FUNDAMENTAL STUDY ON PREDICTION OF CONCRETE DETERIORATION CAUSED BY CALCIUM LEACHING OVER 100 YEARS

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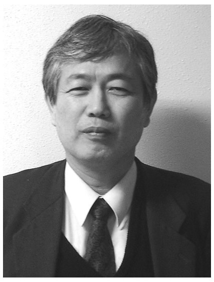
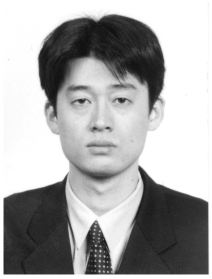

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The purpose of this study is to propose an experimental method for predicting the long-term leaching of calcium from concrete and the resultant concrete. The proposed method combines an electro chemical test and a diffusion test. The estimated number of years for which calcium leaches is obtained by a technique of combining the results from the tests. Further, the concrete deterioration caused by this leaching of calcium can be predicted by examining the specimen after leaching has halted. The validity of the method is demonstrated by comparing predicted results with an investigation of an existing structure in use for 100 years. Next, the influence of mix proportion on concrete deterioration caused by Ca leaching is investigated using the method. From the results, the Vickers hardness and Ca/Si molar ratio of the bulk at the same DCT (Diffusion Conversion Time) are high in the case of (1) high unit cement content, (2) cement containing mainly belite, and (3) low water-cement ratio.

Key Words: calcium leaching, deterioration, hundred years, experimental prediction method

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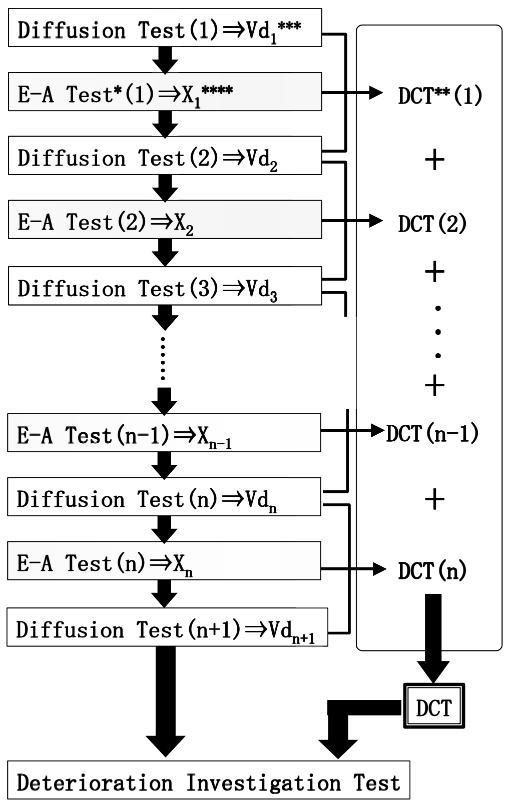
1. INTRODUCTION

As the calcium hydrate contained in concrete dissolves into water around the concrete structure, the concrete becomes porous. This type of deterioration, known as “concrete deterioration caused by calcium leaching”, progresses very slowly in comparison with other deteriorations such as the alkali-aggregate reaction or chloride attack. Consequently, it has not generally been considered when designing ordinary concrete structures. However, in the design of special concrete structures requiring service lives of several hundred years or more, this type of deterioration must be considered. For instance, in the case of a water supply facility or a dam the remains in contact with water for over 100 years, it is impossible to ignore this deterioration.[1] Also, when a cement material is used for the solidification and disposal of incinerated ash containing toxic substances, the long-term stability of the material must be estimated from the viewpoint of environmental preservation. Moreover, the half-life of the radioactive elements in high-level radioactive waste material is over 100 years, so it is necessary to guarantee a service life of disposal facilities for radioactive waste over 100 years. In order to minimize environmental effects and prevent early deterioration of the concrete by weathering or carbonation, etc, current plans call for constructing such facilities underground. If this is done, they will be in contact with groundwater and thus prone deterioration caused by calcium leaching. This means that it is necessary to estimate durability in consideration of concrete deterioration caused by calcium leaching over 100 years.

For the reasons outlined above, it is important to establish a prediction method for deterioration caused by calcium leaching and to estimate the durability of concrete over the long term. However, although research on the long-term durability of concrete under the influence of deterioration caused by calcium leaching has begun, there remain many unsolved issues. Further, most studies of this type of deterioration have been done using cement paste or mortar [2]. Therefore, it can be said that current evaluations of the long-term durability of concrete with deterioration caused by calcium leaching are inadequate.

The purposes of this study are (1) to verify the validity of an experimental prediction method for concrete deterioration caused by calcium leaching over 100 years and (2) to clarify the mix proportion with best resistance to such deterioration. Incidentally, it is assumed here that deterioration of concrete in contact with water occurs due to calcium leaching only. To achieve these aims, an already reported experimental prediction method for mortar deterioration due to calcium leaching [3] is applied, and the validity of its application to concrete is examined. Also, it should be noted that the predictions made in this study are for 100 years, while previous studies have investigated time periods of 10 years order [3]. Moreover, the influence of the mix proportion of concrete on deterioration caused by calcium leaching is evaluated using this method.



