A MODIFIED MODEL OF PARTICULATE DISPERSION FOR MIGRATION OF SOLUBLE SUBSTANCES FROM SOLIDS INTO SURROUNDING LIQUIDS

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Soluble substances contained in various solids such as plastics, bitumen and concrete slowly migrate into surrounding liquids. These phenomena are analyzed by a modified particulate dispersion model proposed by the authors in this paper. The model is based on the assumption that a part of a solute initially forms a solid solution in the continuous phase of the solids, and the remainder is dispersed particulately.

Basic equations based on this model have been solved numerically. The adequacy of the model was determined by a comparison of calculated curves with experimental results. Leaching of metal compounds from three kinds of plastics using dilute nitric acid was carried out. It was confirmed that the mass fraction of solid solution of solute governed the curve features in the early stage of leaching and the volume fraction of particulate solute was preferential in the later stage.

Introduction

The migration of soluble substances from various solids into surrounding liquids has been noted, especially in the field of the food industry, but only a few reports are available on this phenomenon. Several papers deal with the theoretical aspects of the migration of monomer and adjuvants from polystyrene but fail to discuss particulate solutes.[3,4] The particulate dispersion of solute is implied in a report dealing with the leaching of nuclides from solidified radioactive wastes.[5] One of the present authors proposed a model for this phenomenon assuming particulate dispersion of a solute with reference to the experimental results of the leaching of lead contained in heat stabilizers added to commercial rigid polyvinyl chloride (PVC) plates.[1] In work reported in the preceding paper, curves were calculated by use of this model and were found to coincide reasonably well with those obtained experimentally except at the early stage of leaching.

To obtain greater agreement between calculated curves and observed data on leaching, a modified model is proposed, based on the assumption that a solute partially forms a solid solution in a continuous phase.

Experimental verification was made using three kinds of plastics containing metal compounds. The calculated curves were found to be quite superimposable on those obtained experimentally throughout the entire process of leaching.

1. Model Formulation

Basic differential equations of the original particulate dispersion model proposed in the preceding paper[1] are given as Eqs. (1), (2), (4) and (5). Material balance with reference to diffusion of a solvent in the continuous phase and penetration into particles is obtained by Eq. (1). The accumulation rate of solvent in solute particles per unit volume of solid is given by Eq. (2). A newly proposed modification of the model is shown by Eq. (3) in which the mass flux of a solvent reaching the diffusion front (coordinate $x = X$) and rate of generation of dissolved solute equivalent to that of penetrated solvent are equated. The rate of accumulation of a solute in the continuous phase is represented by Eq. (4) in the same manner as Eq. (1). The rate of accumulation of dissolved solute inside solute particles is given by Eq. (5), where the rate of generation of dissolved solute is equivalent to that of solvent penetration.

$$\frac{\partial C_N}{\partial t} = D_N \frac{\partial^2 C_N}{\partial x^2} - k_N a(\lambda_N C_N - S_N) \tag{1}$$

$$\frac{\partial S_N}{\partial t} = k_N a(\lambda_N C_N - S_N) \tag{2}$$

$$-D_N \frac{\partial C_N}{\partial x}\bigg|_{x = X} = C_H \frac{\partial X}{\partial t} \tag{3}$$

$$\frac{\partial C_P}{\partial t} = D \frac{\partial^2 C_P}{\partial x^2} - k_P a(\lambda_P C_P - S_P) \tag{4}$$

$$\frac{\partial S_{\mathrm{P}}}{\partial t}=k_{\mathrm{P}}a(\lambda_{\mathrm{P}}C_{\mathrm{P}}-S_{\mathrm{P}})+k_{\mathrm{N}}a(\lambda_{\mathrm{N}}C_{\mathrm{N}}-S_{\mathrm{N}}) \qquad (5)$$

