Pergamon

Cement and Concrete Research 30 (2000) 1815–1825

CEMENT AND CONCRETE RESEARCH

Leaching tests on different mortars using accelerated electrochemical method

Hiroshi Saito[a,]*, Akira Deguchi[b]

[a]Project Promotion Department, Technical Research Institute, Obayashi Corporation, 640, Shimokiyoto 4-chome, Kiyose, Tokyo 204-8558, Japan
[b]Nuclear Power Engineering Department, Tokyo Electric Power Company, 1-3 Uchisaiwai-cho 1-chome, Chiyoda, Tokyo 100-0011, Japan

Received 24 January 2000; accepted 31 July 2000

Abstract

In designing radioactive waste repositories, it is necessary to predetermine the degree of concrete performance change due to leaching degradation. Leaching tests were carried out on different mortars using an electrochemical method. With this method, a potential gradient is applied across the specimen, which accelerates the dissolution of cement hydrate from mortar in contact with water. Tests were carried out using various sand/cement ratios, water/cement ratios, and pozzolanic admixture [blast-furnace slag (BF) and silica fume (SF)] replacement for a part of the cement to determine differences in the quality and quantity of cement hydrate. The amount of Ca^{2+} ions entering the water varied depending on the mix proportions. It decreased with sand content, but increased with water/cement ratio, and it varied with the kind of pozzolanic admixture and the replacement ratio. The pore volume of the degraded specimens increased as a result of cement hydrate dissolution. The water permeability of the mortar specimens increased by about one to two orders of magnitude due to leaching degradation. The compressive strength of the degraded mortar specimens decreased by 20% to 60%. There was good correspondence between each performance change and pore volume change due to leaching degradation. Pozzolanic admixture replacement for a part of the cement was very useful in achieving a durable concrete that resists leaching and shows a small loss of performance after leaching. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Acceleration; Microstructure; Degradation; Permeability

1. Introduction

High-level radioactive waste will be isolated several hundred meters under the ground in our country. Lining concrete will be placed through part of the access tunnel when the repository is constructed. Since this concrete will be in contact with water for a long time, the cement hydrate will gradually dissolve. This causes concern that the concrete's water permeability will increase and its strength will decrease. Therefore, in designing the facilities, it is necessary to predetermine the degree of performances changes. It has been shown that there is good correspondence between concrete compressive strength and water permeability, and pore structure of cement hydrate [1–2]. It is conjectured that the pore structure of cement hydrate becomes coarser with dissolution of cement hydrate. However, phenomenon has not sufficiently clarified, because it progresses very slowly, and there has been no acceleration method that can reproduce it experimentally.

The authors have carried out experimental studies on an electrochemical acceleration test method for leaching degradation to clarify its applicability [3]. The method can accelerate cement hydrate dissolution by increasing Ca^{2+} ion moving speed in the pore water by applying a constant potential gradient across a mortar specimen in contact with water. With this method, the ions moving are not the same as under natural condition, but similar deterioration conditions are obtained. Other researchers [4] have used the same method.

In the test, an electrochemical acceleration method was used to degrade different mortar specimens by dissolution of the cement hydrate. Water permeability and compressive strength of the specimens were then measured and the degraded condition was studied.

---

* Corresponding author. Tel.: +81-424-95-0976; fax: +81-424-95-1091.

E-mail address: h.saito@tri.obayashi.co.jp (H. Saito).