*: Electrochemical accelerated test (E-A Test)
**: Diffusion conversion time (illustrated in Figure 4)
***: Diffusion leaching rate (by measurement)
****: Amount of calcium leaching (by measurement)

Figure 1 Flowchart of experimental prediction method

2. OUTLINE OF THE PREDICTION METHOD AND FLOW OF THIS STUDY

The chosen experimental prediction method entails carrying out electrochemical accelerated test and diffusion test. A flowchart of the method is shown in **Figure 1**. A characteristic of this method is that the

Table 1 Properties of materials

Material	Classification	Details
Cement	OPC	Density:3.15g/cm^3, Blaine:3270cm^2/g, CaO:64.2%, SiO_2:21.1%, Al_2O_3:4.8%
Fine aggregate	Land sand from Obitsu	Density:2.63g/cm^3, Absorption:1.41%, F.M.2.26
Coarse aggregate	Crushed stone from Oume	Density:2.64 g/cm^3, Absorption:0.98%, F.M.6.44, Gmax=13mm

Table 2 Mix proportion and basic properties of fresh concrete

Cement	W/C	s/a	Unit content (kg/m^3)				Slump	Air	Remarks
	(%)	(%)	W	C	S	G	(cm)	(%)	
OPC	72	47	109	152	688	1427	0.2	1.0	*
OPC	55	50	175	318	942	960	2.0	2.5	**
OPC	55	50	190	345	910	928	10.0	1.8	**
OPC	55	50	225	409	839	855	20.0	0.8	**

*: same mix proportion as existing concrete member [4]
**: for evaluating the influence of unit cement content

electrochemical accelerated test for a certain period can be converted to the diffusion test period dividing the amount of calcium leached per unit area by the mean diffusion calcium leaching rates. This converted period is known as the 'Diffusion Conversion Time (DCT)'. Using this concept, it is possible to predict the concrete deterioration caused by calcium leaching over the long term.

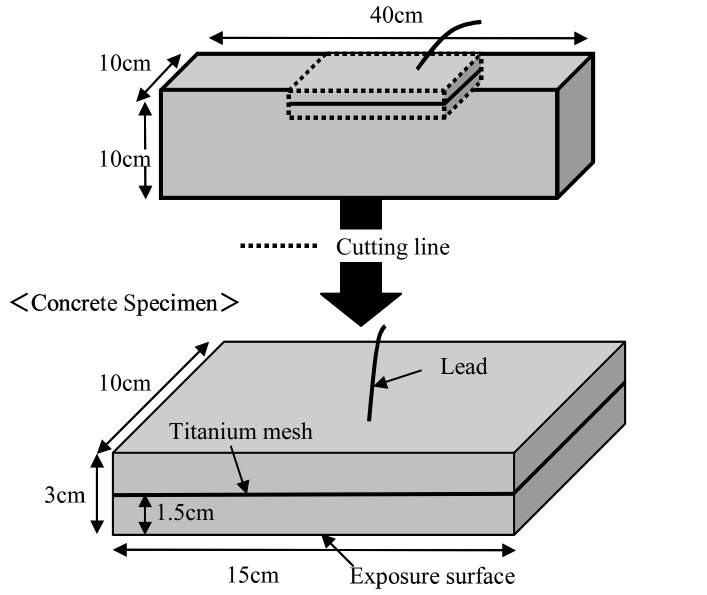
First of all, in order to confirm the validity of this method, predictions for a period of 100 years are compared with surveys of existing concrete structural members that have been in contact with water for 100 years. Here, the mix proportion of the specimen used for prediction was the same as that of the existing concrete member. Later, the long-term influence of unit cement content on concrete deterioration caused by calcium leaching is evaluated using the same method. In addition, the long-term influence of mix proportion on deterioration is summarized from the results of a previous study [3] and this study. The parameters of mix proportion observed in this study are unit cement content, type of cement, and water-cement ratio. Concrete deterioration is evaluated in terms of Vickers hardness test, needle penetration test, and measurement of Ca/Si molar ratio.

3. EXPERIMENTAL OUTLINE

During the leaching of calcium from concrete in the diffusion test and the electrochemical accelerated test, the amount of calcium was measured and the results used to predict the consequent deterioration. Also, in order to predict changes in concrete properties resulting from calcium leaching, physical deterioration and chemical deterioration were experimentally evaluated after the final diffusion test. Specimen preparation, testing methods, and evaluation of property variations are detailed below.

3.1 Fabrication of specimens

The basic properties of materials used in this study are indicated in **Table 1**. The mix proportions and basic properties of the fresh concrete are shown in **Table 2**. The mix proportion of the specimen used to confirm the validity of the prediction method was same as the original mix proportion of the old concrete member that had been in contact with water for 100 years. This mix proportion was determined by referring to previous research [4]. The mix proportions of specimens used to evaluate the influence of unit cement content were 318, 345, 409 kg/m3 as unit cement content with a 55% water-cement ratio. Steel moulds (measuring 10×10×40 cm) were used to form the specimens, as shown in **Figure 2**. A titanium mesh was located 8.5 cm above the basal plane of the mould before concrete casting. This titanium mesh was connected to an electrical lead by soldering, and the junction was covered with epoxy resin before placing it in the mould. The concrete specimens were demolded 24±2 hours after casting, and then cured in moist conditions (20±3 degrees; R. H.: over 90 %) for 28 days. After curing, a 3×10×15 cm section was cut away, as shown in **Figure 2**, using a diamond cutter. This test specimen was then sealed with epoxy resin except an one 10×15 cm surface, which was the exposure surface. This ensured that calcium dissolved from the exposure surface only.



