ANALYSIS OF OLD STRUCTURES AND NUMERICAL MODEL FOR DEGRADATION OF CONCRETE BY CALCIUM ION LEACHING

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Studies related to leaching mechanisms and degree of degradation are carried out on 34 to 104-year-old concrete structures immersed in or in contact with water and subjected to calcium leaching, using numerical analysis techniques and by factual investigation. The analytical model is based on the law of conservation of mass and takes into account changes in diffusion coefficient and porosity with degradation, as well as the solubility equilibrium of calcium. It is assumed that distributions of physical properties such as calcium concentration, porosity, and strength can be estimated. Based on the studies of actual structures, the model is used to investigate the effects of action of water quality and material conditions on degradation rate. The results of the investigations verify that the stages of degradation in different environments can be predicted by the leaching model and that the effects of water-cement ratio and boundary calcium ion concentration on degradation rate are significant.

Key Words: *leaching of calcium, degradation, diffusion, advection, chemical equilibrium, porosity, mechanical properties*

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1. Introduction

Although hydrates of cement in concrete do not easily dissolve in water, they are not completely insoluble and include substances of varying solubility. As a result, deterioration of concrete through, for example, the formation of pores or strength loss is associated with the dissolution of hydrates over the long term. This is true even under the action of water free from components that promote short-term degradation (such as acids, salts, and chlorides). Known as "leaching," this phenomenon causes degradation at a much slower rate than other forms of degradation. It often occurs in combination with degradation due to acid attack or physical damage. Thus, leaching itself has not generally been considered a problem in ordinary structures, and it was only evaluated qualitatively in the past.

However, in structures such as tunnels or pressure vessels, or in hydraulic structures such as waterways and dams, where concrete joints or cracks are present, leaching degradation is likely to occur intensively because of contact with flowing water or water leaks. Once leaching has caused degradation, problems such as salt damage, carbonation, and frost damage are likely to accelerate and be compounded. Accordingly, a quantitative evaluation of the phenomenon by which cement hydrates leach is important.

Similarly, radioactive waste disposal facilities must offer long-term durability for periods from several hundred to several thousand years. These are constructed in hard rock 100 to 1000 meters below the ground, and are assumed to be in an environment where degradation rarely occurs. For such structures, the study of degradation that occurs over the long term, such as by leaching, is more important than short-term forms of degradation.

The migration of calcium ions accompanying leaching also needs to be evaluated quantitatively [1] since the alkali compounds generated by cement hydrates also change the pH of the surrounding environment. As a result, the protection of metallic vessels degrades, the rate of migration of nuclides changes, and the properties of bentonite used in the vicinity are likely to be degraded.

In this study, several old concrete structures (ranging from 34 to 104 years old) are investigated to clarify the actual status of alteration (degradation) of concrete caused by the leaching of calcium ions (abbreviated as Ca^{2+}) under the action of water. Simultaneously, the possibility of evaluating leaching degradation is studied using numerical analysis and models for evaluating physical properties combining chemical equilibrium and mass transfer.

2. Objectives and description of research

Both short-term accelerated tests in the laboratory and analytical methods have been proposed for research into the long-term degradation of concrete used for atomic energy facilities. Past experimental investigations have focused on analysis of solutions with the aim of simulating the pore solution into which hydrates leach, and many batch-type experimental investigations have been carried out with the focus on solid-liquid solubility equilibrium [2], [3]. However, degradation with respect to the passage of time could not be directly evaluated from the results of such investigations. New conditions had to be tentatively set up, such as assumption regarding inflows of water from external sources, to allow for evaluation with respect to the passage of time. Typically, these experimental investigations involved determining the solid-phase components of the hydrates and the components of the pore solution. Moreover, investigations were carried out for to evaluate changes in physical properties as the balance of solid phase-liquid phase components varied, and also to show up differences between accelerated tests and actual phenomena. Although models have been proposed specifically for paste in analytical investigations [3], [4], methods applicable to actual structures have yet to be established. This is because of problems such as: (1) there are practically no models of concrete or mortar that take the aggregate into account; (2) there is no clear method of setting diffusion coefficients; (3) there is no method for estimating physical properties; and (4) no verifications against actual structures have been carried out.

Accordingly, in this study, the results of long-term analysis (34 to 104 years) are first described so as to provide an understanding of the degradation of actual structures subject to the action of water free of toxic substances, such as ground water, river water, and tap water.

Next, with the aim of simplifying the analysis, a model is proposed for (i) estimating long-term changes (degradation) in physical properties that accompany the change (reduction) in amount of solid phase Ca and (ii) mass transfer with the focus on Ca, which is the main substance involved in leaching and the dissolution of hydrates. An analytical method is proposed for sequentially applying a chemical model related to dissolution of

Table 1 Mix proportions and environmental conditions of actual structures studied

Item	Notation	A	B	C	D	E	F	G	H	I
Structure	–	Inside the slab of waterworks facilities	Outside the slab of waterworks facilities	Bulkhead joints of waterworks facilities	Building foundation	River weir waterway bulkhead	River weir waterway bulkhead	River weir waterway abutment	Outside the slab of water supply facilities	Upstream of dam body
Materials	–	Concrete	Concrete	Mortar	Concrete	Concrete	Concrete	Concrete	Concrete	Concrete
Location	–	Tokyo	Tokyo	Tokyo	Yokohama	Niigata	Niigata	Niigata	Atami	Hiroshima
Age (years)	–	34	104	104	70	76	41	68	35	60
Water quality	–	Tap water	Ground water	Tap water	Ground water	River water	River water	River water	Ground water (70% seawater)	River water
Water condition	–	Flowing water	Still water	Flowing water	Still water	Flowing water	Flowing water	Flowing water	Still water	Still water
Measured compressive strength (N/mm^2)	f'c	36.0	13.2	–	43.4	19～27	–	19～27	55.0	17.9
Estimated water-cement ratio	W/C	0.6	0.72	0.72	0.55	0.6	0.6	0.6	0.4	1.0
Estimated fine aggregate ratio (%)	s/a	44	32.5	100	42	32	42	32	40	32
Estimated unit water content (kg/m^3)	W	170	109	253	170	151	170	151	170	155
Estimated unit cement content (kg/m^3)	C	283	152	352	309	252	283	252	425	155
Estimated unit fine aggregate content (kg/m^3)	S	847	688	1595	799	640	808	640	723	662
Estimated unit coarse aggregate content (kg/m^3)	G	1078	1427	–	1104	1359	1116	1359	1084	1407
Specific gravity of cement	ρ_C	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.15
Specific gravity of fine aggregate	ρ_S	2.6	2.51	2.51	2.6	2.6	2.6	2.6	2.6	2.6
Specific gravity of coarse aggregate	ρ_G	2.6	2.51	2.51	2.6	2.6	2.6	2.6	2.6	2.6
Volume ratio of paste per unit volume (m^3/m^3)	Pvol	0.26	0.16	0.36	0.27	0.23	0.26	0.23	0.30	0.20
Weight per unit volume of paste (kg/m^3)	Wp	1744	1660	1659	1787	1744	1744	1744	1951	1518
Measured CaO by EDX (wt%)	Rca	36.3	57.3	31.9	28.9	49.8	55.7	52.9	50.2	55.3
Total Ca concentration calculated from EDX (mol/L)	C_{P0}	11.3	17.0	9.4	9.2	15.5	17.3	16.5	17.5	15.0
Weight of cement in 1m^3 of paste (kg/m^3)	Cpaste	1090	967	965	1153	1090	1090	1090	1394	759
Weight of CaO in cement (wt%)	CaO	65	61	61	63	63	65	63	65	63
Total Ca concentration estimated from cement volume (mol/L)	C_{P0}	12.7	10.5	10.5	13.0	12.3	12.7	12.3	16.2	8.5

hydrates, the Ca^{2+} migration model, and a model for evaluating changes in physical properties.

The proposed model is then verified using the results of the studies on actual structures. This enables the degradation mechanisms and input values assumed in the model to be validated.

Finally, the effects on degradation of various fluctuations assumed to have acted on the actual structures, such as material conditions and environmental conditions, are evaluated using the verified analytical model.

3. Studies of actual structures

3.1 Overview of the structures

Table 1 shows the mix proportions and environmental conditions of the structures studied. The water acting on all the structures was considered to be sluggish; that is, it was assumed that no chemical degradation due to acids occurred. Structures aged between 34 and 104 years were selected.

Samples A, B, and C were taken from various structural components of a water supply facility located 7 m below ground in Tokyo. Sample A is from the concrete slab of a waterway repaired 34 years ago. Sample B is from a concrete slab located on the exterior of a 104-year-old structure. Sample C is brick mortar from a bypass wall in the same waterway as B, and subject to the action of tap water for 104 years [5].

