leaching data. The general form of the BIKO equation is given by

$$f_t = \sum_{i=o}^{n} f_i = f_o + f_1 + f_2 + f_3 + \cdots \qquad (52)$$

$$= f_o + \frac{Z_1 k_1 t^{\frac{1}{2}}}{1 + k_1 t^{\frac{1}{2}}} + \frac{Z_2 k_2 t}{1 + k_2 t} + \frac{Z_3 k_3 t^{3/2}}{1 + k_3 t^{3/2}} . \qquad (53)$$

where

f_t: the total fraction leached

Z_i: the fraction of a component subjected to leaching as described by the i-th term

k_i: the reciprocal time constant for a specified component subjected to leaching as described by the i-th term.

This polynomial can be used to describe the leaching process provided the functions used are selected pertinently in order to fit the leaching data.

The data for the leaching of ^{90}Sr from basalt were analyzed with the BIKO equation to give(16),(19)

$$f_t = f_1 + f_2,$$

$$= 7.5 \times 10^{-5} \frac{0.065\ t^{\frac{1}{2}}}{1+0.065\ t^{\frac{1}{2}}} + 2.7 \times 10^{-4} \frac{5\text{x}10^{-5}\ t}{1+5\text{x}10^{-5}\ t} . \qquad (54)$$

The calculated values by using Eq. 54 agree very closely with the experimental values. Brownell et al. confirmed further the applicability of the BIKO equation to the leaching data of various silicates.

Similar analytical treatment on the data for leaching of ^{137}Cs from the cement-waste solid was carried out to give

$$f_t = f_1 + f_2 + f_3$$

$$= -3.49 \times 10^{-2} \frac{-1.68\ t^{\frac{1}{2}}}{1-1.68\ t^{\frac{1}{2}}} + -0.106 \frac{0.978\ t}{1-0.978\ t}$$

$$+ 0.116 \frac{1.39\ t^{3/2}}{1+1.39\ t^{3/2}} . \qquad (55)$$

As seen in Table 6, the calculated values agree very well with the experimental data. This polynomial seems plausible to predict the amounts leached from various types of waste solids.

It was assumed that the each term in Eq. 52 had the characteristic physicochemical meaning such as;

f_o; the fraction initially removed by rinsing

f_1; the fraction due to diffusion and/or ion exchange

f_2; the fraction due to chemical attack and diffusion combined with chemical attack

f_3; the fraction due to the terminal end of the leaching process.

It is of interest that the each term in Eq. 52 can be assigned a significance in terms of the physicochemical process contributing to the leaching process. However, it must be pointed out that the BIKO equation is a polynomial derived from the diffusion equation. The each term of Eq. 52 may not always therefore necessitate the characteristic physicochemical meaning other than diffusion.

In addition, these meanings which are provided by the mathematical treatment lacking the reasonable experimental evidences are doubtfull in many respects.

The term f_1 was taken as the fraction due to diffusion and/or ion exchange. As is well known, the ion exchange which occurred in the heterogeneous system is generally controlled by diffusion , film diffusion through the boundary Nernst film or internal diffusion through the matrix of waste solid, hence the above description is irrational.

From the similarity between the term f_2 and a rate equation of second-order chemical reaction,

$$f = C_0 k\, t / (1 + C_0\, k\, t), \qquad (56)$$

where k is the rate constant, C_0 is the initial concentration of the reactant, the term f_2 is supposed to contain the contribution of chemical reaction. In their study, Brownell et al. assumed that the reaction was second-order respect to the leachate, namely pseudo second-order reaction. However, it is difficult to obtain the reaction mechanism which satisfies the above assumption. The experimental evidence supporting this assumption therefore is essential. After all, the BIKO equation is so excellent for representing the leaching data that the each term in the BIKO equation need not require the physicochemical meaning other than diffusion without reasonable experimental evidences.

2.4 Graphical Representation of Leaching Data

The method of graphical representation has many advantages which favor their use in representing data. One of the most important of these advantages is that a graph may reveal significant features in data which might be overlooked in a tabular or formular representation. Furthermore, direct differentiation may be performed to obtain tangent from a curve, in many cases this operation being easy and practical.