*Specimen was sealed with epoxy resin, except on the exposure surface.

Figure 2 Outline of concrete specimen

3.2 Diffusion test

The aim of the diffusion test is to measure the diffusion calcium leaching rate. After a fixed period of electrochemical accelerated testing, the specimen was placed into deionized water, and the amount of calcium leaching into the deionized water was measured. The duration of the test was set at 7 days so as to minimize the influence of changes in environmental conditions as ions leached from the concrete into the deionized water and in consideration of the accuracy of the ion chromatograph used ion concentration measure. In order to distribute the ion concentration in the deionized water uniformly, it was stirred every 24 hours. Here, the aim of using deionized water was to avoid any influence of ion concentration on calcium leaching rate, and thus obtain basic information about calcium leaching. The leaching rate was calculated by dividing the amount of calcium ions in the deionized water by the duration of the diffusion test (7 days), as shown by Equation (1).

$$V_d = \frac{X_d}{T \cdot S} \tag{1}$$

where, V_d : calcium leaching rate per unit area (mg/h・cm^2)

X_d : amount of leached calcium during test (mg)

T : duration of test [=24×7 (hours)]

S : area of exposed surface [=10×15 (cm^2)].

3.3 Electrochemical accelerated test

The electrochemical accelerated test rapidly removes calcium from concrete into an immersion solution using electrochemical method. An outline of the electrochemical accelerated test is shown in **Figure 3**. A cathode made from titanium was placed at the bottom of a plastic container, and the specimen was suspended 1 cm above the base. The container was filled with deionzed water up to the level of the anode within the specimen. Titanium mesh was used for the electrodes because the ionization tendency of titanium is extremely low.

The immersion solution was deionized water, and this was replaced every 24 hours in order to maintain the solution in unsaturated condition and prevent crystallization of calcium ions.

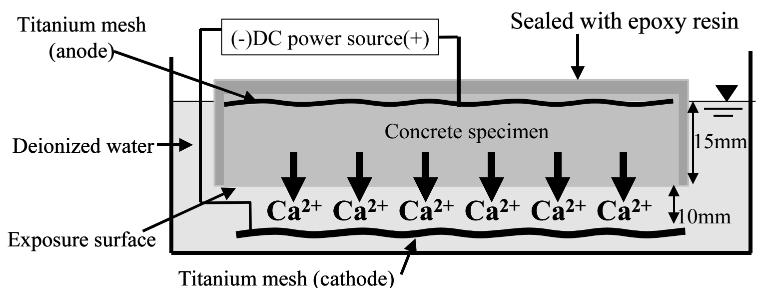


Figure 3 Outline of electrochemical accelerated test

The current density was set to 10.0(A/m2) for the surface area of the exposure surface, and test periods of 0, 120, 240, 480, 720, 1,200, and 1,500 (hours) were selected. Calcium ions must be removed at comparatively high current density because the mobility of calcium ions is low. The heat released in the specimen increases at higher voltages with a high current density, so current density was determined after running a pilot test.

The amount of calcium in the deionzed water was measured using ion chromatography.

There is a possibility of oxygen being released near the anode as a result of an anodic reaction, and this phenomenon would alter the properties of the concrete around the anode. Therefore, a region measuring 3 mm in diameter around the electrode was excluded from evaluation when looking at deterioration. However, no deterioration of the concrete around the electrode was seen in this particular study.

3.4 Methods of evaluating deterioration

The needle penetration test and the Vickers hardness test were carried out to evaluate physical deterioration. Also, the Ca/Si molar ratio was measured to evaluate chemical deterioration.

a) Needle penetration test

After the final diffusion test, the specimen was cut in a perpendicular direction trough the exposure surface using on ISOMET LOWSPEED SAW (BUEHLER Ltd.). Then, a needle penetration test was implemented according to JSCE guidelines [5] on the bulk part of the concrete on the cut face. From the results, the uniaxial compressive strength was estimated. The needle penetration load was set to a constant 10 kgf (98N), and the intrusion of the 0.56 mm diameter needle was measured.

b) Vickers hardness test

The Vickers hardness of the bulk concrete was measured using a microhardness tester (Akashi Co.). The loading duration and load were set to 10 seconds and 0.025N, respectively. Also, the measured value was taken as the average value of 20 samples.

c) Ca/Si molar ratio

In order to evaluate the elemental composition of the concrete hydrates, the Ca/Si molar ratio of the cement matrix was measured using energy-dispersible X-rays (with JSM-5310 LV by JEOL Ltd.). Also, one measured value was taken as the average value of 20 samples.

4. OUTLINE OF EXPERIMENTAL PREDICTION METHOD AND CONFIRMATION OF VALIDITY

4.1 Outline of experimental prediction method

The experimental prediction method presented by the authors in a previous study [3] was used to predict the concrete deterioration caused by calcium leaching in this study. The concept behind this method is described in this section.

The basic idea is to access the relationship between the amount of leached calcium and DCT through a combination of the electrochemical accelerated test and the diffusion test.