Sample D is from a reinforced concrete building with four stories above ground and one story below ground constructed 70 years ago at a location about 100 m from the coast in Yokohama. Concrete was taken about 70 cm below the ground water level and also from 4 m below this structure. The results of ground water analysis indicate that chloride ions account for only 1/200 to 1/400 of the water, so the effect of seawater was negligible.

Samples E, F, and G are concrete from the river weir in Niigata. Sample E is from a 76-year-old wall, F is from a 41-year-old abutment, and G is from a 68-year-old abutment under continuous action by flowing water [6].

Sample H was taken from the slab of a waterworks facility 50 to 60 m under the ground on the coast at Atami, and is about 35 years old. An analysis of the ground water acting on H showed that various ions equivalent to 70% of the concentration of seawater were present in the ground water.

Sample I is from the body of a gravity dam in Hiroshima, taken from the upstream side of the dam. River water had acted on this concrete for about 60 years.

Table 2 Method of studying actual structures

Category	Items studied	Test method
Materials and mix proportions	Mix proportion analysis	Cement Association of Japan F-18
	Existing data	—
Physical properties	Compressive strength	JIS A1108
	Vickers hardness	JIS Z2244
	Porosity	Mercury porosimetry
Chemical properties	Elemental analysis	EDX
Environmental conditions	Ion concentration of water	Ion chromatography

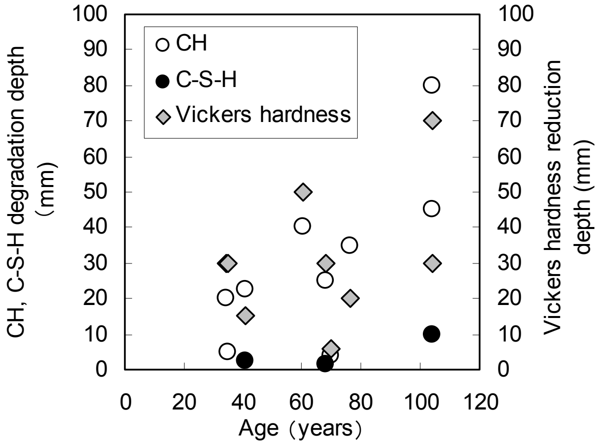

Fig. 1 Results of studies on degradation depth of actual structures

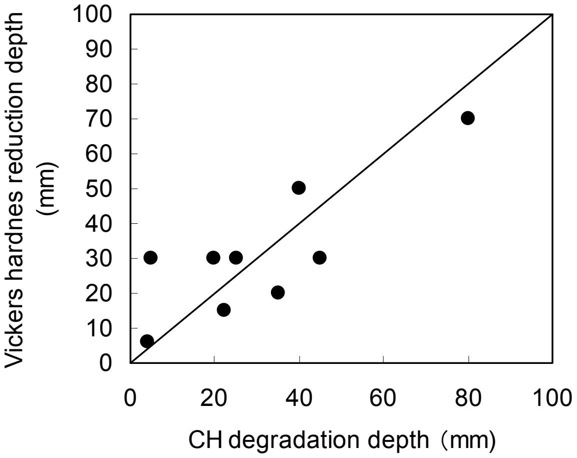

Fig. 2 CH degradation depth and Vickers hardness reduction depth

3.2 Study method

From each of the structures mentioned above, core samples of diameter 50 to 150 mm and of depth 100 to 400 mm were taken perpendicular to the surface on which water had been acting. The studies listed in **Table 2** were carried out.

The mix proportion of the samples B, C, and I were determined as specified by the Cement Association of Japan. In other cases, estimates were made by reference to the compressive strength and past data.

The compressive strength (at 1 to 3 points) was measured at sound points on the structure at a depth of a few hundred millimeters from the surface. The samples near the surface were cut in the vertical direction, the cut face was ground and polished, and Vickers hardness (square-shaped diamond weight used as indenter; load 15 to 30 gf; loading rate 10 seconds) was measured at 10 to 30 points at random on the paste part (avoiding the aggregate) at a constant depth from the surface. The sound part of the sample, which was in the deepest position from the surface, was crushed into small 5-mm squares and the porosity (average of 2 to 4 mortar pieces after removing the coarse aggregate) was measured using a mercury porosimeter.

To determine chemical properties, atomic analysis was carried at an average of 4 points randomly chosen at a constant depth from the surface (avoiding the aggregate) using an energy dispersive X-ray spectrometer (EDX).

Analysis of the ion concentration in the water acting on each sample was performed using an ion chromatography.

3.3 Results of studies of actual structures

Figure 1 shows the degradation depth of cement material on which water had been acting for a period of 34 to 104 years (as indicated in **Table 1**). Although the data in the figure shows large variation, $Ca(OH)_2$ ("CH"), degradation depth (depth at which the solid-phase Ca concentration begins to fall), C-S-H degradation depth (depth at which the solid-phase Ca concentration drops steeply to nearly zero; that is, the depth at which C-S-H disappears), and Vickers hardness reduction depth (maximum depth at which the Vickers hardness distribution begins to drop off) all tend to increase with age. The leaching of C-S-H in all structures of age 34 years to 104 years was less than 10 mm, and there were many cases where no C-S-H had been lost. The CH degradation depth was in the range 10-100 mm, and it increased considerably with age. The Vickers hardness began to drop off at the same depth as the CH degradation depth. The degradation depth increased with age.

Figure 2 shows the relationship between CH degradation depth and Vickers hardness reduction depth. Although the variation is rather large, it can be deduced that the Vickers hardness tends to fall at almost the same depth as the CH leaching limit. Surface parts in contact with water had visibly reduced hardness due to CH leaching, with the coarse aggregate becoming exposed in locations subject to rapid flow conditions and mortar becoming so fragile that it could be scraped out with a finger even under still-water conditions.

4. Modeling the dissolution of cement hydrates

4.1 Identification of properties of cement composites

The objective of this research is to estimate changes in the amount of hydrate compounds as cement hydrates dissolve, and to determine the ensuing changes in chemical and physical properties of cementitious materials. Accordingly, it is very important to accurately identify the initial conditions of cement hydrates so that their status after degradation can be accurately predicted, particularly because the dissolution reaction mode has to be determined and the amount of Ca initially in the hydration products has to be quantitatively determined.

Generally, the primary hydration products of ordinary Portland cement include CH (about 25%) and C-S-H (about 60%). In addition, small quantities of monosulfate hydrate ("AFm") and ettringite ("AFt") are also assumed to be generated [7].

If the mix proportion is known or can be estimated by analysis or by other means, the amount of Ca in the cement of the paste only, excluding the aggregate, can be calculated from equation (1), and assuming from equations (2) and (3) that 25% of the total Ca quantity in the cement hydrate is CH and 75% is C-S-H, the form ratio of Ca in the hydrate can be broadly identified. In practice, AFm and AFt are present, but the quantities of these hydrates are very small compared to CH and C-S-H. Furthermore, comparison of the bonding strength of insoluble salts, or the solubility product Ksp that expresses ease of dissolution, shows that AFm is log Ksp = -29 [8], [9] and AFt is log Ksp = -44 [8], [9]. These are extremely low values compared to the CH value of log Ksp = -5.05 to -5.25 [2], [8], [9], [10]. They are also very low compared to the C-S-H value of log Ksp = -7 to -26 [2], [9], [11], [12], which is taken to be insoluble (but varies widely depending on the Ca/Si ratio). Therefore, the Ca present in AFm and AFt was considered to be nominally part of the C-S-H. Based on this assumption, these small quantities of hydrates, which are actually insoluble, are taken as being more soluble in the model than in the real world. As mentioned later, this will tend to increase the degradation rate in the analysis, thereby giving results on the safe side.

$$C_{paste}\cdot CaO/100/56 = C_{P0} \qquad (1)$$

$$C_{P0}\cdot 0.25 = C_{CH} \qquad (2)$$

$$C_{P0}\cdot 0.75 = C_{CSH} \qquad (3)$$

Here, C_{paste}: Weight of cement per m^3 of paste in concrete (kg/m^3); *CaO*: Percentage of CaO in cement by weight (wt%); C_{P0}: Concentration of all Ca included in 1 liter of paste (mol/l); C_{CH}: Concentration of Ca in CH in 1 liter of paste (mol/l); and $C_{C\text{-}S\text{-}H}$: Concentration of Ca in C-S-H in 1 liter of paste (mol/l).