PII: S0008-8846(00)00377-X

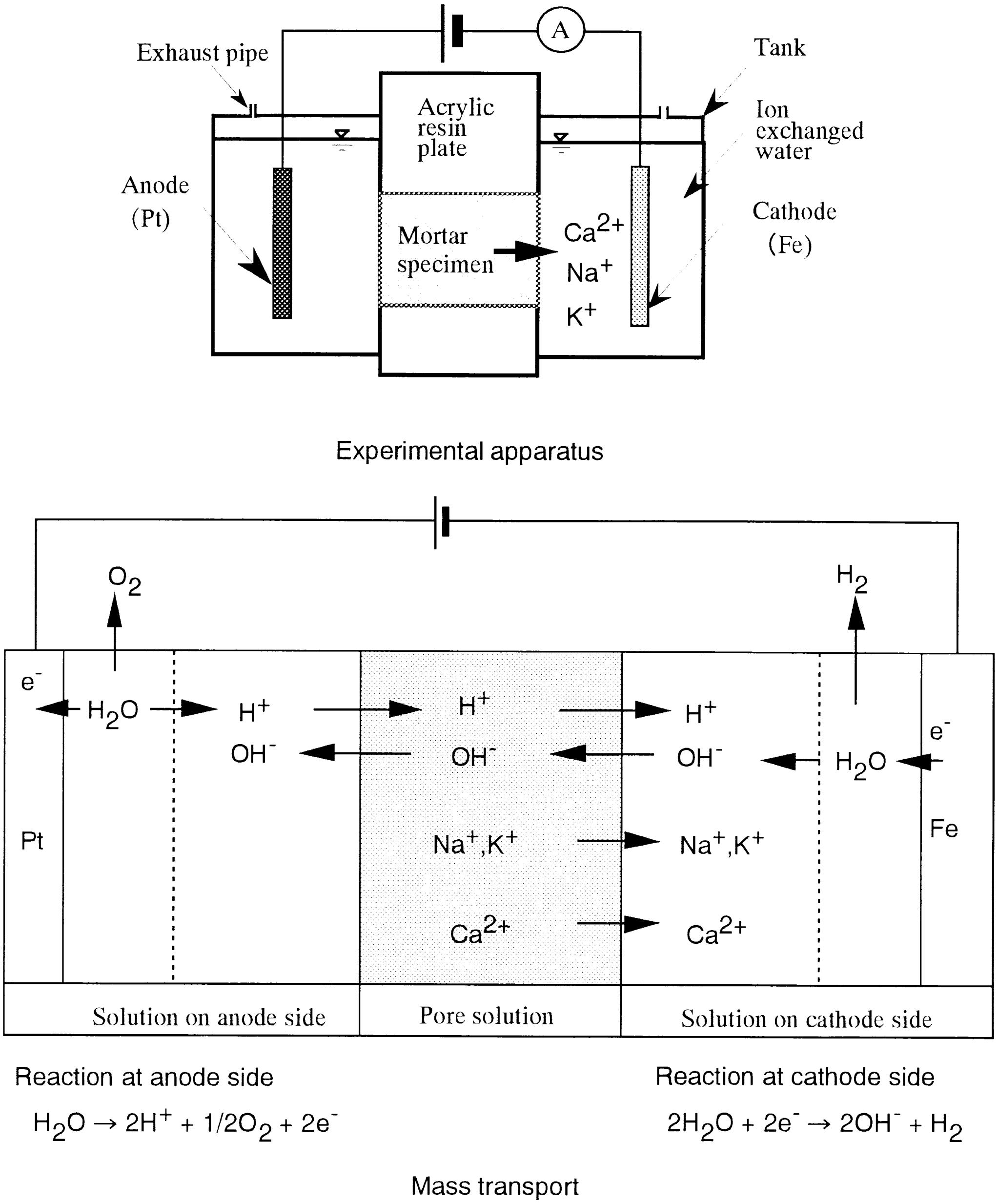

Fig. 1. Experimental apparatus and mass transport in this test.

This report describes test results and discusses the changes in water permeability and compressive strength due to dissolution of the cement hydrate.

2. Electrochemical acceleration test method

There is a chemical equilibrium between the main hydrates $Ca(OH)_2$ and C–S–H, and their component ions in pore water, as described by the following chemical reactions (Reactions (1) and (2))

$$Ca(OH)_2 \rightleftarrows Ca^{2+} + 2OH^- \qquad (1)$$

$$C-S-H \rightleftarrows Ca^{2+} + 2OH^- + SiO_2 \qquad (2)$$

Brown and Clifton [5] demonstrated this from the viewpoint of thermodynamics. If the Ca^{2+} ion concentration in the pore water decreases, $Ca(OH)_2$ dissolves, thus supplying additional Ca^{2+} ions to maintain equilibrium. After complete dissolution of the $Ca(OH)_2$, Ca^{2+} ions supplemented by the C–S–H start to dissolve and the C–S–H finally degrades to SiO_2 gel.