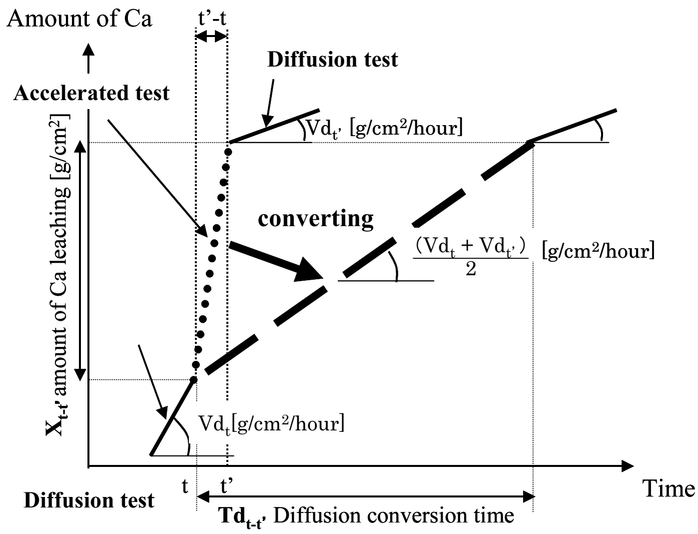


Figure 4 Method of calculating Diffusion Conversion Time (DCT)

The method of assessing DCT is shown in **Figure 4**. If the total amount of calcium leached in the electrochemical accelerated test at $T=t$ is X_t, the amount of calcium leached in the interval $t'-t$ is $X_{t'}-X_t$. If it can be assumed that the leaching rate during this interval is equal to the average of the leaching rates at t' and t ($V_{dt'}$ and V_{dt}), which can be obtained from diffusion tests before and after the electrochemical accelerated test, Equation (2) can be introduced:

$$\frac{X_{t'} - X_t}{T_{d \cdot t'-t}} = \frac{V_{d \cdot t'} + V_{d \cdot t}}{2} \quad (2)$$

Therefore, it is possible to calculate the DCT ($T_{dt-t'}$) as shown in Equation (3).

$$T_{d\cdot t'-t} = \frac{X_{t'} - X_t}{\frac{V_{d\cdot t'} + V_{d\cdot t}}{2}} \tag{3}$$

Here, the combinations of t and t' used in calculating DCT were as follows: (t, t') = (0h, 120h), (120h, 240h), (240h, 480h), (480h, 720h), (720h, 1,200h), and (1,200h, 1,500h).

Base on the above outline and assumptions, it is possible to estimate the DCT of a specimen tested in the experimental prediction method. Moreover, by carrying out physical and chemical experiments an specimen that have experienced calcium leaching, and by grasping the relationship between DCT and physical and chemical deterioration, deterioration caused by calcium leaching can be predicted.

4.2 Confirmation of validity of the method

In order to confirm the validity of this experimental prediction method, a concrete specimen was fabricated with a mix proportion matching that of an existing concrete member that had been in contact with water for 100 years [4]. The long-term calcium leaching and resulting deterioration were then predicted using this specimen. Finally, the predicted results for this specimen were compared with the results of an actual survey of the existing concrete member. The existing concrete member was part of the floor system at a waterworks in Shiba, Tokyo. An outline of this structure is shown in **Figure 5**. The predicted results yielded a DCT value that enabled 101 years of leaching to be simulated in 1,500 hours of current flow. Thus, the acceleration was about 600 times.

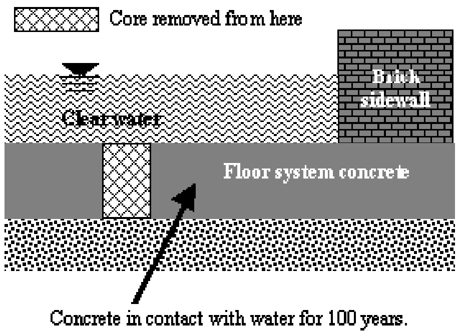


Figure 5 Outline of existing concrete member

The deterioration index used to compare the concrete specimen and the existing concrete member were (1) the relationship between the uniaxial compressive strength obtained from needle penetration test and distance from the exposure surface and (2) the relationship between Ca/Si molar ratio of the bulk and the distance from the exposure surface. Incidentally, the calcium hydrate in the specimen and in the existing concrete member was identified using powder X-ray diffraction equipment. This confirmed that $Ca(OH)_2$ did not exist in the range 0-15 mm from the exposure surface.

The relationship between DCT and the amount of calcium leaching per unit surface area is shown in **Figure 6**. This demonstrated that the amount of calcium leaching increased with increasing DCT almost linearly. The rate of calcium leaching was expected to decrease exponentially, because calcium leaching appears to follow the diffusion rule. However, **Figure 6** shows clearly that the calcium leaching rate measured in this study changed little with increasing DCT. This resulted from the increase in diffusion coefficient due to the concrete becoming more porous as calcium leaching proceeded.