In order to represent the leaching data, several theoretical and emprical formulas have been introduced, but there are no consistency in the treatment of data among them. This situation makes it difficult to perform the inter-conversion of the parameter which indicate the leachability, resulting in the considerable confusion in the inter-comparison of the leaching data. In the present situation, it may be desirable that the original data are shown in the form of graphs along with the parameter which represents the leachability and is obtained by applying the data to a analytical formula.

It was also proposed by IAEA(20) in the paper entitled "Leaching testing of immobilized radioactive waste solids, A proposal for a standard method" that the results shall be represented by a plot of the cumulative leaching fraction against the total time of leaching,

$$\left(\frac{a}{A}\right)\left(\frac{S}{V}\right) \quad \text{versus } t$$

or

$$\left(\frac{a}{A}\right) \quad \text{versus } t^{\frac{1}{2}}$$

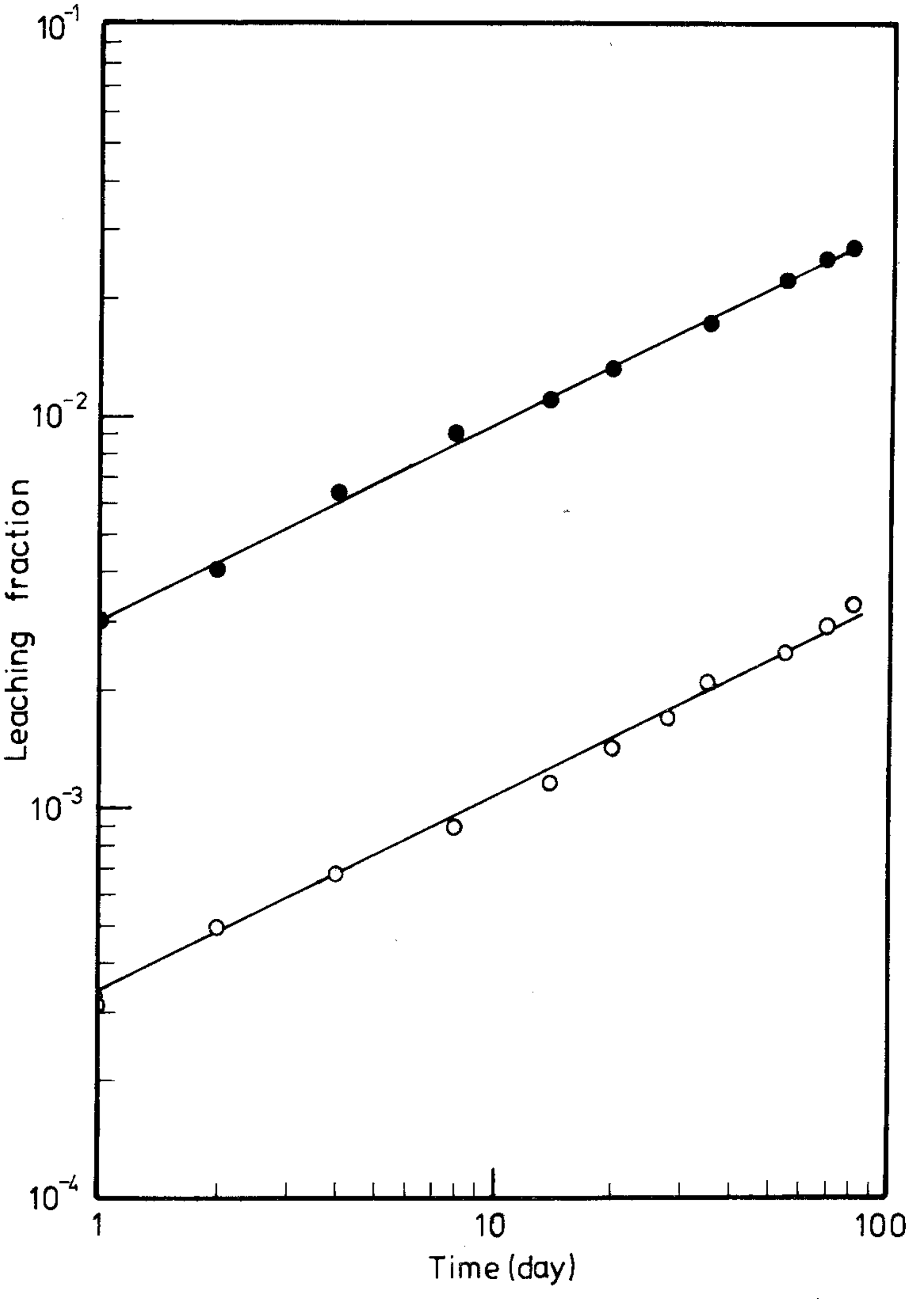

Fig. 5 Variation of leaching fraction as a function of t

The examples of this type of plots are shown in Figs. 1, 2 and 3.