Furthermore, cement hydrate dissolution seems to correspond to a movement of related ions. This suggests that if dissolution speed is determined by ion movement speed, then increasing the ion movement speed will

Table 1
Mix proportions of mortar

Type of test		W/C	S/C	BF replacement ratio (%)	SF replacement ratio (%)
Test on different sand contents	No. 1	0.41	1.62	0	0
	No. 2	0.41	1.00	0	0
	No. 3	0.41	0.57	0	0
	No. 4	0.41	0.25	0	0
Test on different water/cement ratios	No. 5	0.32	0.67	0	0
	No. 6	0.41	0.77	0	0
	No. 7	0.50	0.89	0	0
	No. 8	0.60	0.97	0	0
Test on admixture replacement ratios	No. 9	0.41	1.00	30	0
	No. 10	0.41	1.00	50	0
	No. 11	0.41	1.00	70	0
	No. 12	0.41	1.00	0	10
	No. 13	0.41	1.00	0	20

accelerate dissolution speed. This led to the application of a potential gradient to increase the rate of ion movement. According to electrochemical principles, ions in solution move toward opposite electrodes under a direct-current potential gradient, i.e., cations move toward the cathode and anions move toward the anode. In an infinite dilute solution, the rate of movement under a 1-V/cm gradient is defined as mobility, and each ion has its own characteristic value.

Fig. 1 shows the experimental apparatus used in the test and the mass transport concept applied. The specimen was clamped between two glass vessels, each containing 1 l of ion-exchanged water. Each vessel also had a small pipe for exhausting the gas produced by electrolysis. One vessel contained an anode (Pt) and the other a cathode (stainless steel). These were connected to a DC power source to provide a potential gradient across the specimen. Ca^{2+} ions in the pore solution moves rapidly to the cathode, and thus hastens cement hydrate dissolution. In this electrochemical reaction, cations in the pore solution, such as Na^+, K^+, and Ca^{2+}, move toward the cathode, while anions, such as OH^-, move toward the anode. Under natural conditions, Ca^{2+} and OH^- ions resulting from dissolution move in the same direction. Thus, with this experimental arrangement, the OH^- ions move in the wrong direction. Further, a small current (of several mA) flows during the test, so water electrolysis occurs at the same time at both electrode, forming a few H^+ and OH^- ions and producing H_2 and O_2 gases. This also does not occur under natural condition. Nevertheless, these differences do not affect the dissolution mechanism, but only ion transport efficiency and solubility because of the different pH conditions. Consequently, this method of acceleration with an electric field produces leached samples in a short time without altering the assumed degradation mechanism.

Table 2
Qualities of pozzolanic admixture

	Relative surface area	Specific gravity	CaO [%]	SiO_2 [%]	Al_2O_3 [%]
BF	4360 cm^2/g	2.91	42.6	33.3	15.1
SF	19.6 m^2/g	2.22	> 0.3	94.2	>0.3

3. Experiment

3.1. Mortar specimens

Table 1 shows mix proportions of the mortar specimens. Ordinary Portland cement, Toyoura Sand (as specified in the former JIS standards; solid volume ratio 57.2%) and pozzolanic admixtures [blast-furnace slag (BF) and silica fume (SF)] were used in these tests. The qualities of pozzolanic admixtures are shown in Table 2. The mix proportions are grouped into categories A and B. Water/cement ratio and sand/cement ratio were changed in group A. Parts of the cement were replaced by pozzolanic admixtures in group B. In the sand content test, the water/cement ratio was 0.41 and four sand/cement ratios were used: 1.62, 1.00, 0.57, and 0.25. These ratios were chosen to achieve four levels of *S*/Slim (Sand volume (*S*) divided by solid volume ratio (Slim)). In the water/cement ratio test, ratios of 0.32, 0.41, 0.50, and 0.60 were chosen, and *S*/Slim was held constant at 50%. The resulting sand/cement ratios were from 0.67 to 0.97. In the pozzolanic admixture replacement test, the replacement ratios were 30%, 50%, and 70% for BF, and 10% and 20% for SF. Certain chemical admixtures were added so as to obtain a flow of about 200 mm, as occasion demanded. The specimens were cylindrical, 2.5 cm in diameter and 10 cm high. They were cured in water at 20°C for 4 weeks for group A and for 8 weeks for group B.