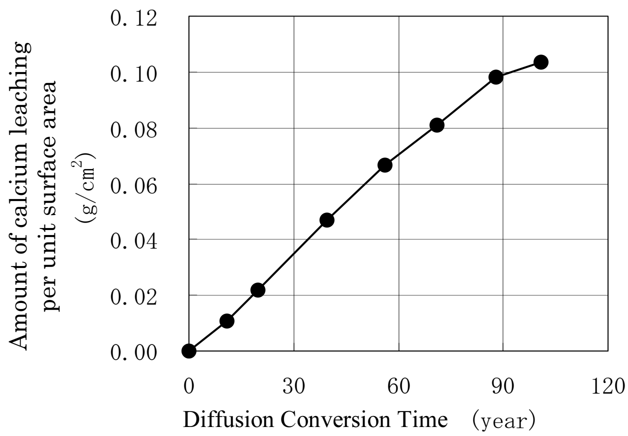


Figure 6 Relationship between DCT and amount of calcium leaching per unit surface area

The relationship between uniaxial compressive strength, for both of the concrete specimen and the existing concrete member, and distance from the exposure surface is shown in **Figure 7**. The region of the concrete specimen surveyed was up to 12.5 mm from the exposure surface. On the other hand, the existing concrete member was surveyed up to 20 mm from the exposure surface. The figure shows that the predictions for the concrete specimen correspond well with the survey of the existing concrete member. **Figure 7** also shows that the uniaxial compressive strength falls as the measurement point closes on the exposure surface.

The relationship between Ca/Si molar ratio, for both the concrete specimen and the existing concrete member, and distance from the exposure surface is shown in **Figure 8**. Again, the region surveyed in the concrete specimen was up to 12.5 mm from the exposure surface, while the existing concrete member was surveyed in the range 10-30 mm from the exposure surface. The Ca/Si molar ratio in the non-deteriorated region of the existing concrete member and the concrete specimen was 2.12 [4] and 2.25, respectively.

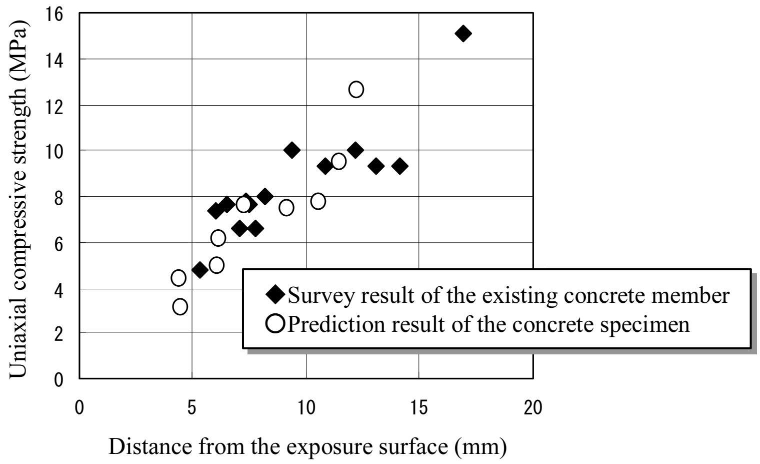


Figure 7 Relationship between uniaxial compressive strength of concrete
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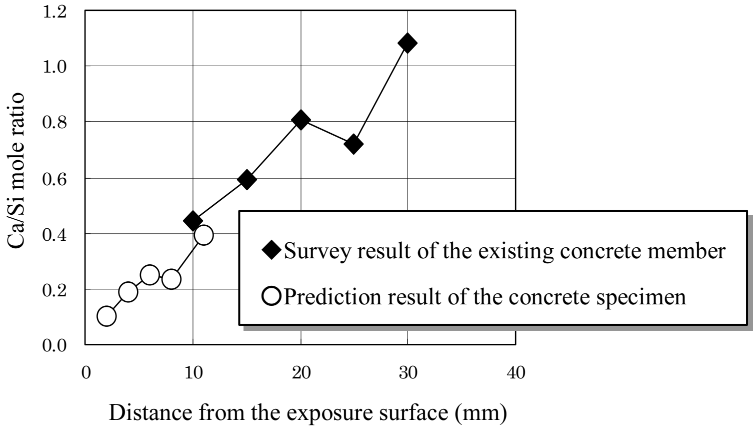

Figure 8 Relationship between Ca/Si molar ratio of concrete specimen and existing concrete member and distance from exposure surface

Figure 8 shows that the Ca/Si molar ratio fell as the measurement point approached the exposure surface. This is because calcium gradually dissolved out from the exposure surface, and it explains why the uniaxial compressive strength was low near the exposure surface. This makes it clear that clear that the concrete specimen and the existing concrete member satisfy are of the assumptions of this study, which is that the deterioration of concrete in contact with water occurs results from calcium leaching only.

These results verify that the strength decline caused by calcium leaching in the bulk can be quantitatively predicted using the experimental prediction method.

5. <u>INFLUENCE OF UNIT CEMENT CONTENT ON DETERIORATION CAUSED BY CALCIUM LEACHING</u>

In this chapter, by applying the above experimental prediction method to concretes with various unit cement contents, calcium leaching and resulting deterioration are predicted. From the results, the influence of unit cement content on deterioration caused by calcium leaching is examined.

First, in order to confirm that the decrease in Vickers hardness of the bulk concrete was caused by calcium leaching, the relationship between Ca/Si molar ratio and bulk Vickers hardness is discussed. Concrete deterioration is evaluated from the viewpoint of the relationship between distance from the exposure surface and the bulk Vickers hardness or Ca/Si molar ratio for concretes with different unit cement contents. These relationships are discussed using concrete specimens whose DCTs are within 40 years.

Finally, with reference to the result of the previous report [3], the influence of mix proportion on the deterioration caused by calcium leaching is summarized at the end of this chapter.