In the case that the fraction leached is represented by the relation

$$f = k\ t^{\alpha}, \tag{57}$$

where k and α are the parameter, the plot of log f against log t is very convenient for obtaining the parameters k and α. The data given in Fig. 1 are replotted in the form of log f against log t as seen in Fig. 5. The relation is almost linear in both cases, and the slope of this relation is about $\frac{1}{2}$.

3. Concluding Remarks

3.1 Kinetics of the Leaching Process

For more than half a century, the dissolution of salts, metals, silicate glasses etc., in water and aqueous solutions have been the subject of numerous experimental and theoretical investigations. From the time of the classical works of Nernst(22) and Brunner,(23) it has been accepted that these processes are governed by diffusion even if these are accompained by a chemical reaction, with very few exception.(24) Since the leaching process belongs to the category of dissolution, this process may also be controlled by diffusion either internal or external diffusion. In spite of the work of Nernst, it has been frequently claimed that certain leaching processes are controlled by a chemical reaction. In the study of leaching kinetics, the rate determining step has been erroneously determined by several workers who unfortunately obtained no or almost no experimental evidences enough to support their conclusion. As is well known, the rate-determining step is not revealed by the time dependence of fraction leached alone. In order to distinguish clearly between diffusion-controlled and chemical reaction-controlled process, following matters should be examined.

(i) In the most cases, the kinetics of leaching was studied under the condition that the leachant was not stirred. The fact that a relationship exists between the rate of dissolution and the speed of rotation of the stirrer is always considered as a proof of the fact that the process is controlled by diffusion.

$$(\text{rate of dissolution}) \propto (\text{rate of stirring})^S,$$

the value of S was determined by several workers; S = 1 (Wildermann), 2/3 (Brunner), and 4/5 (Nernst).(25) The effect of agitation of the leachant must therefore be examined to clarify the kinetic behavior of the leaching process. Although at high rotation speeds the effect of agitation becomes less pronounce, this by no means proves the change of rate-determining step into chemical reaction.(26)

(ii) The effect of temperature on the leaching rate is more pronounced in the case of chemical reaction-controlled process. If the process is controlled by diffusion, the apparent activation energy is comparable to that for diffusion of water molecule. In the previous paper, the apparent activation energy of 4 - 5 kcal/mol was obtained for the leaching of ^{137}Cs from the cement composites.(4) This value is comparable to that for diffusion of water

In the case of diffusion-controlled process, as pointed out by Berthoud(27) the rate equation is sometimes similar to that of the chemical reaction-controlled process, especially first-order rate equation. Therefore, the above-mentioned examinations are essential to obtain the kinetic behavior of leaching process. It is obvious that in the diffusion-controlled process the observed leaching rate does not depend on any specific feature of the chemical mechanism; the rate is governed by the diffusion coefficient of the species tested and the structure of the matrix of composite (porous structure). Thus, it is also important to obtain the structural informations about the matrix of composite for understanding the kinetic behavior of leaching.

3.2 Prediction of Amounts Leached

Although the kinetics and mechanism of leaching process are of very interest, and are of very importance to develope the durable composite for incorporating wastes, in order to predict the amounts leached from the waste composites, these detailed informations are not necessarily essential. In such a case , it is perhaps convenient to use the simple formula rather than the complex one which requires somewhat troublesome numerical treatments. For this purpose, Eq. 7 (diffusion equation obtained from a plane source model) has several advantages; simplicity in its numerical treatment and popularity in its use.

As seen in Figs. 2 and 3, the linearity between f and time which is one of the criteria for the validity of Eq. 7 is not always obtained throughout the leaching time tested for cement composites. However, as shown in Fig. 6, it can be regarded that the leaching process consists of two stages; the initial and latter stages. The initial leaching process can be described by the following relation,

$$f_i = m_i t^{\frac{1}{2}}, \qquad (58)$$

and corresponding relation for the latter stage is

$$f_1 = m_1 t^{\frac{1}{2}} + \alpha, \qquad (59)$$

where m is the coefficient defined by Eq. 8, and α is the intercept of the line described by Eq. 59, which corresponds to the contribution of initial leaching process.