3.2. Measurements and procedures

3.2.1. Cement hydrate structure prior to test

After curing, the characteristics of the cement hydrate structure were measured using a method proposed by Nishikawa and Suzuki [6]. The hydrate constituent was measured by X-ray diffraction, the $Ca(OH)_2$ content by TG–DTA, and the Ca/Si molar ratio by chemical analysis. Pore volume and pore distribution within the range 3 nm to 60 μm in diameter were measured by the mercury intrusion method.

Table 3
Test conditions

Potential gradient	10 V/cm
Water	Ion exchanged water
Temperature	Room temperature (about 25°C)
Test period	A group; 4 months B group; 6 months

Table 4
$Ca(OH)_2$ content and Ca/Si molar ratio

		$Ca(OH)_2$ [%]	Ca/Si molar ratio of C–S–H	Remarks
Sand content	No. 1	19.4	2.0	S/C = 1.62
	No. 2	18.7	2.1	S/C = 1.0
	No. 3	19.5	1.9	S/C = 0.57
	No. 4	19.9	2.0	S/C = 0.25
Water/cement ratio	No. 5	17.0	1.9	W/C = 0.32
	No. 6	18.7	2.0	W/C = 0.41
	No. 7	21.3	1.9	W/C = 0.5
	No. 8	21.4	1.9	W/C = 0.6
Admixture replacement	No. 9	10.6	1.8	BF = 30
	No. 10	7.1	1.6	BF = 50
	No. 11	3.9	1.5	BF = 70
	No. 12	9.4	1.5	SF = 10
	No. 13	3.5	1.2	SF = 20

3.2.2. Leaching acceleration tests

The leaching acceleration tests were carried out by the proposed electrochemical method under the conditions indicated in Table 3. Chemical reaction rates, such as the dissolution of cement hydrates, are strongly influenced by temperature. To exclude any temperature influence, the tests were carried out in an air-conditioned room at 25 ± 2°C. Monitoring indicated that the temperature of solution on the cathode side occasionally changed by about 2°C, but for most of the test period, it was maintained at 25°C. The test periods were 4 months for the test on group A, and 6 months for the tests on group B. Test periods were varied so as to obtain a suitable deteriorated thickness for the study of changes in water permeability and compressive strength due to deterioration.

The solutions on both the anode and cathode sides were replaced once a week, the solution around the cathode was filled up to 1 l, and its Ca^{2+} ions concentration was determined by atomic absorption analysis. After the acceleration test, the specimens were removed from the apparatus and the deteriorated thickness was measured. The deteriorated region was easily distinguished visually by density change from cement hydrate dissolution.

3.2.3. Changes of cement hydrate structure after test

Each specimen was divided into two pieces by cutting at the deterioration boundary using a diamond cutter. The deteriorated thickness ranged from about 0.8 to 2.2 cm, corresponding to the degree of deterioration. The mineral composition and pore volume of each piece were measured using the method described in Section 3.2.1.

3.2.4. Water permeability and compressive strength

The water permeability of each piece was determined by Eq. (3)

$$Q = K_w A \Delta H / L \tag{3}$$

where Q is the water flow volume [m^3/s], K_w is the water permeability coefficient [m/s], A is the cross-section of flow [m^2], ΔH is the water head [m], and L is the specimen length [m].

The compressive strength of each was determined by Eq. (4)

$$\sigma = \alpha P / S \tag{4}$$

where σ is the compressive strength [N/mm^2], P is the maximum load [N], S is the cross-section of specimen [mm^2], and α is the correction coefficient that corresponded with specimen height.