5.1 Relationship between Vickers hardness and Ca/Si molar ratio

In order to confirm that the decrease in bulk Vickers hardness of the concrete was caused by calcium leaching, the relationship between Ca/Si molar ratio and bulk Vickers hardness is discussed. The Ca/Si molar ratio is the ratio of calcium quantity in moles to silicon quantity in moles in a unit area of the bulk material. The amount of calcium decreases with leaching. However, silicon seems to remain in the concrete as silica gel in spite of calcium leaching, and so the amount of silicon remains approximately constant [6]. Consequently, the Ca/Si molar ratio of the bulk material is an index, albeit semiquantitative of calcium in the bulk part.

Figure 9 shows the relationship between Vickers hardness and Ca/Si molar ratio of the bulk part of a concrete specimen that leaches calcium according to the experimental prediction method. From this figure, it is clear that Vickers hardness decreases with a decrease in Ca/Si molar ratio. By the examination of this result and **Figure 7** and **Figure 8**, it is obvious that calcium dissolved from material near the exposure surface first, and thereafter calcium began leaching from deeper in the concrete. Also, the bulk concrete became porous as a result of calcium leaching, and the Vickers hardness decreased.

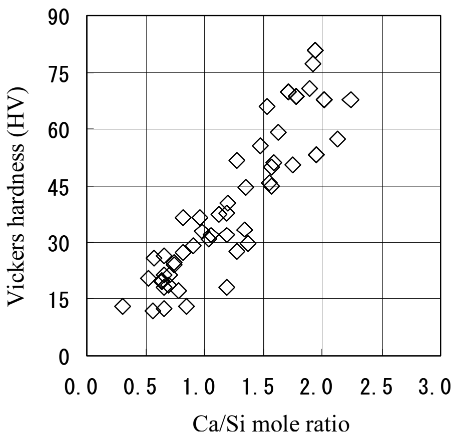

Figure 9 Relationship between Vickers hardness and Ca/Si molar ratio of the bulk concrete

5.2 Influence of unit cement content on decrease in Vickers hardness and Ca/Si molar ratio with calcium leaching

In this section, the influence of unit cement content on calcium leaching and the corresponding decrease in Vickers hardness and Ca/Si molar ratio is discussed.

Concrete with three different unit cement contents was used in this study, 318, 345, and 409 kg/m^3. The cement was ordinary Portland cement, and the water-cement ratio and sand-aggregate ratio were 55% and 50%, respectively. The relationship between Vickers hardness and DCT is shown in **Figure 10**. **Figure 10-(a)**, **(b)**, and **(c)** were for the regions 0-4 mm, 4-8 mm, and 8-12 mm from the exposure surface, respectively.

Figure 10(a) shows that with a DCT 0-3 years, the greater the distance from the exposure surface, the smaller the decrease in Vickers hardness. Also, for a given DCT, the Vickers hardness increases as distance from the exposure surface increases. This demonstrates that the Vickers hardness first begins to fall near the exposure surface. Thereafter, the region of reduced Vickers hardness expands further into the concrete as DCT increases. Also, the fall in Vickers hardness stagnates at a value of about 10-20 HV, while the deterioration continues in regions deeper than points that reach 10-20 HV. In a report on concrete deterioration caused by calcium leaching due to contact with river water for 80 years [7], it was shown that the Vickers hardness approached 10-20 HV at points where it could be measured. From these results, it is inferred that Vickers hardness falls no further than about 10-20 HV.

In the region 0-4 mm from the exposure surface, the Vickers hardness fell particularly significantly with a DCT of 0-3 years in comparison with other locations. Thereafter, it fell slowly, and ultimately approached 10-20 HV. It was concluded that this region is the ‘calcium leaching layer’, and here the concrete strength falls dramatically. In Particular, in the case of 318 kg/m^3 in unit cement content, the fall in Vickers hardness reached its constant value and the area became a calcium leaching layer DCT = 2 years.

In the region 4-8 mm from the exposure surface, the reduction in Vickers hardness with DCT = 2-3 years was not as great as nearer the surface. This is because the deterioration caused by calcium leaching began near the exposure surface. Also, the fall in Vickers hardness halted earlier, as the unit cement content was less. From this result, it can be predicted that the appearance of a calcium leaching layer will be earlier as the unit cement content is reduced.