On the other hand, since the mix proportion is generally unknown when evaluating old structures, it was decided to identify the components in the hydration products by the procedure given below.
(1) Take perpendicular core samples from the surface
(2) Measure the elemental distribution of the paste by EDX
(3) Assume that the part within the core in which the Ca distribution is constant has not suffered degradation. Take the weight ratio of CaO here as R_{Ca}, the weight ratio of all the CaO in the paste initially.
(4) Calculate the aggregate quantity from area measurements at the core ends and estimate the mass per unit volume of paste W_p (kg/m^3)
(5) Calculate $C_{PO} = W_P \cdot R_{Ca}/56$ where 56 = molecular weight of CaO (g/mol)
(6) Calculate C_{CH} and $C_{C\text{-}S\text{-}H}$ from equations (2) and (3)

Table 1 shows the results of calculating the total Ca quantity initially in the paste in the 34 to 104-year-old structures by the two different methods together with the estimated mix proportions. The CaO quantity included in the cement was decided after referring to past literature and data [5], [13], [14].

Although a discrepancy of about ±30% is seen between the proportions estimated using actually measured values (by EDX) and the values obtained from the amount of cement, the results can be said to be approximately the same. Since the air content is ignored when estimating the mix proportion, an error of 10% can anyway be expected between the two sets of values. Furthermore, the effects of Ca in the aggregate or the effects of moisture

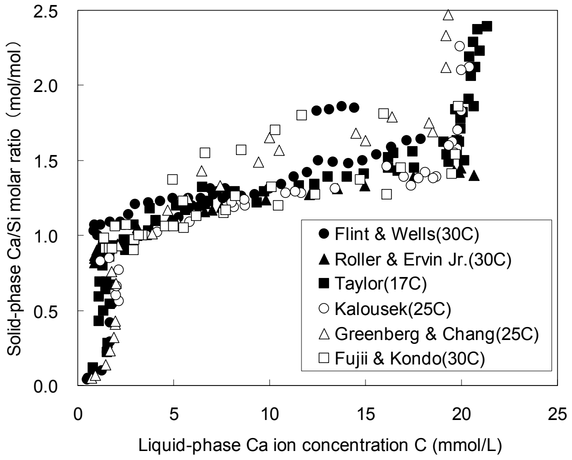

Fig. 3 Relationship between solid-phase calcium-silica ratio C/S and liquid-phase calcium ion concentration [3]

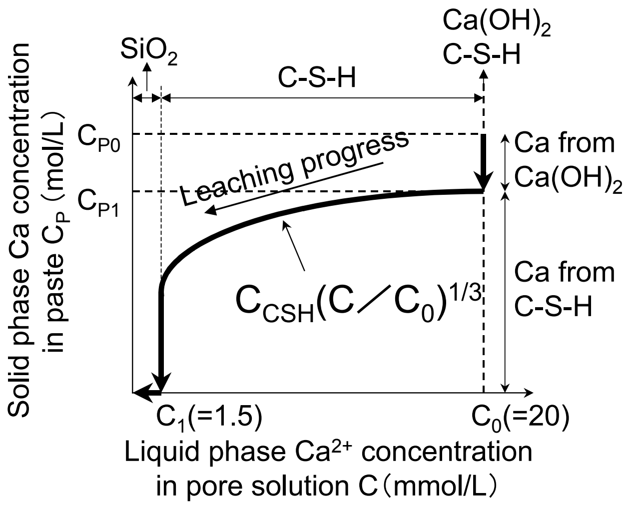

Fig. 4 Equilibrium model of solid-phase calcium concentration and liquid-phase calcium ion concentration [16]

and paste non-uniformity may also contribute to the error in the EDX method. Regarding the non-uniformity of the material, however, since the error is reduced in the EDX method by performing measurements at a large number of points, the effect of the aggregate or moisture is anticipated to be large. On the other hand, in making estimates from cement quantity, the amount of cement and the quantity of CaO in the cement are the only variables. Although the CaO content of cement has varied slightly over time according to the year of manufacture, it is generally about 60% to 65% [13], [14]. If this value is assumed not to vary significantly, then the estimation accuracy may be considered dependent on the cement quantity.

In any case, since the difference in estimated Ca by the two methods is relatively small, it was decided to adopt the total Ca concentration estimated from the results of measurement by EDX in this research.

Strictly speaking, the type of cement used influences the conditions for determining cement hydrates composition. Even for the same ordinary Portland cement, the percentages of the main components, namely C_3S and C_2S, vary with year of manufacture. It is also likely that the component percentages of the hydration products, CH and C-S-H, would vary [13]. However, it is difficult to identify the percentages of these components, either by estimation or analysis, at the present stage. Accordingly, it was decided to apply the conditions (equation (2), (3)) for determining the composition to represent the present-day ordinary Portland cement.

4.2 Dissolution reaction of cement hydrates

The solubility equilibrium relationship for CH and C-S-H, the main hydration products, is considered to be as given by equation (4) [3], [4]. As degradation progresses, Ca^{2+} and hydroxyl ions (OH^-) dissolve from the solid phase CH and C-S-H. With further progress of dissolution, the silica gel decomposes.

The reactions basically proceed from left to right under conditions suitable for degradation to take place; that is, the reaction moves from the solid phase to the liquid phase. However, due to the effects of boundary conditions and the time-dependent ion distribution, the reaction moves from right to left, with Ca^{2+} in the liquid phase solidifying and being deposited on the micropore wall. Accordingly, from mass transfer considerations, when the concentration of Ca^{2+} in the liquid phase is judged to be supersaturated according to solid-phase equilibrium-related models, a reversible reaction is employed in which CH is deposited and the solid-phase Ca concentration, *Cp,* increases.

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^-$$
$$\text{C-S-H} \Leftrightarrow Ca(OH)_2 + H_4SiO_4 \Leftrightarrow Ca^{2+} + 2OH^- + H_4SiO_4 \qquad (4)$$

4.3 Solubility equilibrium related to calcium ions

The primary solubility equilibrium relationship of liquid phase Ca^{2+} in the pore solution and the solid phase Ca in

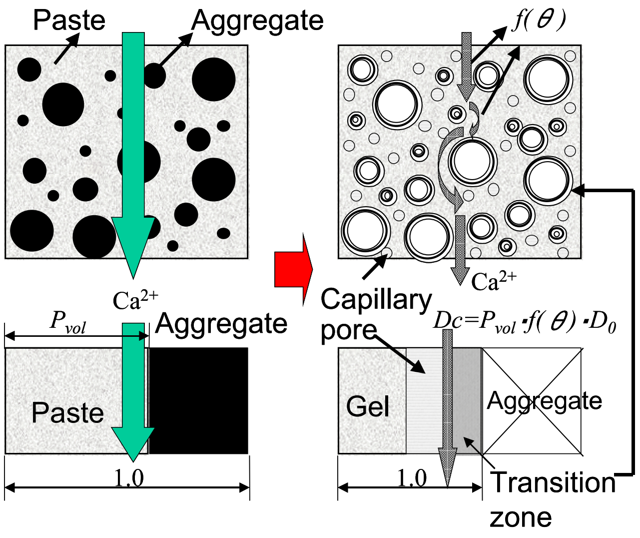

Fig. 5 Pore and micropore torsion modeling

the hydrate has been verified to hold good through a large number of experiments (involving testing the contact between solutions simulating the pore solution and cementitious materials) [3] as shown in **Fig. 3**. The time taken for a new solubility equilibrium to be reached after a change in solid-liquid contact ratio or replacement of the solution, that is the solubility time, has been measured in such tests and found to be comparatively short (several days to a few months) [15]. In the analysis carried out here, degradation is expressed using a combination of the dissolution phenomenon and the phenomenon of migration of dissolved components within the material. Under the conditions assumed for actual structures, the solubility rate governing the dissolution phenomenon will be very large compared to the rate of transfer (migration). Consequently, the overall degradation rate is governed by the rate of migration of each component (diffusion control). In view of this, the effect of Ca dissolution rate is not considered, and it is assumed that solubility equilibrium is reached instantaneously. In this analytical model, it was decided to adopt the equilibrium relationship between the solid phase Ca concentration and the liquid phase Ca^{2+} concentration shown simplified in **Fig. 4**. On the basis of the experiments shown in **Fig. 3**, it was assumed that the solid-phase silica concentration does not change. In other words, it was assumed that CH dissolves during the initial stage of dissolution and that the Ca^{2+} concentration of the pore solution remains at the saturated level (C_0=20 mmol/l). Next, once the CH has been depleted, the dissolution of C-S-H starts, and the concentration of the pore solution falls. As dissolution progresses further, and when the Ca concentration of the solid phase falls below a certain value, the decomposition of C-S-H begins to progress rapidly and silica gel is formed. The liquid-phase concentration maintains a constant value (C_1=1.5 mmol/l) until finally, at the stage when the solid-phase Ca concentration reaches zero, the liquid-phase concentration falls toward zero.

