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Long-term forecast of Ca leaching from mortar and associated degeneration

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Abstract

The purpose of this study is the long-term forecast of Ca leaching from mortar and degeneration with Ca leaching. First, a technique for long-term forecasting of Ca leaching from mortar was constructed. Here, Ca is made to dissolve out by combining the electrochemical acceleration test with the diffusion test; it was converted on the basis of Ca leaching rate in real time and was carried out to a long-term forecast of Ca leaching. Next, the long-term forecast technique of mortar degeneration with Ca leaching was constructed. Here, Ca is made to dissolve out by the electrochemical acceleration test, and the mortar was evaluated experimentally. The result of the accelerated degeneration test was checked with the real time conversion result obtained by the long-term forecast of Ca leaching. Finally, predicted results of the degradation with Ca leaching were compared with the survey result of existing structures used for 30 years.

Keywords: Leaching; Mortar; Acceleration; Degradation

1. Introduction

The degradation phenomenon called “leaching” in cement paste is the phenomenon in which the organization becomes sparse by the dissolution of various components in the surrounding water. Since the rate of progress is very slow, degradation by leaching is not often a problem in normal concrete structures. However, it is necessary to evaluate the durability of concrete with Ca leaching in hydraulic structures such as dams, which remain in water in the long term, and radioactive waste disposal facilities, which must guarantee long-term soundness, etc. However, the research on long-term durability of concrete with Ca leaching has just gotten under way.

Therefore, long-term forecast of Ca leaching from mortar and degeneration of the mortar with Ca leaching was the purpose of this study. The following were carried out: ① the construction of a long-term forecast technique of Ca leaching from mortar; ② the construction of a long-term forecast technique of the degeneration with Ca leaching from mortar; and ③ the comparison of predicted results of mortar degeneration with Ca leaching and actual survey results from a real concrete member.

In ①, long-term forecast technique of Ca leaching was constructed. Here, Ca was made to dissolve out by combining the acceleration test with the diffusion test. The acceleration test allows Ca to dissolve out at 200–300 times the speed of normal diffusion phenomena. However, the correlation with the amount of Ca leaching in real time is not proven, and Ca leaching by diffusion phenomena requires a very long test period, since the process is very slow. Therefore, the prediction method constructed in this study combines the acceleration test with the diffusion test and utilizes both advantages.

In ②, a long-term forecast technique of the degeneration with Ca leaching from the mortar was constructed. The long-term forecast was carried out under the assumption that “the physical property change of the mortar is determined by leaching of Ca^{2+}, when $Ca(OH)_2$ remains in the mortar” [1,2]. Here, physical degeneration after Ca leaching was evaluated by the acceleration test, and it was also evaluated experimentally by various measurements. The physical property change of the mortar in the result may be different from that with Ca leaching only by the diffusion, since Ca

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leaching in this study was done in the combination of diffusion test and acceleration test. However, Saito et al. [3,4] have confirmed that the degeneration with accelerated Ca leaching by the electrical method and degeneration with Ca leaching under the real diffusion environment becomes approximately equal, so the effect of the difference of leaching condition on the degeneration seems to be small in this study.

In ③, the prediction method constructed in this study was compared with survey results from a real concrete member. Here, long-term forecast results of the degeneration of the mortar with Ca leaching found in ② were compared with the survey results of waterworks facilities used for 30 years.

2. Experimental procedures

2.1. Specimens

The properties of materials used are shown in Tables 1 and 2. The mixtures and basic properties of mortar are shown in Table 3. In this experiment, three kinds of cement were used: Ordinary Portland cement (OPC); high-early-strength Portland cement (HPC); and low-heat Portland cement (LPC). The water–cement ratio was established at three levels when the OPC was used. A $4 \times 4 \times 16$ cm steel mould was used. Titanium mesh was placed at 3.5 cm from the bottom of the specimen, and the lead wire was connected beforehand to the edge of the titanium mesh. After curing at 20 ± 1 °C, indoor, for 28 days, the specimen was cut off at $2.5 \times 4 \times 10$ cm. A plane of 4×10 cm was made to be the exposure surface, and the specimens were sealed with epoxy resin except for the exposure surface.