4. Cement hydrate structure prior to test

4.1. Mineral composition of cement hydrate

Each specimen contained $Ca(OH)_2$, C–S–H, and monosulfate. This was verified by X-ray diffraction. Table 4 shows the $Ca(OH)_2$ content in each specimen obtained by the TG–DTA method. The $Ca(OH)_2$ content varies with time. Therefore, it was measured after 4 weeks of wet curing in the sand content and water/cement ratio test. On the other hand, it was measured after 8 weeks of wet curing in the admixture replacement test. In the sand content test, the $Ca(OH)_2$ content was 18.7% to 19.9%. These values are similar and are independent of sand content. In the water/cement ratio test, the $Ca(OH)_2$ content was 17.0% to 21.4%. It was similar for water/cement ratios of 0.5 and 0.6, but seemed to decrease slightly with water/cement ratio. In the BF replacement test, the $Ca(OH)_2$ content was 10.6% to 3.9%. It decreased with replacement ratio. In the SF replacement test, the $Ca(OH)_2$ content was 9.4% and 3.5%. It also decreased with replacement ratio. The $Ca(OH)_2$ content was 4% to 10% in the pozzolanic admixtures replacement test. It decreased by one-fifth to a half

Table 5
Pore volume at beginning of test

		PV [cm^3/cm^3]	PV/V_p [cm^3/cm^3]	Remarks
Sand content	No. 1	0.164	0.303	S/C = 1.62
	No. 2	0.169	0.257	S/C = 1.0
	No. 3	0.184	0.238	S/C = 0.57
	No. 4	0.226	0.254	S/C = 0.25
Water/cement ratio	No. 5	0.145	0.203	W/C = 0.32
	No. 6	0.171	0.240	W/C = 0.41
	No. 7	0.240	0.336	W/C = 0.5
	No. 8	0.253	0.354	W/C = 0.6
Admixture replacement	No. 9	0.155	0.236	BF = 30
	No. 10	0.146	0.221	BF = 50
	No. 11	0.180	0.274	BF = 70
	No. 12	0.180	0.273	SF = 10
	No. 13	0.162	0.246	SF = 20

PV: pore volume per unit specimen volume.
PV/V_p: pore volume per cement paste volume.

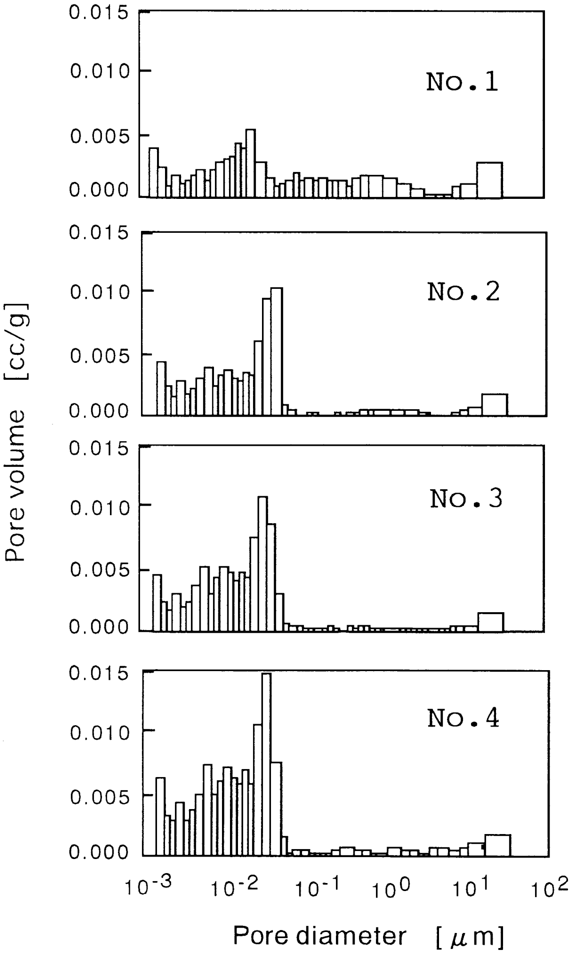

Fig. 2. Pore size distribution (S/C).

compared with specimen No. 2 shown in group A, which had the same mix proportion and no pozzolanic admixture.