5. Modeling the migration of calcium ions and changes in physical properties

5.1 Law of conservation of mass relating to calcium ions

A mix of ions exists in the pore solution of cement hydrates, and equilibrium is always maintained as a result of diffusion when there is a difference in concentration inside and outside a pore. Here, methods are investigated for estimating the migration of Ca, which forms the highest proportion of cement and which has the greatest influence on the degradation that accompanies dissolution of cement hydrates. Although concrete is the actual subject of this analysis, the effects of aggregate (transfer path torsion) on the mass transfer path, as indicated in **Fig. 5**, are taken into account on the assumption that the materials do not permeate the aggregate. The concentrations are for the pore solution in the paste.

The law of conservation of mass as it applies to Ca^{2+} in the pore solution of the paste can be expressed as equation (5). Using the boundary conditions and the initial conditions given in equations (5), (6), and (7), the solid-phase Ca concentration and the liquid-phase Ca^{2+} concentration of paste in concrete is estimated by the first-order finite difference method (the Crank-Nicolson Implicit Method):

$$\frac{\partial(\theta\cdot C)}{\partial t}=\frac{\partial}{\partial x}\left(D_c\frac{\partial(\theta\cdot C)}{\partial x}\right)-\frac{\partial(v_d C)}{\partial x}+\frac{\partial C_p}{\partial t} \qquad (5)$$

$$C(t,\,0)=Cout(t) \qquad (6)$$

$$C(0,x)=C_0 \qquad (7)$$

Here, C: Ca^{2+} concentration of the pore solution in the paste (mmol/l); t: time elapsed since leaching began (s); D_C: apparent diffusion coefficient of Ca^{2+} in pore solution of the paste, considering the torsion of micropores, etc. (m^2/s); x: depth from the water boundary (mm); θ: porosity (m^3/m^3), C_p: solid-phase Ca concentration in the paste (mol/l), C_{PO}: initial solid-phase concentration of Ca in the paste (mol/l); and v_d: Darcy velocity due to hydraulic gradient. Also, *Cout(t)* indicates the boundary concentration (mol/l), for which changes with time might be taken into account. However, for calculations under given conditions where the boundary conditions vary with time according to specific functions and converge to fixed values, the degradation rate is governed by the converged value regardless of the form of the function [17]. In view of this, the boundary condition was taken as a fixed value that does not vary with time in this study.

Table 3 Coefficients k_n [20] related to degree of hydration of each mineral

Mineral	k_1	k_2	k_3
Alite C_3S	0.25	0.70	0.90
Belite C_2S	0.46	0.12	0.00
Aluminate phase C_3A	0.28	0.77	0.90
Ferrite phase C_4AF	0.26	0.55	0.90

5.2 Change in porosity with calcium leaching

The pores (in practice, these are voids among water, since saturated conditions are applicable, but "pores" is used in the general sense here) in hydrates can be broadly classified as entrapped air, entrained air, capillary pores, and gel pores. Only the capillary pores, which account for the largest percentage in ordinary materials and with normal mix proportions, were assumed to become migration paths for Ca^{2+} in this study. The migration rate of small-diameter gel pores that exist between layers of crystalline hydrates is extremely small, at about 1/100 to 1/1000 the rate of capillary pores, according to past literature [4]; therefore, it was considered negligible in the analysis. The capillary pore count is assumed to increase as the leaching of hydrates progresses. The change in porosity indicated in equation (8) is used to correct the concentration shown in equation (5) and the diffusion coefficient shown in equation (11). The first term on the right-hand side of equation (8), θ_0, is the initial porosity at the start of leaching. The second term indicates the increase in porosity as Ca is leached. The third term indicates the increase in porosity with leaching of elements other than Ca, such as Na, K, and Si [18]. This equation is an experimental one obtained from the results of laboratory experiments and tests on actual structures. Soluble components such as NaOH or KOH leach out of the pore solution in the initial stage of hydration, but the porosity is considered to increase when alkali or silica components present in insoluble hydrates leach out with degradation of the hydrates.

$$\theta = \theta_0 + \frac{M_{CH}}{d_{CH}}(1-V_c)(C_{P0}-C_P) + \alpha(1-V_c)(C_{P0}-C_P) \qquad (8)$$

Here, θ_0: initial porosity of paste (m^3/m^3); M_{CH}: molecular weight of CH (74 g/mol); d_{CH}: density of CH (2,230 g/l); V_c: volumetric ratio of cement in paste (m^3/m^3, $= 1/(d_c \cdot W/C+1)$; d_c: specific gravity of cement; W/C: water-cement ratio); α: Correction factor for porosity due to leaching of components other than Ca (taken as 0.003 here from the results of past experiments [18]).

If there are no measured values, and if paste that does not include aggregate is being analyzed, then the initial porosity θ_0, is taken as the theoretical capillary porosity as proposed by Powers [19] and indicated by equation (9).

$$\theta_0 = \frac{W/C - 0.36 \times \bar{F}}{W/C + 0.32} \qquad (9)$$

Here, W/C: water-cement ratio and $\bar{F}$ mean degree of hydration. $\bar{F}$ is 1.0 for hydrates after a long period, but it was decided to determine the degree of hydration of hydrates during the hydration stage by referring to equation (10) as proposed by Dalziel and Gutteridge [20].

$$F = 1 - \exp\left[-k_2(t-k_3)^{k_1}\right] \qquad (10)$$

Here, F: degree of hydration, t: age of material (days), and k_n: coefficient given in **Table 3**. The degree of hydration is determined for each mineral in **Table 3**. Therefore, the percentage of each mineral in the cement used is estimated, the degree of hydration of each is calculated, and then the mean degree of hydration of the cement as a whole is calculated according to the effective percentage of each of the minerals. This is then input in equation (11). The composition of cement compounds in present-day ordinary Portland cement is C_3S - 50%, C_2S - 9%, C_4AF - 9%. If the percentage compositions are not known, the above-mentioned values are used.

On the other hand, in the transition zone at the interface of paste and aggregate, there are a large number of pores. Accordingly, in analyzing cases such as mortar or concrete where aggregate is present, the porosity of the transition zone needs to be considered in addition to the porosity indicated in equation (9).

However, no model has been presented in the literature up till now for quantitatively estimating the porosity of the transition zone. Furthermore, at ages greater than 35 years, the mean degree of hydration (determined from equation (10)) reaches 1.0, and the actual structures to be analyzed later were all 34 to 104 years old. Therefore, porosity of the samples was obtained using a mercury porosimeter, with all pores assumed to be located in the paste, and the calculated specific volume using the mix proportion estimated beforehand was used. This implies that the transition zone around the coarse aggregate is not taken into account, but the transition zone around the fine aggregate is. It was mentioned earlier that the theoretical analysis focused only on capillary pores, but pores due to small pockets of entrapped air or entrained air may also be included when using mercury porosimeter data.

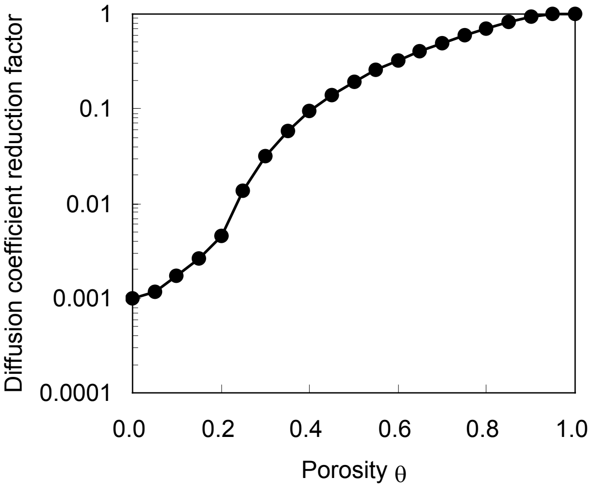

Fig. 6 Relationship between porosity and diffusion coefficient reduction factor *f(θ)*

5.3 Change in diffusion coefficient with calcium leaching

The significance of the diffusion coefficient varies widely depending on whether the pore solution only or all of the dilute solution totally unaffected by the matrix is taken to be the diffusion medium. If the micropores are considered to be groups of large, uniform capillary pores, and if the solid regions (hydrate and aggregate) are considered to have no effect at all on diffusion, then the migration distance along the actual path of the micropores is longer than the matrix length due to torsion; as a result, the apparent diffusion coefficient is lower. Also, if the quantity of pores decreases, the diffusion coefficient falls simultaneously. Considering this, and taking the diffusion coefficient D_0 in water solution as the basis, the diffusion coefficient D_c of the pore solution as the quantity of pores and the matrix torsion vary is calculated by equation (11).

$$D_c = P_{vol} \cdot f(\theta) \cdot D_0 \qquad (11)$$

Here, the coefficient P_{vol} is a correction factor related to the analysis of concrete or mortar. Since aggregate is assumed to block the migration path of ions, if the volume ratio of paste is 30%, then P_{vol} is taken to be 0.3. Also, $f(\theta)$ is a reduction factor applied to the diffusion coefficient to reflect micropore torsion, as shown in equation (12) and based on research carried out by Garboczi and Bentz [21].