The boundary conditions are

$$C_{\mathrm{N}}=0, \qquad \text{at} \quad t=0, \quad x\geqq 0$$

$$C_{\mathrm{N}}=C_{\mathrm{N}0}, \qquad \text{at} \quad x=0$$

$$k_{\mathrm{N}}a=0, \qquad \int_0^t k_{\mathrm{N}}a(\lambda_{\mathrm{N}}C_{\mathrm{N}}-S_{\mathrm{N}})dt \geqq (1-H)C_{\mathrm{PS}}$$

$$S_{\mathrm{N}}=0, \quad t=0, \quad x\geqq 0$$

$$X=0, \quad t=0$$

$$C_{\mathrm{P}}=0, \quad t=0, \quad x\geqq 0$$

$$C_{\mathrm{P}}=0, \quad x=0$$

$$S_{\mathrm{P}}=0, \quad t=0, \quad x\geqq 0$$

$$k_{\mathrm{P}}a=0, \qquad \int_0^t k_{\mathrm{P}}a(\lambda_{\mathrm{P}}C_{\mathrm{P}}-S_{\mathrm{P}})dt \geqq (1-H)C_{\mathrm{PS}}.$$

The loss of solute is given by

$$Q=\int_0^X \left\{ \int_0^t k_{\mathrm{P}}a(S_{\mathrm{P}}-\lambda_{\mathrm{P}}C_{\mathrm{P}})dt + (C_{\mathrm{H}}-C_{\mathrm{P}}) \right\}dx. \qquad (6)$$

These equations were converted into nondimensional form and solved using an explicit finite difference method successively, since a simultaneous solution was impractical because of time-consuming computation. Nondimensional capacity coefficients of both solvent and of solute are three times as large as the volume fraction of the solute particles,* so that they can be represented by the unified term kaX_0^2/D.

Several examples are shown in **Fig. 1**, where parameter H is denoted as a fraction of the solid solution (FSS) of a solute. The curve with $H=0$ is identical to that of the original model in the preceding paper.[1] According to the original model, migration progresses rapidly after a considerable time delay, but the slope of each curve varies less throughout the entire range of migration with increasing values of H for the modified model.

2. Experimental

To verify the adequacy of the calculated curves based on the present model, the following experiments were carried out.

2.1 Samples used

1) Solid samples
  a) Vinyl ester resin (Showa Kobunshi Co., Ltd., R802)
    Initiator: methyl ethyl ketone peroxide
    Accelerator: cobalt naphthenate
  b) Epoxy resin (Asahi Denka Kogyo Co., Ltd., ER4200)

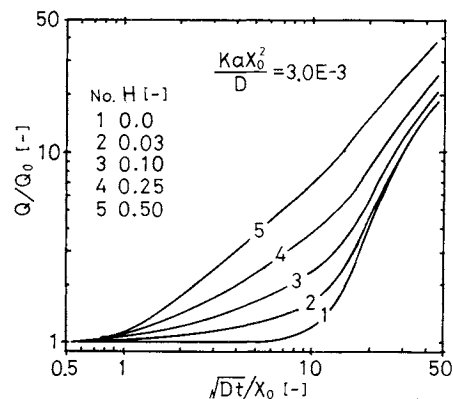* This relation is derived in Section 4.2.

Fig. 1. Examples of calculated curves based on modified particulate dispersion model.

Hardener: (ibid., EH513)
2) Particulate solute Zinc oxide (volume-average diameter using a photo-transmission method of 1.5 μm.)
3) Solvent Dilute nitric acid of concentrations 1% and 3%.

2.2 Preparation of specimen

Specimens rectangular in shape, 100 mm long, 30 mm wide and 3 mm thick were molded in a silicon rubber mold, followed by aging for about two months at room temperature to obtain sufficient hardness.

2.3 Experimental procedure

Each specimen was placed in a test tube and batch leaching was carried out with 150 ml solvent thermostated at 313 K. At prescribed time intervals, 10 ml of leachate was withdrawn and a solvent of equal volume was supplied. Zinc concentration was measured by an atomic absorption spectrophotometer (Nippon Jarrel Ash Co., Ltd., AA782B) to determine the amount of zinc leached from the specimen.

The adequacy of the following approximations was evaluated in the preceding paper.[1]

1) Each specimen can be taken as a semi-infinite medium.

2) Concentration of the solute at the specimen surface is regarded as zero owing to infinite dilution of solute in the leaching bath.

3) No agitation of the bath is necessary, since mass transfer resistance in the liquid film along the specimen surface can be ignored in comparison with that inside the specimen.