2.2. Electrochemical acceleration test

The electrochemical acceleration test is to accelerate Ca leaching using the electrochemical technique [5]. The outline of the acceleration test is shown in Fig. 1. Titanium mesh was placed as a negative electrode at the bottom of the plastic container. The specimen was kept 1 cm above the bottom of the container. The surrounding ion exchange water was kept at the same level as the embedded titanium mesh in the specimen. The ion exchange water was changed every 24 h. The current density was 10.0 A/m^2 to the exposure surface of the mortar. The five lengths of current application were 100, 200, 400, 800 and 1200 h.

Table 1
Physical and chemical properties of cements

Type of cement	Specific gravity, g/m^3	Specific surface, cm^2/g	CaO, %	SiO_2, %	Al_2O_3, %
OPC	3.15	3270	64.2	21.1	4.8
HPC	3.14	4490	65.3	21.2	4.5
LPC	3.22	3500	63.8	26.6	2.6

Table 2
Aggregate properties

Aggregate	Specific gravity, g/m^3	Solid content, %	Absorption, %	Fineness modulus
Sand	2.60	66.3	1.84	2.54

As a result of preliminary tests, the current density was chosen considering both the facts that Ca^{2+} mobility is low, and that heat production at high current density is undesirable. Using ion chromatography, the amount of Ca leaching was measured.

2.3. Diffusion test

The diffusion test was carried out in order to correlate Ca leaching rate by diffusion phenomena with the results of the acceleration test. The immersed specimens allowed to dissolve out for 7 days, then the acceleration test began. After the chosen accelerated testing period ended, the specimen was again allowed to dissolve out. The amount of Ca that dissolved out after immersion for 7 days in the solution was measured. The leaching rate is shown in Eq. (1). By dividing the amount of Ca that dissolved out in ion exchange water after 7 days of immersion, the leaching rate was calculated.

$$V_d = \frac{X_d}{\Delta t A} \tag{1}$$

where V_d = leaching rate per unit area (g/s m^2); X_d = amount of Ca that dissolved by the diffusion (g); Δt = diffusion test period (s; here, 604 800 s); and A = exposure surface area of specimen (m^2; here, 0.0040 m^2).

2.4. Measurement techniques

After the chosen accelerated testing period ended, the specimen was perpendicularly cut off from the exposure surface. Using the microhardness tester, Vickers hardness was measured every 2.5 mm from the exposed surface. The test force was 0.025 N, and the test force duration was 10 s. Also, the compression strength was measured within 2 cm from the exposed surface. For this measurement, a sample

Table 3
Mixtures and basic properties of mortar

Mix	Water–cement ratio, %	Water, kg/m^3	Cement, kg/m^3	Sand, kg/m^3	Flow value, cm	Air content, %
OPC 0.40	0.40	250	626	1251	155	0.5
OPC 0.55	0.55	313	568	1136	195	1.0
OPC 0.70	0.70	364	521	1041	240	2.0
HPC 0.55	0.55	314	568	1136	200	0.5
LPC 0.55	0.55	313	571	1141	200	1.0

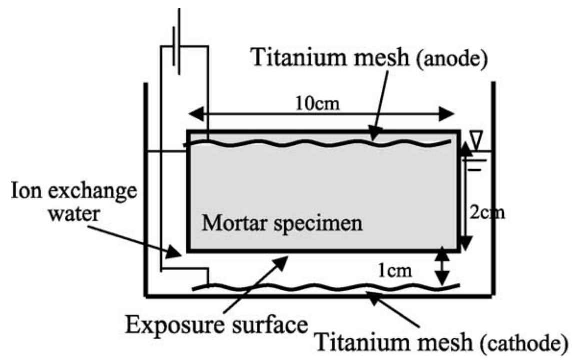

Fig. 1. Outline of electrochemical acceleration test.

of 2 × 2 × 2 cm was cut down from specimen after the chosen acceleration test period.