Table 4 also shows the Ca/Si molar ratio of C–S–H obtained by chemical analysis. In group A, the Ca/Si molar ratios of C–S–H were 1.9 to 2.1, and were similar. In group B, it decreased with BF replacement ratio within the range of 1.8 to 1.5, and it decreased with SF replacement ratio within the range of 1.5 to 1.2. This showed that SiO_2-rich C–S–H was formed under a SiO_2-rich environment because of BF and SF replacement.

4.2. Pore structure

Table 5 shows the pore volume of each specimen. Because cement hydrate content varies with the mix proportion, the PV/V_p value (pore volume divided by volume ratio of cement paste) is also shown in Table 5 to allow comparison of the pore structures. In the sand content test, PV/V_p was similar for sand/cement ratios under 1, but it was 20% higher with a sand/cement ratio of 1.62. It is deduced from the pore distribution, described later, that this difference is due to the formation of a transit zone. In the water/cement ratio test, PV/V_p increased with water/cement ratio within the range 0.2 to 0.35, indicating that cement hydrate structure became coarser with increasing water/cement ratio. In the BF replacement test, PV/V_p was similar, 0.22 to 0.24 for replacement ratios of 30% and 50%, but it was 0.27, slightly higher for a replacement ratio of 70%. In the SF replacement test, PV/V_p slightly decreased with replacement ratios of 10% to 20% within the range 0.27 to 0.25. As mentioned above, PV/V_p was distributed within the range 0.22 to 0.27, which was similar to the value of 0.26 for no replacement. Therefore, it was judged that each specimen had a similar pore volume.

Figs. 2–4 show pore distributions. In the sand content test, the pore distribution was similar for sand/cement ratios under 1, with most pores under 50 nm in diameter. However, for a sand/cement ratio of 1.62, there were also pores of 50 nm to 2 μm in diameter and they comprised about 40% of the total pore volume. It has been reported that pores in this near size range result from a transit zone formed

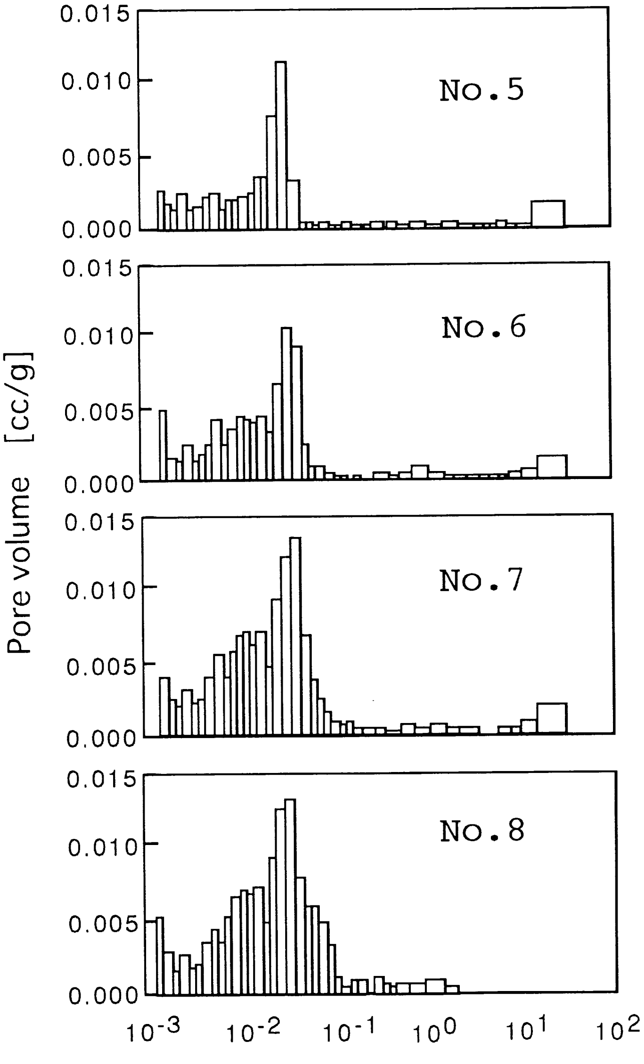

Fig. 3. Pore size distribution (W/C).