3. Comparison of Calculated Curves with Experimental Results

3.1 General description

The instantaneously leached amount, i.e. instantaneous loss defined as the intercepts of extrapolated leaching curves on the ordinate, is given by

$$Q_0=(1-H)C_{\mathrm{PS}}d_p/2, \qquad (7)$$

where Q_0 should be proportional to the content of the particulate solute. (See appendix.)

This relation was confirmed by the experimental results shown in **Fig. 2**. However, particle diameters estimated on the basis of slopes of the curves in Fig. 2 may be regarded as those of the aggregated particles discussed below.

Calculated results are plotted in log-log graphs paper with the square root of nondimensional time on the abscissa and nondimensional loss (ratio of the loss of solute to the instantaneous loss) on the ordinate as shown in Figs. 3 to 7. Experimental results are plotted on the same graphs with the square root of actual time instead of nondimensional time, using a parallel shift along the abscissa to obtain optimum superposition with the calculated curves.

Parameter C_{NO}/C_{PS} is the molar ratio of equilibrium concentration of the solvent at the specimen surface to content of the solute in the specimen, where the value of C_{NO} is determined experimentally as shown in Tables 1 to 3.

The parameter H is determined by a trial method, checking the fitness of the early stage of both calculated and experimental curves. The apparent diffusion coefficient D is determined by comparing the non-dimensional time of the calculated curve with the actual time of experimental data.

3.2 Leaching of zinc from vinyl ester resin

Experimental results using 1% and 3% nitric acid are shown in **Figs. (3)** and **(4)** respectively. The parameter values are tabulated in **Table 1**.

3.3 Leaching of zinc from epoxy resin

Experimental results using 1% nitric acid are shown in **Fig. 5** and the parameter values in **Table 2**.

3.4 Leaching of lead from commercial rigid PVC plates

Experimental data in reference to the preceding papers[1,2] and calculated curves for non-heat-treated and heat-treated specimens are plotted in **Figs. 6** and **7** respectively. Parameter values are listed in **Table 3**.

4. Discussion

4.1 Existence of solid solution

Unfortunately, no quantitative examination has yet been made, but the following experimental facts provide indirect support for the present considerations.

1) Twenty grams of liquid resin or hardener was immersed in 60 ml of distilled water. The pH of the water fell significantly after 3 days, but on adding zinc oxide it remained at near neutrality as shown in **Table 4**. Thus, the dissolution of zinc may occur by an acid-base reaction.

2) Since commercial PVC contains a small amount of lead soap of fatty acid as a lubricant, it may form a solid solution due to its affinity to a
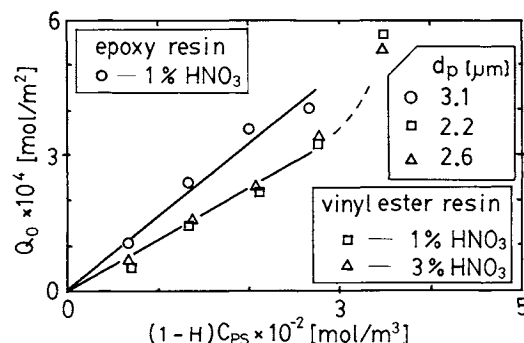

Fig. 2. Relation between instantaneous loss of solute and content of particulate solute. Particle diameters estimated on the basis of the slopes are shown.

polymer.

4.2 Non-dimensional capacity coefficient of mass transfer (NDCC)

It is well known that the following relation holds with respect to mass transfer from or toward a sphere in a stagnant medium.

$$kd_p/D = 2 \tag{8}$$

The specific surface area of particles per unit volume of medium is shown by

$$a = 6(1-\varepsilon)/d_p , \tag{9}$$

where $(1-\varepsilon)$ is the volume fraction of the particles. Substituting Eqs. (8) and (9) into the formula defining NDCC, we obtain

$$\frac{kad_p^2}{4D} = \frac{kaX_0^2}{D} = 3(1-\varepsilon) . \tag{10}$$

That is, NDCC is directly proportional to the volume fraction of particles. The proportionality of the NDCC obtained by superposition is shown in **Fig. 8**, where the slopes of the curves are significantly lower than that given by Eq. (10). This discrepancy probably arises by aggregation of particles accompanied by mass transfer resistance at the interface of primary particles.

4.3 Fraction of solid solution (FSS)

The values of FSS determined in a trial by numerical method are uniform for an individual sample, though they may be affected by agitation intensity at the time of specimen preparation.