3. Results and discussion

3.1. Long-term forecast of Ca leaching

The prediction method constructed in this study is to combine the acceleration test with the diffusion test and to calculate the relationship between real time and amounts of Ca leaching. Here, calculated real time is called the diffusion conversion period.

The outline of the calculation for the diffusion conversion period is shown in Fig. 2. For example, an amount $(X_{t'} - X_t)$ of Ca dissolved out over the time from t to t', with X_t dissolving out after t h and $X_{t'}$ dissolving out after t' hours. When the amount $(X_{t'} - X_t)$ dissolves out in the diffusion phenomena, the average leaching rate is assumed as an average of leaching rate V_{d_t} from the diffusion test after t h of the acceleration test and leaching rate $V_{d_{t'}}$ from

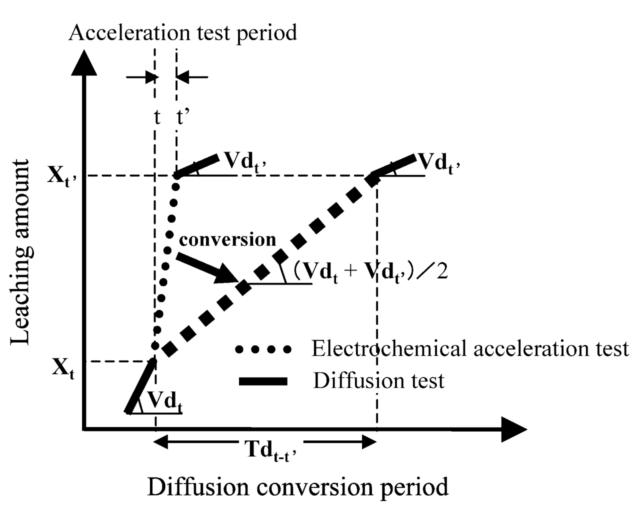

Fig. 2. Outline of the calculation for the diffusion conversion period.

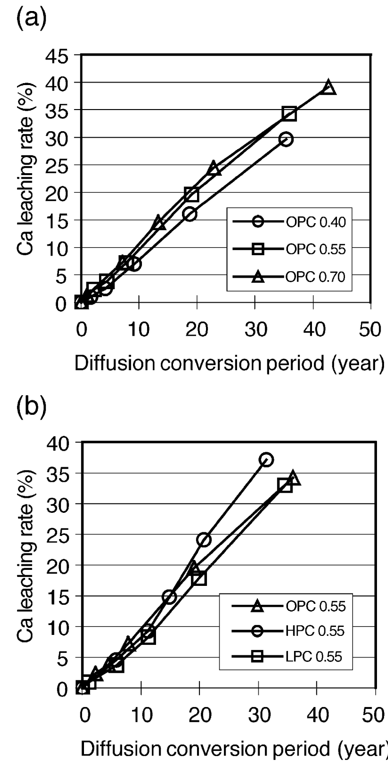

Fig. 3. The relationship between Ca leaching rate and diffusion conversion period.

the diffusion test after t' h of acceleration test. The relation shown in Eq. (2) is obtained.

$$\frac{X_{t'} - X_t}{T_{d_{t-t'}}} = \frac{V_{d_t} + V_{d_{t'}}}{2} \qquad (2)$$

Therefore, it is possible to calculate the necessary time for $X_{t-t'}$ to dissolve out by diffusion phenomena, as it is shown in Eq. (3). In this study, the combination of t h and