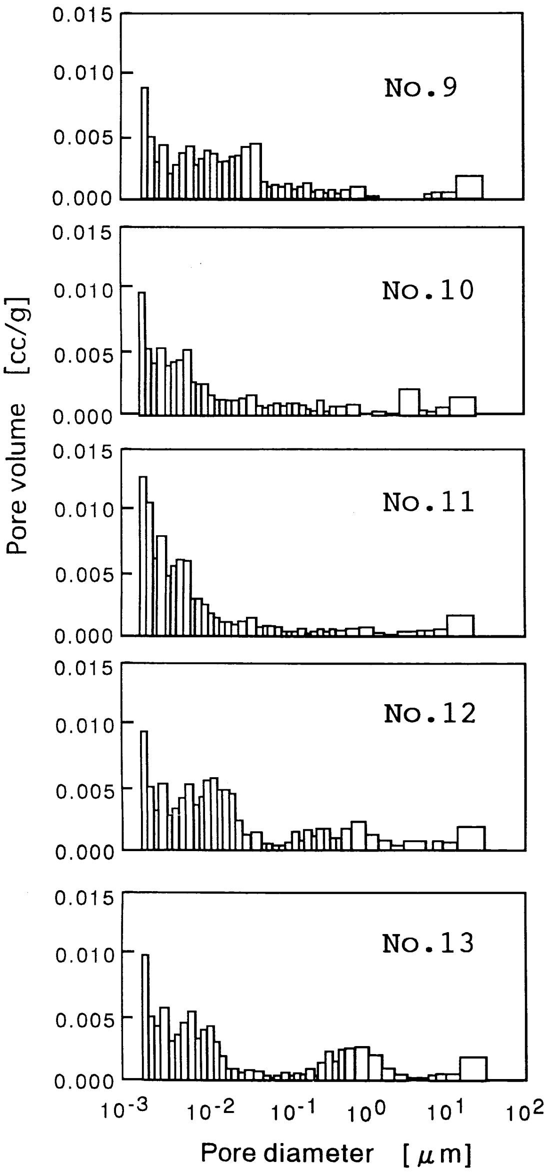

Fig. 4. Pore size distribution (BF, SF).

around the sand particles [7]. In the water/cement ratio test, most pore diameters were less than 50 nm, because the sand/cement ratio was less than 1. Generally, there were many pores 20 to 50 nm in diameter for sand/cement ratio less than 1. In the BF replacement test, the small pore volume ratio increased with BF replacement ratio. However, in the SF replacement test, the pore distribution was similar irrespective of replacement ratio, and it showed a characteristic with two peaks at about 1 μm and 10 nm in diameter.

5. Quantity of dissolved Ca^{2+}

Fig. 5 shows the cumulative quantity of dissolved Ca^{2+} ion in the sand content test. It expresses value per unit mortar volume. It differs for each sand/cement ratio. Thus, the results reflect the differences in cement content per unit mortar volume. That is, the decrease in Ca^{2+} ion quantity with sand content is due to the decrease in cement content, i.e., the decrease in cement hydrate volume. Fig. 6 shows the cumulative quantity of dissolved Ca^{2+} ion in the water/cement ratio test. In the test, the smaller the water/cement ratio, the greater the cement content per unit mortar volume. The quantity of dissolved Ca^{2+} ion decreased with cement content. This is the opposite of the test results for sand content, and demonstrates that the quantity of dissolved Ca^{2+} ion is affected not only by the quantity of cement hydrate, but also by its quality. That is, the tighter the cement hydrate, the smaller the quantity of Ca^{2+} ion.