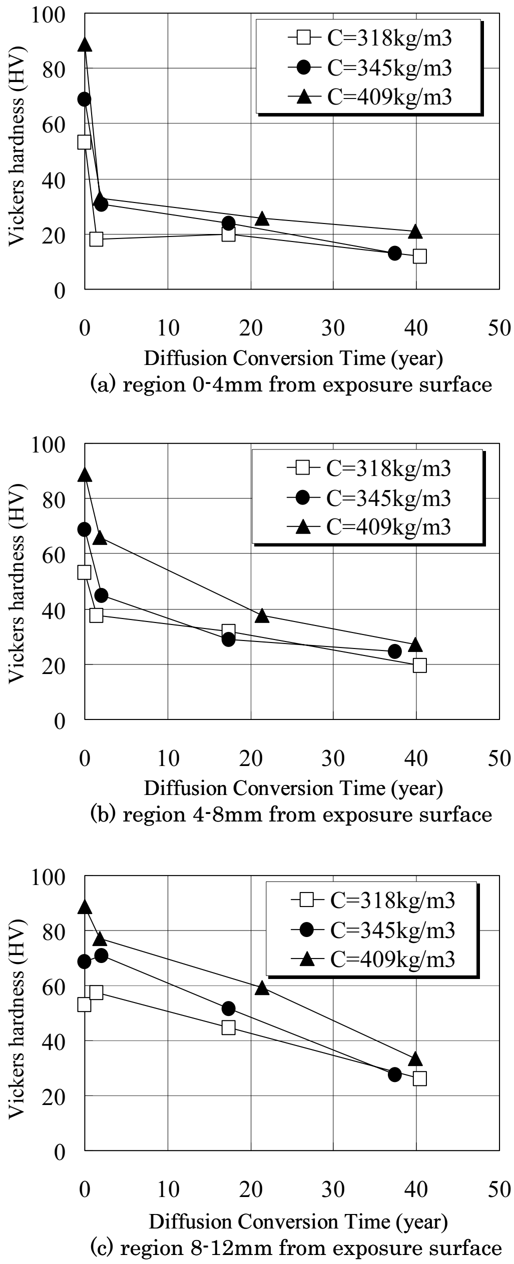

Figure 10(a)~(c)
Relationship between Vickers hardness
and Diffusion Conversion Time

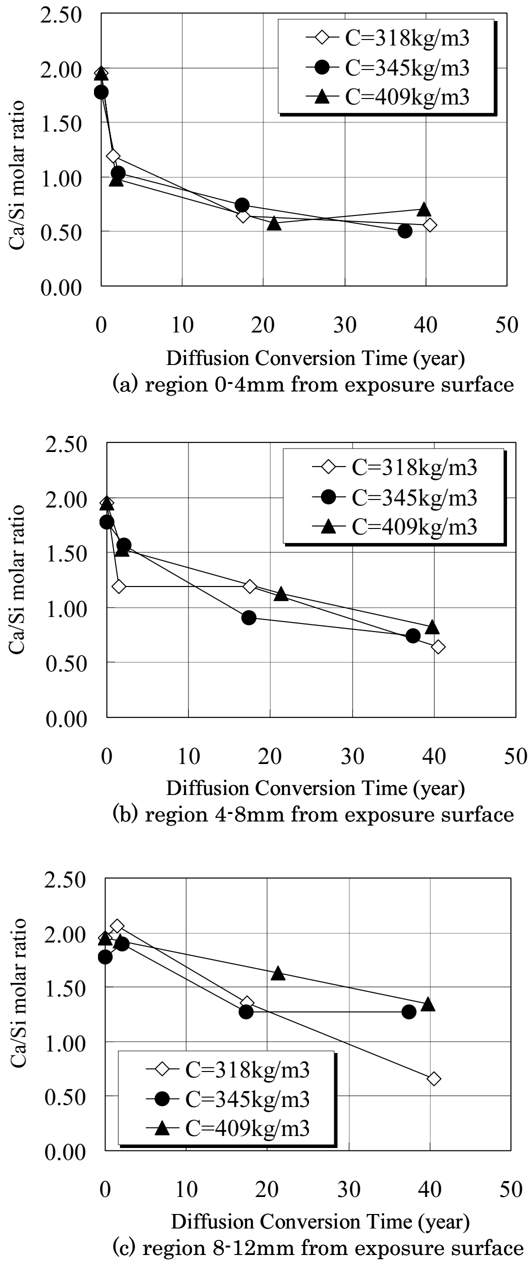

Figure 11(a)~(c)
Relationship between Ca/Si molar ratio
and Diffusion Conversion Time

In the region 8-12 mm from the exposure surface, no notable reduction in Vickers hardness was seen. It is thus clear that the fall in Vickers hardness as a result of calcium leaching does not progress very rapidly in regions relatively far from the exposure surface. Also, the Vickers hardness decreased in an almost rectilinear pattern for DCT up to 40 years. Therefore, it was concluded that this region is an 'intermediate layer', or the transition region between sound concrete and calcium leaching for DCT up to 40 years. Finally, the Vickers hardness at the same DCT increased as the unit cement content increased.

Figure 11 shows the relationship between Ca/Si molar ratio and DCT. **Figure 11-(a)**, **(b)**, and **(c)** are for the regions 0-4 mm, 4-8 mm, and 8-12 mm from the exposure surface, respectively. **Figure 11** shows that the influence of unit cement content on Ca/Si molar ratio was inconspicuous in the 0-8 mm region. However, in the 8-12 mm region, the higher the unit cement content, the higher the Ca/Si molar ratio. Incidentally, there is more calcium per unit concrete volume when the unit cement content is higher, so calcium remains around the exposure surface even under conditions where all calcium in a low unit cement content specimen has leached away. For this reason, calcium leaching from deep regions is suppressed in the case of high unit cement content.

Summarizing the above results, it is concluded that the appearance of a calcium leaching layer is early and the progress of calcium leaching is fast when the unit cement content is low.

Incidentally, as calcium leaching progresses, the fall in Vickers hardness of the concrete comes to a halt at 10-20 HV, as already noted. Comparing **Figure 10** and **Figure 11**, it is obvious that the fall in Ca/Si molar ratio also halts when the Vickers hardness reaches 10-20 HV. This result shows that the leaching of calcium from the solid-phase paste into the pore solution of the concrete slows in the region where the fall in Vickers hardness halts. According to the solid-liquid equilibrium model of Buil [8], the amount of calcium leaching from the solid phase to the liquid phase falls with leaching of the calcium hydrate. Therefore, the reason for the halt in Vickers hardness decline is that the amount of calcium leaching from the solid phase becomes less as the calcium concentration in the solid phase decreases.