Equations for variations in the diffusion coefficient due to micropore torsion and due to changes in the quantity of micropores have in the past been verified by the percolation model and through experiments. If porosity is restricted to the vicinity of 0.18, then the relationship shown in **Fig. 6** may be used.

$$f(\theta) = \left[0.001 + 0.07 \cdot \theta^2 + 1.8 \cdot (\theta - 0.18)^2 \cdot H(\theta - 0.18)\right] \qquad (12)$$

Equation (8) is used for the porosity, θ, which is a parameter. $H(x)$ denotes the Heaviside function (equal to 1.0 when x>0 and equal to 0.0 at all other times). Since $f(\theta) \leqq 1.0$, $f(\theta)$ becomes 1.0 at $\theta \geqq 0.92$, as shown in **Fig. 6**.

The diffusion coefficient D_0 in water solution can be calculated theoretically from the electrical ionic mobility using Einstein's equation. Equation (13) is the equation for calculating the theoretical diffusion coefficient in water solution.

$$D_0 = k \cdot T \cdot \frac{u}{e \cdot Z} \cdot \left(1 + \frac{\partial \ln \gamma}{\partial \ln C}\right) \qquad (13)$$

In this equation, k is the Boltzman constant (1.38 x 10^{-23} J/K), T is the absolute temperature (K), u is the ion mobility (m^2/V/s), λ is the limiting ionic equivalent conductivity in dilute solution (Ca^{2++} is 59.5 S cm^2/equiv., 25°C) divided by the value of the Faraday constant (96,485 C/mol), e is the elementary electrical charge (1.6×10^{-19}C), Z is the valence of the ion, and C is the Ca^{2+} concentration. The terms within parentheses ( ) in equation (13) are correction terms based on the Debye-Huckel theory to take into account the effect of concentration or the mutuality effect of multiple ions. The activity coefficient γ is given by equation (14).

$$\log\gamma = \frac{-A \cdot Z^2 \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} \qquad (14)$$

Here,

a: ion size parameter (cm). This is a value related to the distance between nearby ions. In this analysis, only Ca is considered. From the radius of Ca^{2+} ions, this value is taken here to be 2 x10^{-8}.

A: constant ($= 1.82 \cdot 10^6 \cdot d_0^{0.5} \cdot (\varepsilon_r \cdot T)^{-1.5} =$ 0.506 $mol^{-0.5} dm^{1.5}$ (20 ℃))

B: constant ($= 50.3 \cdot 10^8 \cdot d_0^{0.5} \cdot (\varepsilon_r \cdot T)^{-0.5} =$ 3.28*10^7 $cm^{-1} mol^{-0.5} dm^{1.5}$ (20 ℃))

d_0: density of pure solvent (taken as 1 here)

ε_r: relative dielectric constant (relative dielectric constant of water is $87.7 - 0.40 \cdot (T-273) + 9.40 \cdot 10^{-4} \cdot (T-273)^2 - 1.41 \cdot 10^{-6} \cdot (T-273)^3 = 80.1(20℃)$)

T: absolute temperature (K) *I*: ionic strength (mol/L), defined by equation (15)

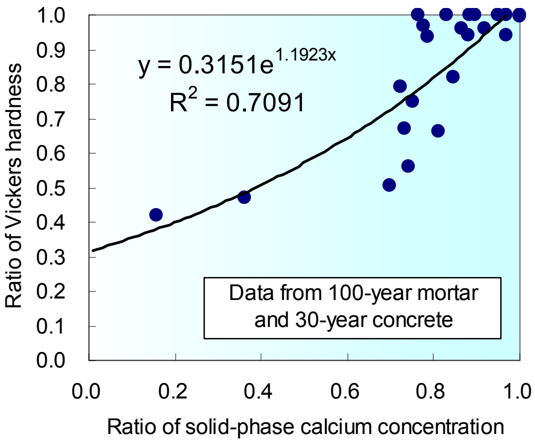

Fig. 7 Relationship between solid-phase calcium concentration ratio and Vickers hardness

$$I = \frac{1}{2}\sum_i Z_i^2 \cdot C_i \qquad (15)$$

In principle, the various ions in the pore solution should be considered in equations (13) to (15), but as long-term degradation is under consideration, the probability that Na and K will leach out first is high. The quantity of other kinds of ions is small, and their effects, even if considered in the analysis, amount to no more than 20% [25]. Accordingly, the effects of ions other than Ca are ignored here for the purpose of simplifying the analysis.

5.4 Migration of calcium ions due to advection

Mass transfer with the migration of pore solution -- that is, the advection rate -- is in principle taken to be zero in still water conditions, such as under the action of ground water. Where the environment was a waterway and where a hydraulic gradient existed, the Darcy velocity was calculated according to equation (16) and used in the analysis. However, changes in the coefficient of permeability with increasing porosity were ignored.

$$q = v_d \cdot A = k_w \cdot A \cdot \frac{h}{L} \qquad (16)$$

$$k_w = 0.126 \cdot 10^{-13} \cdot \exp(4.58 \cdot W/C) \qquad (17)$$

Here, *q*: flow rate (m^3/s); v_d: Darcy velocity (m/s); *A*: cross-sectional area of permeable medium (m^2); k_w: coefficient of permeability of medium (m/s); *h*: difference in head; *L*: length of medium (m); and *W/C*: water-cement ratio. The regression equation (17) for concrete with a maximum coarse aggregate size of 25 mm was used for the coefficient of permeability, from experimental results by Murata [26].

5.5 Changes in physical properties with calcium leaching

Physical properties such as strength and coefficient of permeability are likely to degrade as porosity increases or as chemical bonding of hydrates weakens through the leaching of hydrates. A method that might be considered for evaluating mechanical properties and estimating strength with porosity as the intermediate parameter would be to compare the porosity and strength of Ca, which is the main component of hydrates. Here, the change in physical properties is investigated by comparing the solid phase Ca concentration ratio with the Vickers hardness ratio of actual structures. **Figure 7** shows the regression data for structures A and C. The correlation between solid phase Ca concentration and Vickers hardness ratio is verified by this figure. Thus, if the Ca concentration is known, the hardness ratio can be estimated.

Furthermore, if the porosity or compressive strength can be evaluated, other physical properties such as Young's

Table 4 Relationship between analysis model and applicable structures

Category	Sub-category	Type and description of model	Applicable to
Disolution of hydrates	Composition of initial hydrates	Calculation from cement content	Mix proportion known
		By EDX	Mix proportion not known
	Solubility equilibrium chemical reaction	Reversible model considering precipitation	All
	Solid–liquid equilibrium relationship	Past results of solubility tests	All (temperature effects ignored)
Migration of ions	Boundary conditions	Constant value	All
	Initial porosity	Powers' model	Paste or test data cannot be acquired
		Results of mercury porosimeter tests	Test data can be acquired
	Change in porosity	Equations based on experimental data	All
	Degree of hydration	Dalziel and Gutteridge model	Age below 35 years
	Diffusion coefficient	Garboczi and Bentz model (volume of aggregate, tortuosity), Einstein equation, Debye-Hückel theory	All
	Advection speed	Darcy flow rate calculation model	Flow or hydraulic gradient exists
Physical properties	Micro hardness	Relationship with solid–phase calcium concentration	All
	Strength/permeability coefficient	Model estimated from porosity	All