4.4 Decrease in FSS by heat treatment of commercial rigid PVC plates

A lead compound added to PVC serves as a heat stabilizer which captures hydrogen chloride produced from the degradation of PVC. It is evident that the decrease in FSS results from the faster change of lead into a slightly soluble product, i.e. lead chloride, in the continuous phase than that inside the particles.

4.5 Factors governing curve features

Features in the early stage of the leaching curves are predominantly affected by FSS. The effects of
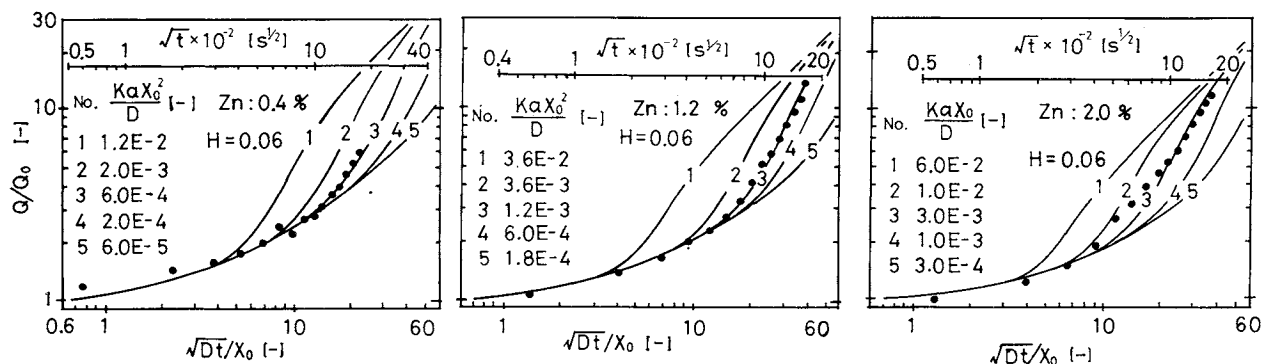
Fig. 3. Comparison of calculated curves with experimental results for leaching of zinc from vinyl ester resin using 1% nitric acid at 313 K. Results for zinc contents of 0.8% and 1.6% are omitted.
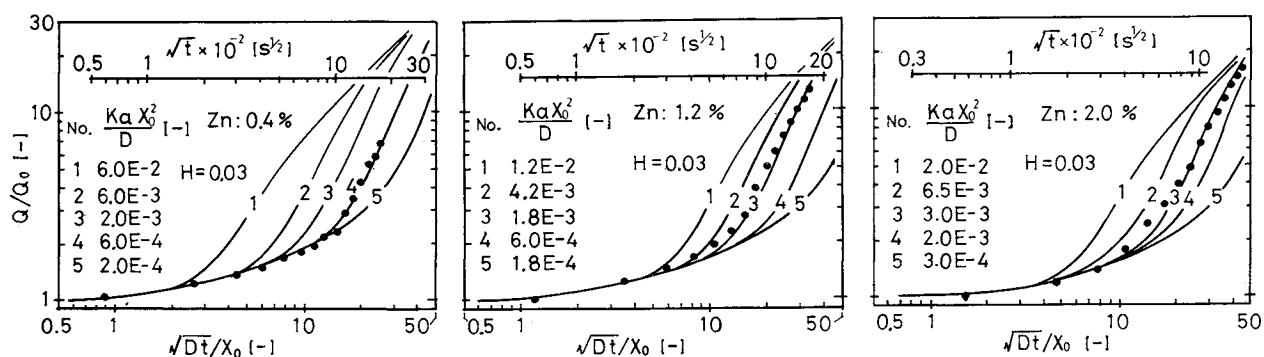

Fig. 4. Comparison of calculated curves with experimental results for leaching of zinc from vinyl ester resin using 3% nitric acid at 313 K. Results for zinc contents of 0.8% and 1.6% are omitted.