Although this method can not describe the whole leaching process by a single formula, it is very convenient to simulate the leaching process in the longer leaching time. If it is not necessary to simulate the initial leaching stage, this equation can be used for predicting the amounts leached at the longer leaching time, especially in the case of safety assessment for the disposal of waste solids.

If the detailed mechanism of the leaching process is known, the rate equation can be derived from the rate-controlling steps. Unfortunately, in many cases the leaching process is so complicated that the mechanism is not always obtained. Therefore, it is practically convenient in such cases to use polynomial for representing the leaching data. As seen in Table 6, this method gives the best fitting, hence this method can be useful if it is not necessary to take the theoretical basis into account.

Although in this paper the probability of occuring the process controlled only by a chemical reaction was excluded, the intermediate case controlled by diffusion and a first-order reaction simultaneously was discussed in Sec. 2.2. This type of rate equation was derived first by Danckwerts to analyze the adsorption process attributed to not only diffusion but also simultaneous reaction. Recently, Terashima and Godbee suggested that this type of equation may be used to analyze the leaching data. As confirmed by Godbee, this method gives fairly good approximation, however, this requires a very troublesome numerical treatment. This

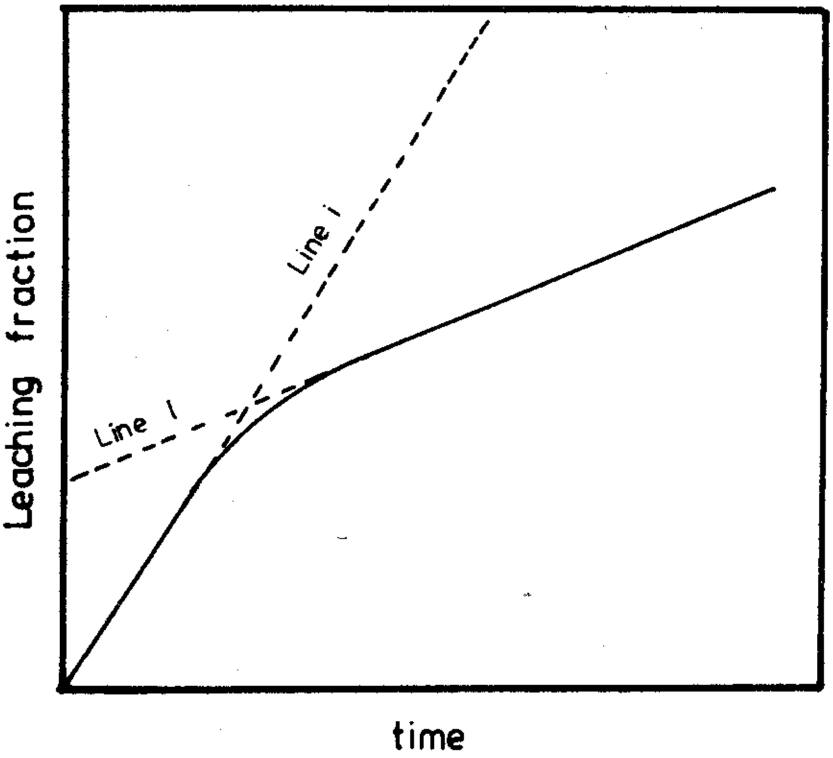

Fig. 6 Schematic leaching curve

Table 7 Composition of specimens

Sample no.	Cement	Waste	Wa/C**
1	P	15% Na_2SO_4	60
2	S	"	60
3	S	"	36
4	P	"	33
5	P	12% $H_3BO_3^*$	33
6	P	15% Na_2SO_4	33
7	S	"	42
8	P	"	42

* Neutralized with NaOH to give the solution pH of 12.

** The ratio of cement and waste.

probably makes it difficult to use this method in the safety evaluation for disposal and storage of solid wastes.

In this paper, the methods for predicting amounts leached have been discussed by using several experimental and theoretical formulas. It was found that the simple diffusion equations such as Eqs. 7 and 19 are not necessarily sufficient for predicting the amounts leached. However, the approximated equation, Eq. 59 is found to be useful for this purpose. If the mechanism of leaching is not clear, the use of polynomial such as Eq. 48 or Eq. 53 (BIKO equation) is useful.

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