Table 5 Input values into analytical model

Conditions of the analysis	Notation	A	B	C	D	E	F	G	H	I
Age (years)	–	34	104	104	70	76	41	68	35	60
Average annual temperature (℃)	T	15.6	15.6	15.6	15.2	13.2	13.2	13.2	16.0	16.0
Hydraulic gradient	h/L	6.7	–	5.6	–	2.2	1.3	0.7	–	0.4
Permeability coefficient (m/s)	kw	2.0E-13	–	3.4E-13	–	2.0E-13	2.0E-13	2.0E-13	–	1.2E-12
Volume of cement in paste (m^3/m^3)	Vc	0.35	0.31	0.31	0.37	0.35	0.35	0.35	0.44	0.24
Measured porosity in motar (m^3/m^3)	–	0.18	0.26	0.25	0.17	0.16	0.23	0.15	0.20	0.30
Converted initial porosity of paste (m^3/m^3)	θ_0	0.41	0.71	0.69	0.36	0.33	0.51	0.31	0.38	0.67
Basic diffiusion coefficient of Ca ion (m^2/s)	D_0	4.69E-10	4.69E-10	4.69E-10	4.65E-10	4.43E-10	4.43E-10	4.43E-10	4.74E-10	4.74E-10
Initial diffusion coefficient of Ca (m^2/s)	D_c	1.61E-11	5.95E-11	1.24E-10	1.07E-11	5.59E-12	3.31E-11	4.03E-12	1.51E-11	6.41E-11
Darcy velocity (m/s)	v	1.3E-12	–	1.9E-12	–	4.3E-13	2.7E-13	1.3E-13	–	4.6E-13
Initial Ca concentration in solid phase (mol/L)	C_{P0}	11.3	17.0	9.4	9.2	15.5	17.3	16.5	17.5	15.0
Ca concentration after leaching of $Ca(OH)_2$ in solid phase (mol/L)	C_{P1}	8.5	12.7	7.1	6.9	11.6	13.0	12.3	13.1	11.2
Boundary Ca^{2+} concentration (mmol/L)	C_{out}	0.22	1.0	0.22	1.3	0.26	0.26	0.26	7.0	0.58

modulus and Poisson's ratio can be estimated, although these quantities are not investigated here. Note also that the coefficient of permeability can be evaluated using equations (8), (9), and (17). The coefficient of permeability is an important factor when evaluating the performance of concrete with respect to leakage prevention and as an engineered barrier (for the sorption of nuclides, for instance [1]), but instances in which changes to the coefficient of permeability are evaluated with leaching of Ca are rare. The correlation between Ca leaching on one hand and porosity and the coefficient of permeability on the other is likely to become an important topic of study henceforth.

6. Verification of analytical model and evaluation of effects on degradation rate

The analytical model described in sections 4 and 5 consist of equations describing changes in solid-liquid equilibrium, Ca^{2+} migration, and quantity of pores within the material. However, equations and coefficients suitable for the environment of each sample being analyzed should be chosen in each case (so, for instance, advection need not be considered under still water conditions) and the models of the diffusion medium. **Table 4** shows the relationship between instances of the analytical model and the type of structures to which each is applicable. This section describes analysis carried out on the basis of this table; that is, after adjusting the equations in the model according to the conditions experienced by the structures sampled in **Table 1**.

When the various structures are investigated taking only age in years as a parameter, the results exhibit very large variations. This can be attributed to the considerable influence of individual environmental conditions and material properties. Accordingly, the analytical model of sections 4 and 5 is verified in this section, the individual differences in the results of studies of the actual structures are verified in the analytical model, and the effects of individual factors on the degradation rate are evaluated.

6.1 Values input into the analytical model from actual studies

Table 5 shows the values input into the analytical model. As described above, mix proportion was estimated by referring to strength, aggregate area ratio, and past data. Measurements of mortar porosity by the mercury

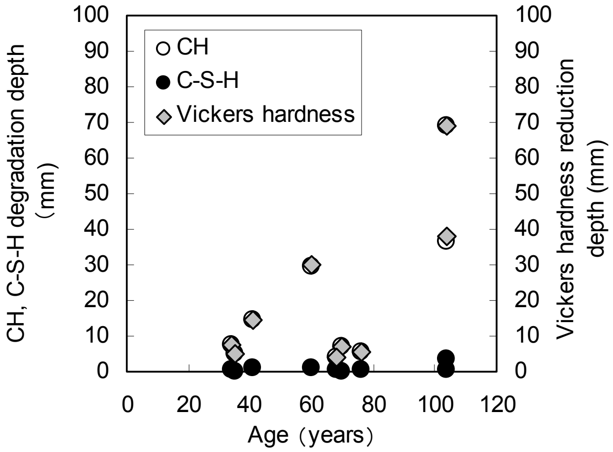

Fig. 8 Results of analysis on degradation depth of actual structures

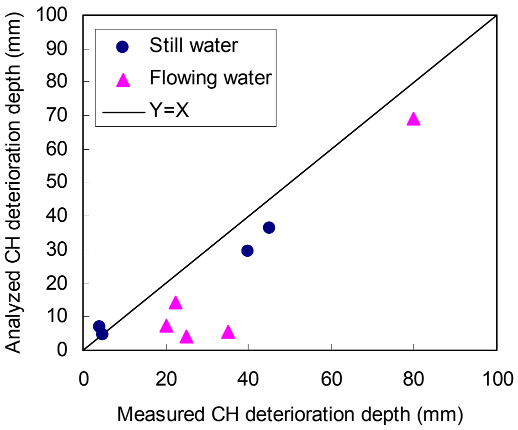

Fig. 9 Comparison of measured and analysis results of CH degradation depth

porosimeter method for each core were converted into paste porosity values and used in the analytical model. The initial solid phase Ca concentration, C_{P0}, was taken as the mean Ca concentration in the solid phase over the region of minimal internal variation, as extracted from the concentration distribution measured by EDX. The measured values of boundary Ca^{2+} concentration, C_{out}, were used for samples D, H, and I, while typical values [27] such as those of river water were used for other samples. The mean annual temperature was the average value over the past 10 years in the nearest city.

6.2 Comparison of actual studies and analysis

The results of analysis for various degradation depths corresponding to age at the time of the actual studies are summarized in **Fig. 8**. A comparison of **Fig. 1** and **Fig. 8** shows that both CH and C-S-H degradation depths and Vickers hardness reduction depth tend to increase with the passage of time. Numerically, also, the results of the analysis closely match the actually measured values.

On the other hand, **Fig. 9** compares the measured values and results of analysis of CH degradation, taking the condition of the reaction water as the parameter. Under some conditions, the calculated values of degradation depth are smaller than the measured values for samples A, C, E, F, and G, which were subject to the effects of flowing water at the boundary or the effects of a hydraulic gradient. However, the measured and analytical values were practically the same for B, D, H, and I, which were samples subject to static water conditions, indicating that the predicted results are generally good in this situation.

Figure 10 compares the solid-phase Ca concentration distribution and Vickers hardness distribution for still water conditions (samples B, D, H and I). **Figure 11** gives the same comparison for sample A, which is typical of the flowing water cases, and G. The accuracy of prediction in still water conditions for both distributions is satisfactory, although there are some appreciable differences in the measured and analytical values under flowing water conditions.

The CH and C-S-H leaching areas are quite distinct as a result of the dissolution equilibrium model used in this analysis. While the predicted solid-phase concentration in the CH leaching area rises almost vertically, the distribution of measured concentration tends to be gently sloping.

Although this may attributed simply to variance in the measurements, the possibility that CH is converted to some other component with time over the long term should also be considered, since the dissolution equilibrium model is based on hydrate dissolution test results in a large quantity of water. A review of the long-term laboratory tests and dissolution test methods, and evaluation through comprehensive chemical analysis of actual structures, are considered necessary future steps.

6.3 Evaluation of basic model in still water conditions

The samples exposed to still water conditions are B, D, H, and I. The mix proportions and environmental conditions vary from sample to sample. Extremely good correlation is obtained between measured and analytical