Table 1. Parameters for leaching of zinc from vinyl ester resin with dilute nitric acid at 313 K

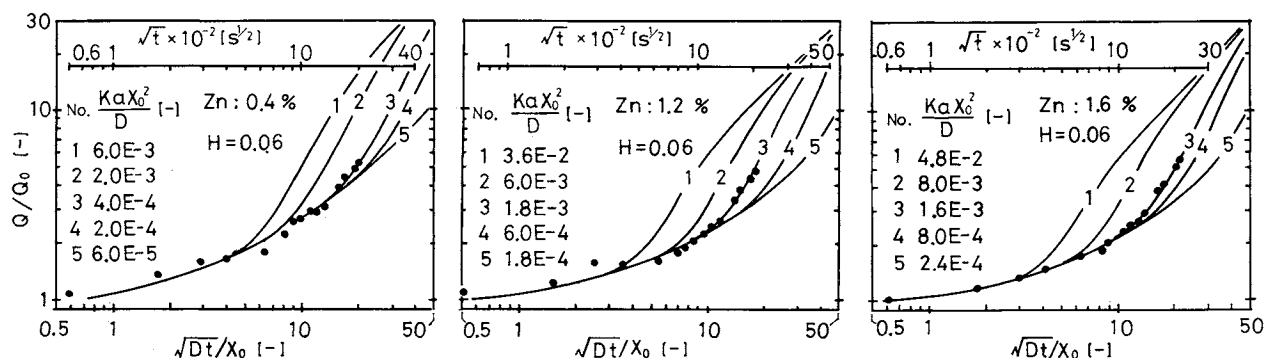| Solvent		1% HNO$_3$					3% HNO$_3$				
$C_{N_0} \times 10^{-2}$	[mol/m^3]	0.63					0.86				
Zinc content	[wt%]	0.4	0.8	1.2	1.6	2.0	0.4	0.8	1.2	1.6	2.0
$C_{PS} \times 10^{-2}$	[mol/m^3]	0.69	1.38	2.07	2.77	3.46	0.69	1.38	2.07	2.77	3.46
C_{N_0}/C_{PS}	[—]	0.46	0.23	0.15	0.11	0.09	0.62	0.31	0.21	0.16	0.13
$KaX_0^2/D \times 10^3$	[—]	0.6	1.2	1.2	2.4	3.0	0.6	1.2	1.8	2.4	3.0
$H \times 10^2$	[—]	6.0	6.0	6.0	6.0	6.0	3.0	3.0	3.0	3.0	3.0
$D \times 10^{15}$	[m^2/s]	0.7	1.4	2.4	1.8	2.1	1.4	3.0	2.4	4.5	4.3

Fig. 5. Comparison of calculated curves with experimental results for leaching of zinc from epoxy resin using 1% nitric acid at 313 K. Result for zinc content of 0.8% is omitted.

Table 2. Parameters for leaching of zinc from epoxy resin with nitric acid at 313 K

Solvent $C_{N_0} \times 10^{-2}$	[mol/m³]	1% HNO₃ 1.3			
Zinc content	[wt%]	0.4	0.8	1.2	1.6
$C_{PS} \times 10^{-2}$	[mol/m³]	0.66	1.32	1.98	2.64
$C_{N_0} \times C_{PS}$	[—]	0.97	0.49	0.33	0.24
$KaX_0^2/D \times 10^3$	[—]	0.4	0.8	1.8	1.6
$H \times 10^2$	[—]	6.0	6.0	6.0	6.0
$D \times 10^{15}$	[m²/s]	0.81	0.95	0.65	0.86

NDCC are initially not apparent but become increasingly so with time, particularly at low values of NDCC.

Conclusions

It is recognized that the suitability of the model is effectively improved by the introduction of a partial solid solution.