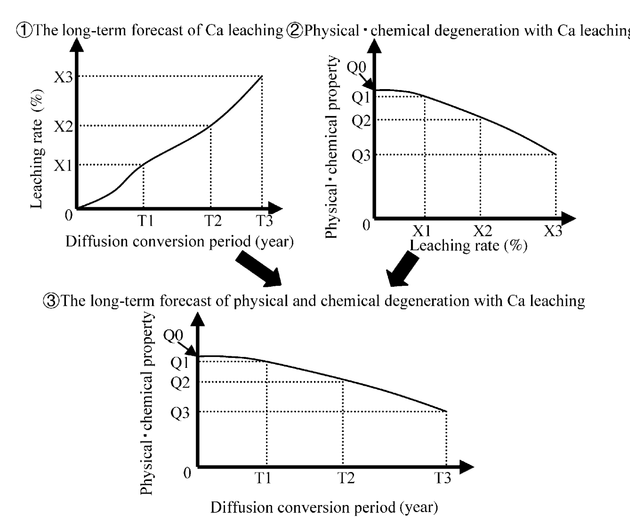

Fig. 4. Outline of the long-term forecast of the degeneration with Ca leaching.

t' h for calculating the diffusion conversion period is (t, t')=(0 h, 100 h), (100 h, 200 h), (200 h, 400 h), (400 h, 800 h), (800 h,1200 h).

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

Using the prediction method constructed above, a long-term forecast of Ca leaching rate was carried out on the basis of the results of the acceleration test and the diffusion test. The Ca leaching rate is calculated as a percentage of the original Ca content in the specimen. The amount of Ca contained before leaching of the specimen was calculated from the CaO content percentage in the cement, mortar mixture proportions and dimensions of specimen.

The relationship between Ca leaching rate and diffusion conversion period after 30–40 years is shown in Fig. 3.