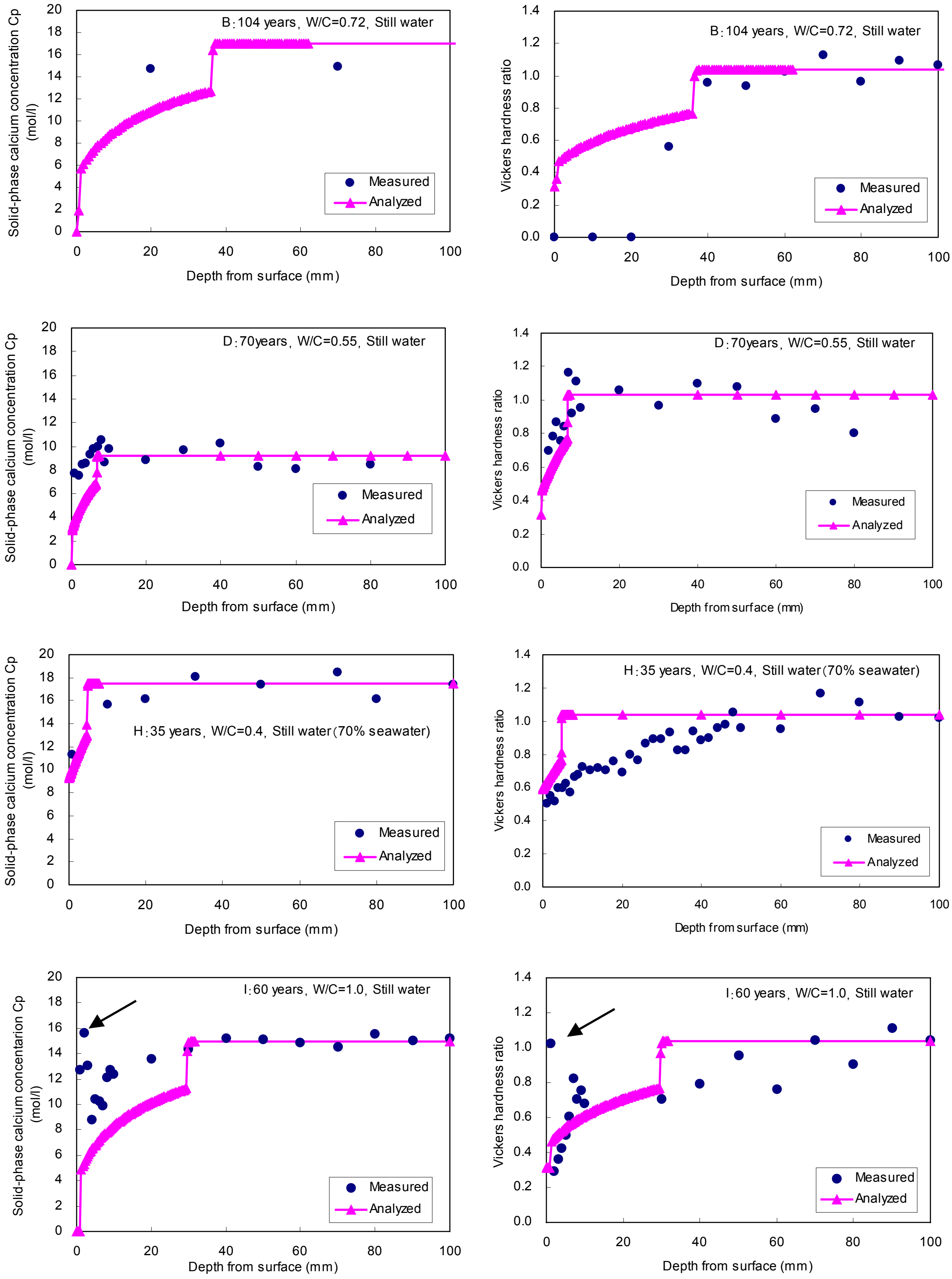

Fig. 10 Comparison of measured and analysis results of solid-phase calcium concentration distribution and Vickers hardness ratio distribution (still water conditions)

values of CH degradation depth, C-S-H degradation depth, Vickers hardness reduction depth, Ca concentration distribution, and Vickers hardness distribution for all cases. The conditions to which the studied samples were exposed were typical of underground structures and radioactive waste facilities. The CH leaching range for 34 to 104-year-old actual structures was roughly 10 to 100 mm, and almost identical values were predicted by the analysis. On the other hand, the C-S-H degradation range could not be verified because the minimum measurable unit in the analysis of actual structures was 1 mm.

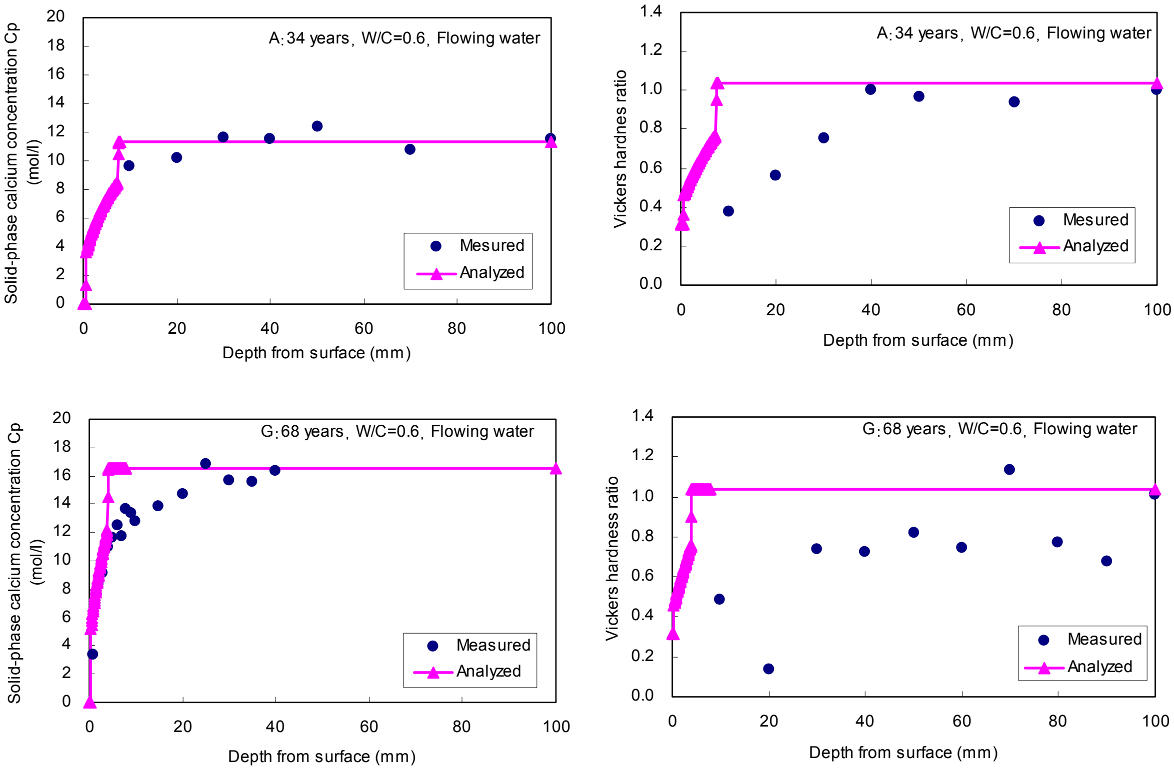

Fig. 11 Comparison of measured and analysis results of solid-phase calcium concentration distribution and Vickers hardness ratio distribution (flowing water conditions)

Although this analysis successfully evaluates the degradation rate at the macroscopic level, the question of how to incorporate variations in leaching rate due to micro cracks and material non-uniformity, which to some degree is apparent in the measured values, is likely to become a topic of further investigation henceforth.

The solid-phase Ca concentration at the surface in sample I is high, and similarly the Vickers hardness ratio is high. This is probably because of the effect of calcium carbonate precipitated on the surface or perhaps the precipitation of hydration products that then reacted with the water. These reactions are not considered in the present model.

For long-term analysis, it is necessary to take into account the effects of reactions involving carbonate ions in the ground water and the effects of other ions.

6.4 Effects of flowing water conditions

Samples A, C, E, F, and G are from structures considered to have been significantly affected by hydrates leaching under the influence of flowing river water or tap water. In these cases, the probability of the analysis underestimating degradation depth is high, as mentioned above.

There is some hydraulic gradient in all these cases, but it is too small and results in a very small value of Darcy velocity. Accordingly, the predicted degradation rate is slower than that actually measured when only diffusion and advection are considered. The error can be attributed to differences in pore diameter, which governs mass transfer due to advection as well as migration due to diffusion, and to the solubility equilibrium relationships in the case of advection. Consequently, for a future more detailed analysis, a model should be developed that considers the effects of pore diameter distribution and physical damage due to flowing water (surface dissolution)[28].