5.3 Influence of mix proportion on fall in Vickers hardness and Ca/Si molar ratio with calcium leaching

This section summarizes the findings on the influence of mix proportion on the fall in bulk Vickers hardness and Ca/Si molar ratio with calcium leaching. The mix proportion factors considered in the investigation were unit cement content, type of cement, and water-cement ratio. The results for unit cement content were based on the results in the above section. Results for type of cement and water-cement ratio were based on the research described in a previous study [3] using mortar specimens.

The previous section showed that, for a given DCT, the Vickers hardness increased as the unit cement content was made higher. Moreover, from the measurements of Ca/Si molar ratio, it was shown that the appearance of a calcium leaching layer occurred later as the unit cement content was increased. Also, calcium leaching did not progress deep inside the concrete in case of high unit cement content.

The results of an earlier study [3], for a given DCT, show that the Vickers hardness increased when using a cement containing mainly belite. Moreover, from measurements of Ca/Si molar ratio, it is known that the appearance of a calcium leaching layer is delayed, and calcium leaching does not progress deep into the concrete, when using a cement containing mainly belite.

For a particular DCT, it has been shown that the Vickers hardness increases as water-cement ratio is reduced. Moreover, measurements of Ca/Si molar ratio showed that the appearance of a calcium leaching layer was delayed, and calcium leaching did not progress deep into the concrete, in the case of a low water-cement ratio.

Putting these results together, it can be concluded that for the mix proportions studied here and in the previous study [3], the bulk Vickers hardness and Ca/Si molar ratio at a particular DCT are high in case of (1) high unit cement content, (2) cement containing mainly belite, and (3) low-water cement ratio.

6. CONCLUSIONS

The results of this study are summarized as follows:

(1) An experimental prediction method constructed in a previous study [3] was used to predict calcium leaching from concrete and the resulting deterioration over 100 years. The predictions were compared with a survey of a real concrete structure that had been in contact with water for about 100 years using the needle penetration test. From this comparison, the validity of the method was confirmed. It is concluded that this experimental method can reliably predict the deterioration of concrete caused by calcium leaching.

(2) The influence of unit cement content on the fall in bulk Vickers hardness and Ca/Si molar ratio due to calcium leaching was examined using the experimental prediction method. Further, the influence of cement type and water-cement ratio, which were examined in a previous study [3], was summarized. From the results, it was clarified that the Vickers hardness and Ca/Si molar ratio of bulk concrete at a particular DCT are high in the case of (1) high unit cement content, (2) cement containing mainly belite, and (3) low water-cement ratio. Also, chemical analysis demonstrated that the fall in Vickers hardness occurs as a result of calcium leaching.

In this study, deionzed water was used as the solution in contact with the concrete in order to obtain fundamental information on the calcium ions leaching from concrete. However, in an actual environment, this solution contains several kinds of ions, and there is a possibility that these ions may have an influence on calcium leaching. Therefore, the solution used in the diffusion test must be made more like that in the actual environment in the future, in order to examine the influence of various ions on calcium leaching.

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REFERENCES

[1] Y. Hurusawa, “Research Trends in Calcium Leaching Deterioration and its Modeling”, Concrete Journal, Vol.35, No12, pp. 29-32, 1997 (in Japanese).
[2] H. Saito, and S. Nakane, “Comparison between Diffusion Test and Electrochemical Acceleration Test for Leaching Degradation of Cement Hydration Products”, ACI Materials Journal, Vol. 96, No.2, pp. 208-212, 1999.
[3] N. Otsuki, S. Hirayama, S. Miyazato, and Y. Yokozeki, “Fundamental Study on Estimation of Ca Leaching from Mortar and Deterioration of Mortar”, Journal of Construction Management and Engineering of JSCE (Japan of Society of Civil Engineering), No. 634/V-45, pp.293-302, 1999 (in Japanese).
[4] Y. Yokozeki, J. Nakasone, K. Kakizaki, K. Watanabe, “Study on the Durability of Underground Concrete Structures Used over 100 Years”, Proceedings of the Japan Concrete Institute, Vol.20, No.1, pp.251-256, 1998 (in Japanese).
[5] The Japan Society of Civil Engineers Rock Mechanics Committee, Fourth Subcommittee, “Guidelines for investigation and testing of soft rock”, pp. 34-36, 1980 (in Japanese).
[6] K. Haga, H. Sakamoto, K. Ishizaki, H. Amano, M. Hironaga, and S. Tamaka, “Solubility Behavior of Cement Material as Artificial Barrior for Radioactive Waste Repository”, Research Report by Chichibu-Onoda Corporation, Vol.133, pp.194-203, 1997 (in Japanese).
[7] M. Hisada, “The Physical Property of the Concrete Collected from the Ookouzu Diversion Channel, Proceedings of 26th Cement Concrete Workshop, pp. 23-28, 1999 (in Japanese).
[8] M. Buil, E. Revertegat, J. Oliver, A Model of the Attack of Pure Water or Under Saturated Line Solution on Cement, ASTM STP 1123, pp. 227-241, 1992.