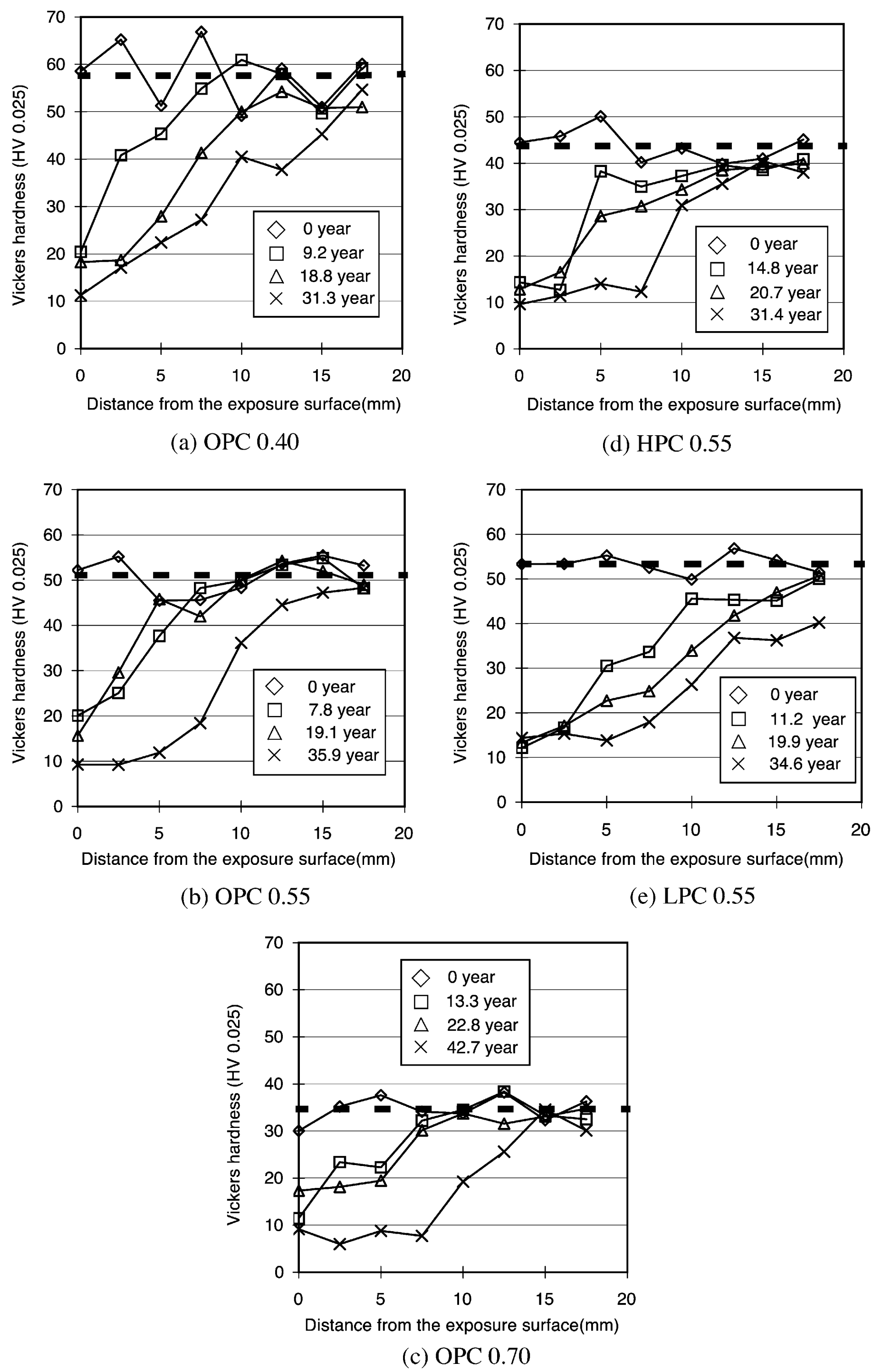

Fig. 5. The relationship between distance from exposure surface and Vickers hardness.

According to this, there is a tendency for the Ca leaching rate to decrease with decreasing water–cement ratio. This seems to be true because the binding power of the hydration products is stronger and the pore structure becomes finer, as water–cement ratio is decreased. There is also a tendency for the leaching rate of the HPC to increase over the leaching rate of OPC and LPC in an equal diffusion conversion period.

3.2. Long-term forecast of the degeneration with Ca leaching

Based on the relation shown in Fig. 4, the long-term forecast of the degeneration with Ca leaching from mortar was carried out. That is to say, based on the prediction method constructed from the results of the diffusion test and the acceleration test previously discussed, the relationship between diffusion conversion period and Ca leaching rate is examined. Then, Ca is made to dissolve out by the acceleration test, and the physical property of the specimen after Ca leaching is evaluated experimentally. Here, the relationship between physical property and Ca leaching rate is examined. Finally, the diffusion conversion period in proportion to each Ca leaching rate is compared with the physical property. By these results, the relationship between physical property and diffusion conversion period can be constructed.

The long-term forecast of the degeneration accompanied by Ca leaching using the prediction method above was carried out. The relationship between distance from exposure surface and Vickers hardness is shown in Fig. 5. The tendency is that with increasing diffusion conversion period, the Vickers hardness is reduced. Also, the tendency is that the Vickers hardness decreases with decreasing distance from exposure surface. This seems to be true because Ca dissolves out from exposure surface.

By comparing the Vickers hardness before and after leaching as the diffusion conversion period is increased, it is possible to carry out the classification shown in Fig. 6. That is to say, the following layers were identified: the layer in which Vickers hardness before and after leaching is equivalent (called sound layer); the layer in which the hardness decreases remarkably (called leaching layer); and a transition zone from sound layer to leaching layer (called intermediate layer). By the classification shown in Fig. 6, it can be considered that the degeneration of the intermediate leaching layers occurs earlier when water–cement ratio is higher. Also, it can be considered that the degeneration of the intermediate layer and the leaching layer of HPC occurs earlier in comparison with LPC and OPC.

In Fig. 7, the relationship between compressive strength of the exposure surface within 2 cm and diffusion conversion period is shown. It can be seen that compressive strength decreases with the increase in the diffusion conversion period in all cases. For an equivalent diffusion conversion period, it can be seen that compressive strength is higher, as the water–cement ratio is smaller. It is thought that this is because compressive strength before Ca leaching is higher, and the lowering of the binding power of the hydration organization does not progress for an equal diffusion conversion period, as water–cement ratio is