6.5 Effects of material conditions

Figure 12 shows predictions of degradation depth of CH and C-S-H after a lapse of 100 years, taking the water-cement ratio W/C in the four still-water cases investigated as the parameter so as to maintain consistency of conditions. It can be observed that the degradation depth increases in almost direct proportion to W/C. Although

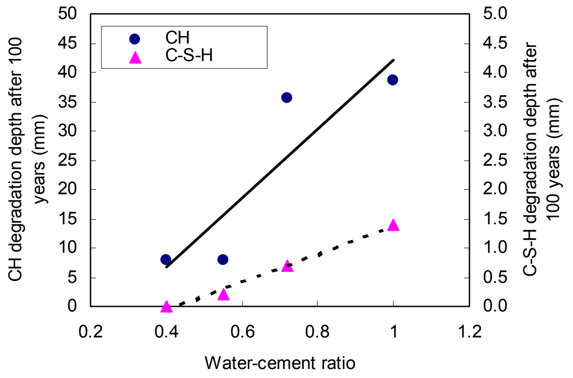

Fig. 12 Relationship between water-cement ratio and CH/C-S-H degradation depth

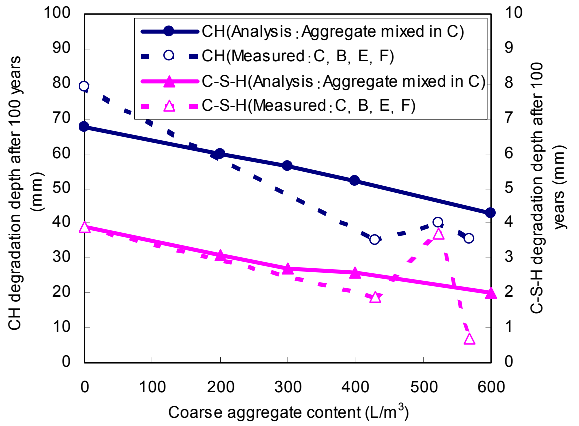

Fig. 13 Effect of quantity of coarse aggregate on degradation depth

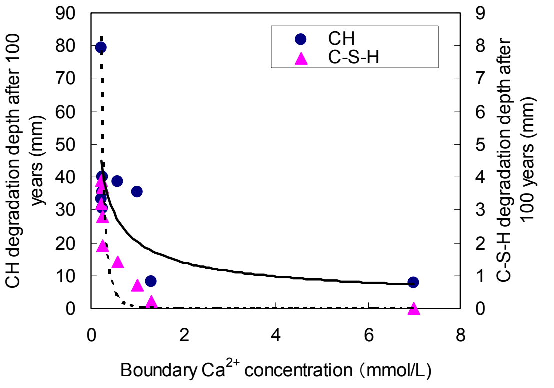

Fig. 14 Relationship between boundary calcium ion concentration and CH, C-S-H degradation depth

the CH and C-S-H degradation depths vary slightly due to the effect of boundary conditions and other differences, the C-S-H degradation depth is less than 1/30 of the CH degradation depth. The CH degradation depth for typical W/C values of about 0.3 to 0.7 is in the range 5 to 40 mm. Variations in W/C bring about a change of nearly 8 times in the degradation depth.

Next, for sample structures that were less than 100 years old, sample B (aggregate volume Gvol = 569 l/m^3), sample E (Gvol = 523 l/m^3), and sample F (Gvol = 429 l/m^3), which were the closest conditions to the sample C, and 100 year-old mortar sample C, the measured effects of the aggregate were compared with extrapolated predictions up to an age of 100 years. In these cases, the year constructed, the water-cement ratio, boundary concentration, and temperature vary slightly as compared to sample C. **Figure 13** shows the results of analysis when aggregate of 200 to 600 l/m^3 was mixed with the mortar of sample C. Both measured and analytical results show a tendency for the CH and C-S-H degradation depth to be reduced directly in proportion to the quantity of coarse aggregate. It can be observed that the mass transfer inhibiting effect is more pronounced in concrete mixed with coarse aggregate than in mortar, and the degradation rate can be inhibited by Ca leaching. Furthermore, it is seen that the effect on degradation rate is less than 2 times over the whole range from coarse aggregate of 600 l/m^3 to mortar, which is a range not employed in ordinary concrete.

6.6 Effects of environmental conditions

Figure 14 shows the predicted degradation depth for the 9 samples studied this time, extrapolated to 100 years, and taking the Ca^{2+} concentration in water acting on the structure, one of the boundary conditions, as a parameter. It is found that the CH degradation depth tends to decrease exponentially with increasing boundary Ca^{2+} concentration. This tendency is similar for C-S-H, also. When the Ca^{2+} concentration at the boundary exceeds 1.5 mmol/l, CH degradation depth drops to an extremely small value and the alteration of C-S-H stops. This is probably because, in the solubility equilibrium model used here, the calcium in C-S-H is fully altered when the liquid phase Ca^{2+} concentration $C_l < 1.5$ mmol/l, and the C-S-H changes to silica gel.

The mean value of Ca^{2+} concentration in the rivers of Japan is 0.2 mmol/l. The mean Ca^{2+} concentration in ground water excluding hot springs is 2.1 mmol/l, and that of ground water considered to originate with precipitation is 0.4 mmol/l on average [25].

From the calculated results above, water with high Ca^{2+} concentration is implied, since degradation rate is inhibited. However, the degradation rate is much higher for river water and ground water considered to originate with precipitation. Moreover, the effect of Ca^{2+} concentration in such low-concentration water on degradation is large; in the Ca^{2+} concentration range 0 to 1.5 mmol/l, the difference in degradation is greater than 10 times.

On the other hand, H is part of a 35-year-old underground structure constructed near the coast, and the ground water includes seawater components such as chloride ions. As shown in **Table 1**, the Ca^{2+} concentration is high, at 7.0 mmol/l, which is about 70% of the value for seawater. As a result, the Ca^{2+} concentration within and outside the concrete was small, the degradation rate was inhibited, and degradation amounted to no more than 10 mm over a span of 35 years. However, as observed from the Vickers hardness distribution in **Figure 10**, the degradation depth actually measured is much larger than that obtained from the analysis. This is because, since Cl^- and SO_4^{2-} ions in the seawater react with the hydrate, Aft may be formed and degradation caused. Therefore, it cannot be said unconditionally that degradation accompanying Ca^{2+} leaching is small in the case that the water acting on the structure is seawater. Accordingly, the analysis needs to be supplemented with a chemical reaction model when the action of such water has to be considered. At the same time, an analytical model that considers collectively the migration of various kinds of ions is necessary.

In this model, the effect of temperature was considered only on the diffusion coefficient, but variations in the solubility equilibrium coefficient may also be anticipated as temperature rises and falls. Thus, other conditions may need to be added to the model. A discussion of such modifications will be taken up henceforth.

7. Conclusion

Changes in the physical properties of concrete accompanying leaching have almost never been predicted in past research. In this research, the state of numerous old structures was evaluated to study the degradation caused by the migration of Ca^{2+} ions in concrete. The factors influencing degradation due to leaching were then evaluated using an analytical model. A method of evaluating physical properties using the relationship between solid-phase Ca concentration and Vickers hardness ratio was proposed. Further, it was shown that various physical properties could be estimated, since porosity after leaching can be calculated using the proposed model. The results obtained of the research are presented and discussed below.

(1) From studies of nine actual structures aged between 34 years and 104 years, it was observed that degradation depth increases almost linearly with structure age. The degradation of hydrated calcium, CH, at the age of 100 years was no more than 100 mm, while that of C-S-H was no more than 10 mm. It was also demonstrated that the CH leaching depth correlates with Vickers hardness.

(2) The dissolution reaction of cement hydrates was modeled, and the solid-phase equilibrium relationships for Ca in dissolution tests carried out in the past were combined into the analytical model. For Ca^{2+} migration, which forms the backbone of the model, the law of conservation of mass was calculated by the first-order finite difference method. A theoretical estimation method taking into account changes in porosity and torsion as well as the progress of hydration was proposed for determining the diffusion coefficient, a very important parameter. While most conventional models were applicable to paste, the proposed one is a wide-ranging analytical model that takes aggregates into account.

(3) A verification of the model, carried out by comparing measurements of actual structures with numerical calculations, showed that degradation depth for different hydrates, Vickers hardness reduction depth, and their distributions could be predicted with good accuracy.

(4) The degradation depth increased almost linearly with rising water-cement ratio, increasing by a factor of about 8 times in the normal range of water-cement ratio. The quantity of coarse aggregate was inversely proportional to the degradation depth. It was observed that for coarse aggregate contents of 0 to 600 L/m^3, the effect on the degradation depth was no more than about 2 times. Regarding environmental conditions, the Ca^{2+} concentration in the water had an extremely large effect. As the Ca^{2+} concentration varied from 0 to 1.5 mmol/l, the degradation depth varied by more than 10 times.

Many models are expected to see improvement as verification of the analytical models takes place and as more data becomes available from actual structures. The improvements to be investigated henceforth are as listed below.

(1) Model that takes into account various ions
(2) Model that takes into account the effect of temperature
(3) Model that takes into account the effect of carbonation
(4) Model that takes into account the distribution of pore diameters
(5) Model incorporating surface dissolution
(6) Model incorporating physical damage
(7) Model that takes into account reactions with seawater

(8) Model that takes into account the type of cement

Some of these models have already been constructed [25], [29] and the authors hope to report on them models at the next opportunity.

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