The values of FSS are predominant factors affecting the early stage of migration and those of NDCC for the later stage. Thus, the results of short-term
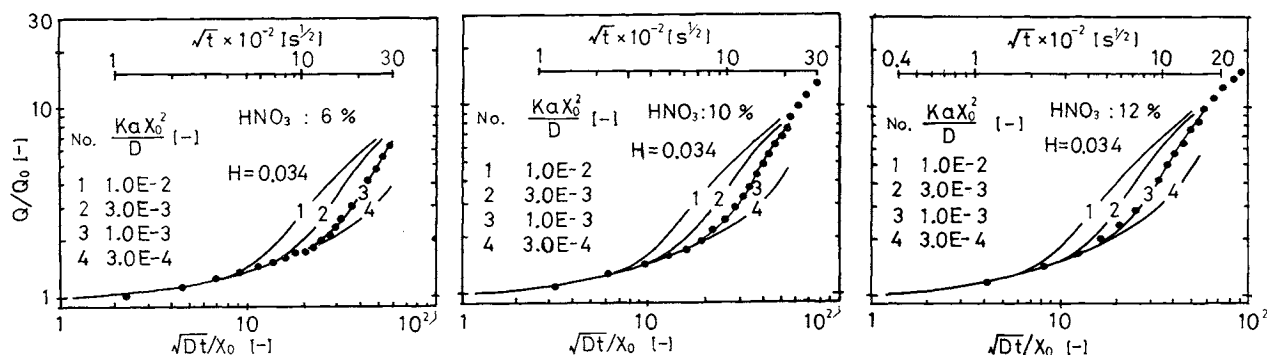
Fig. 6. Comparison of calculated curves with experimental results for leaching of lead from commercial rigid PVC containing 3.6% lead using dilute nitric acid at 313 K. Result for acid concentration of 8% is omitted.
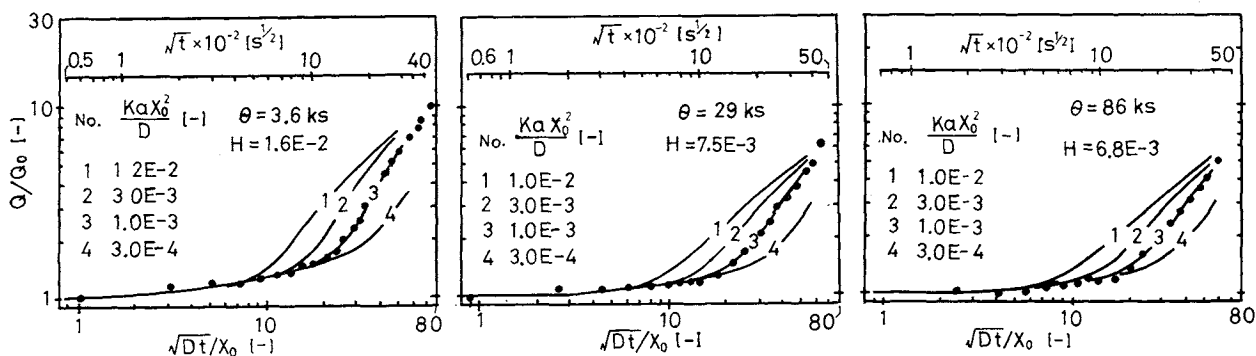

Fig. 7. Comparison of calculated curves with experimental results for leaching of lead from heat-treated commercial rigid PVC containing 3.6% lead using 8% nitric acid at 313 K. Result for heat-treating time of 18 ks is omitted.

Table 3. Parameters for leaching of lead from rigid commercial polyvinyl chloride plates with nitric acid at 313 K

$C_{PS} \times 10^{-2}$	[mol/m³]	2.4							
Heat-treating time θ	[ks]	0				3.6	18	29	86
ϕ	[—]	0.45				0.33	0.16	0.15	0.14
Concentration of solvent	[%]	6	8	10	12	8			
C_{N_0}	[mol/m³]	11.1	15.6	18.7	25.6	15.6			
C_{N_0}/C_{PS}	[—]	0.10	0.14	0.17	0.24	0.20	0.41	0.43	0.46
$KaX_0^2/D \times 10^3$	[—]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$H \times 10^2$	[—]	3.6	3.6	3.6	3.6	1.6	0.81	0.75	0.68
$D \times 10^{16}$	[m²/s]	1.0	1.7	1.6	3.0	0.75	0.74	0.55	0.50

Table 4. Observed values of pH of distilled water in which liquid resin or hardener is immersed

	Vinyl ester resin	Epoxy resin Resin	Epoxy resin Hardener
With ZnO	6.5	7.3	7.3
Without ZnO	3.3	5.9	6.2
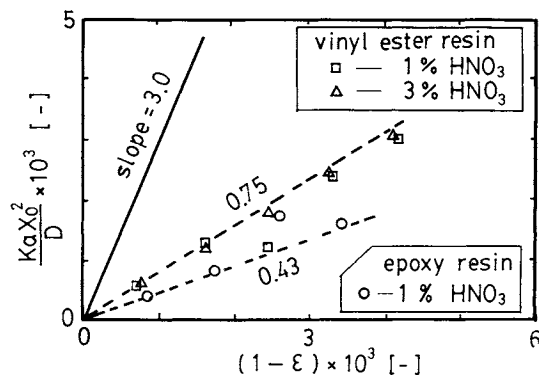
Fig. 8. Nondimensional capacity coefficient of mass transfer vs. volume fraction of particulate solute.

experiments do not always provide pertinent information for predicting long-term migration behavior since FSS and NDCC are independent of each other.