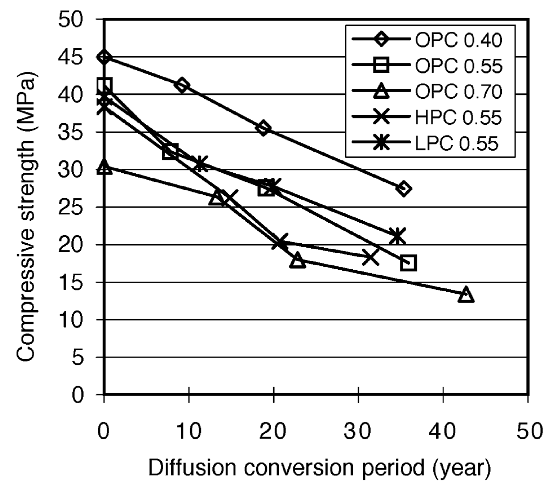

Fig. 7. The relationship between diffusion conversion period and compressive strength.

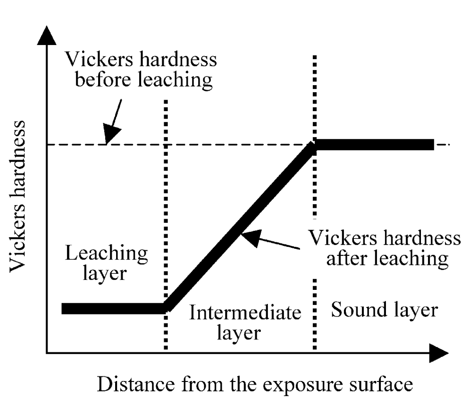

Fig. 6. The distribution of the Vickers hardness before and after Ca leaching.

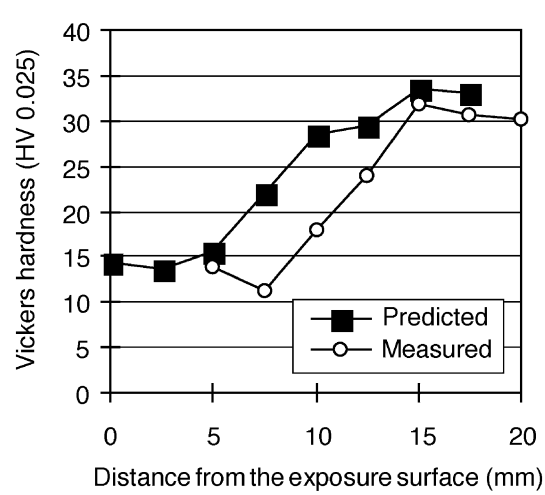

Fig. 8. The predicted and the measured Vickers hardness.

smaller. Also, for an equivalent diffusion conversion period, compressive strength of HPC tends to be lower than that of OPC and LPC.

3.3. The comparison of survey results in real concrete members with predicted results

The comparison was carried out using the survey result of a concrete structure used for 30 years in order to verify the prediction result [6]. The structure for the comparison is the old water supply. The part from which the core was collected is a concrete floor, which has been in contact with drinking water for 30 years. The water–cement ratio of the floor concrete is estimated from survey results to be about 0.70. The predicted and the measured Vickers hardness of above concrete structure are shown in Fig. 8. It can be seen in this figure that reduction of the predicted and the measured Vickers hardness near the surface, which seems to indicate Ca leaching, is in agreement, though construction condition and various other conditions such as the materials are different for the floor concrete as compared with the mortar specimens used in this study.

4. Conclusions

A long-term forecast technique of Ca leaching and a long-term forecast technique of the degeneration with Ca leaching were proposed, and the prediction was carried out. Three kinds of Portland cements and three water–cement ratios from 0.40 to 0.70 were studied, and the results showed that Ca leaching and the degeneration with Ca leaching after 30–40 years could be estimated.

From the predicted result, the effect of cement type and water–cement ratio on degeneration with Ca leaching was examined. As a result, it was confirmed that Ca leaching and degeneration with Ca leaching was suppressed, as pore structure was densified and binding power of the hydration organization was increased.

The survey result of a real concrete structure used for 30 years and the long-term forecast result of the mortar specimen were compared. The predicted result and the survey result are similar regarding the relationship between distance from the exposure surface and Vickers hardness.

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