The value of NDCC introduced theoretically is three times the volume fraction of the particulate solute, but those obtained by graphical superposition of the experimental data are significantly less than the former. The latter may thus possibly be the overall capacity coefficient involving interparticulate resistance of aggregated particles.

Appendix

Derivation of Eq. (7)

Solute particles located in the vicinity of a solid surface are partially excised as shown in **Fig. A-1(a)**. The remaining volume of the particle the center of which is located at $x = x_c$ is given by

$$V = \int_0^{d_p/2 + x_c} \pi \left\{ \frac{d_p^2}{4} - (x - x_c)^2 \right\} dx$$

$$= \pi \left\{ \frac{d_p^3}{12} + \frac{d_p^2}{4} x_c - \frac{1}{3} x_c^3 \right\} \tag{A-1}$$

The nondimensional relation between V and x_c is shown in **Fig. A-1(b)**. It is estimated that both solvent and solute diffuse instantaneously inside the particles, since the mass transfer resistance can be ignored in comparison with that in the continuous phase of solid. Instantaneous loss of solute Q_0 can thus be expressed as follows:

$$Q_0 = n\rho \int_{-d_p/2}^{d_p/2} V dx_c$$

$$= n\rho \frac{\pi}{12} d_p^4 , \tag{A-2}$$

where n is number of particles per unit volume of the solid. Writing $(1-H)C_{PS}$ for the content of the particulate solute, the following relation holds.
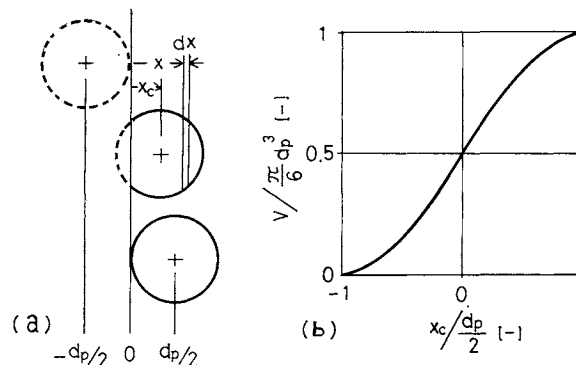
Fig. A-1. Remaining volume of excised sphere in the vicinity of solid surface.

$$(1 - H)C_{PS} = n\rho \frac{\pi}{6} d_p^3 . \tag{A-3}$$

Using Eqs. (A-2) and (A-3), we have

$$Q_0 = (1 - H)C_{PS} d_p/2 . \tag{7}$$

Nomenclature

C	= concentration of diffusant	[mol/m³]
C_{PS}	= content of solute	[mol/m³]
D	= apparent diffusion coefficient	[m²/s]
d_p	= diameter of solute particle	[m]
H	= mol fraction of solid solution	[—]
ka	= individual capacity coefficient of mass transfer	[1/s]
$KaX_0^2/D, kaX_0^2/D$	= nondimensional capacity coefficient of mass transfer, overall and individual, respectively	[—]
Q	= loss of solute	[mol/m³]
S	= amount of diffusant in solute particles per unit volume of solid	[mol/m³]
t	= time	[s]
X	= coordinate of diffusion front	[m]
$X_0(=d_p/2)$	= depth of zone of instantaneously leached solute	[m]
x	= distance	[m]
λ	= partition coefficient	[—]
ρ	= density of solute particle	[mol/m³]
ϕ	= mol-fraction of soluble species	[—]
$1 - \varepsilon$	= volume fraction of particulate solute	[—]
θ	= heat-treating time	[ks]

⟨Subscripts⟩

N	= solvent
P	= solute
H	= solid solution

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