As mentioned, in neither test quantity of dissolved Ca^{2+} ion is explained by the cement content per unit mortar volume or water/cement ratio alone. This shows that a new indicator is needed that incorporates both the quantity and the quality of cement hydrate. Assuming that Ca^{2+} ions move through continuous pores in the cement hydrate structure, we proposed a new index that is equivalent to pore number, or the pore area divided by the circular pore

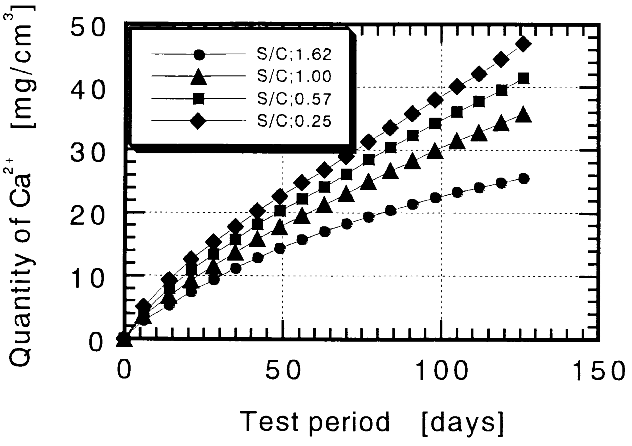

Fig. 5. Cumulative quantity of dissolved Ca^{2+} (1).

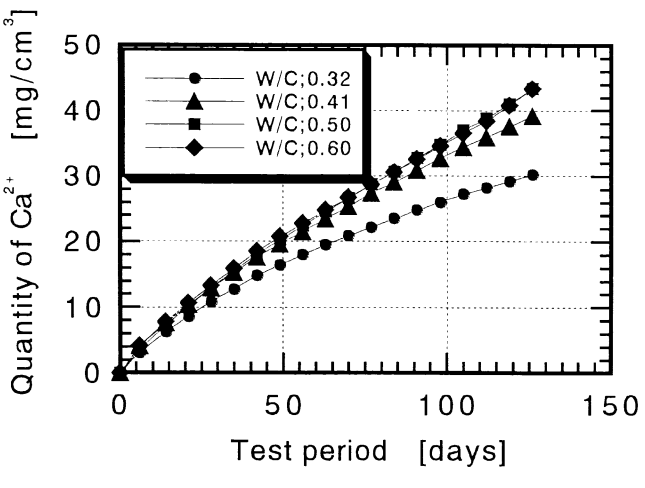

Fig. 6. Cumulative quantity of dissolved Ca^{2+} (2).

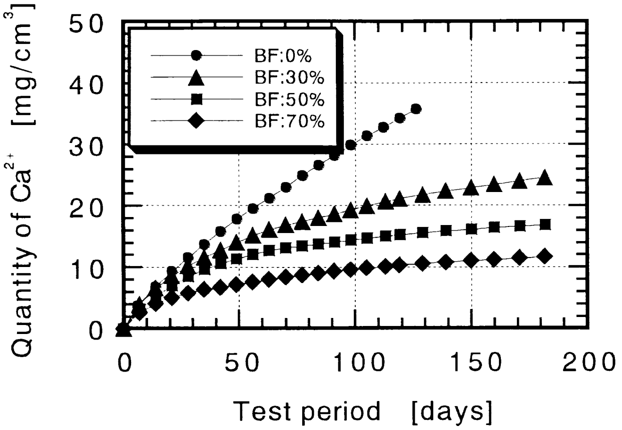

Fig. 7. Cumulative quantity of dissolved Ca^{2+} (3).

area with the average radius obtained from the pore distribution. It was clarified that this index corresponds to the quantity of dissolved Ca^{2+} ion [8].

Fig. 7 shows the quantity of dissolved Ca^{2+} ion in the BF replacement test, and Fig. 8 shows that in the SF replacement test. The greater the BF or SF replacement ratio, the smaller the quantity of dissolved Ca^{2+} ion. Fig. 9 shows the relationship between the pozzolanic admixture replacement ratio and the quantity of dissolved Ca^{2+} ion. The quantity of dissolved Ca^{2+} ion decreased sharply with replacement ratio. Thus, the decrease rate for SF replacement is larger than that for BF replacement. As discussed above, there was 20% to 40% less dissolved Ca^{2+} ion in the pozzolanic admixture replacement test than in the non-replacement test. These results show that the cement hydrate becomes hard to dissolve. This was considered to be because soluble $Ca(OH)_2$ content decreased due to BF or SF replacement.

Based on these results, concrete in which a part of the cement is replaced by pozzolanic admixture is more durable against leaching degradation because of the small $Ca(OH)_2$ content and the tight cement hydrate structure.

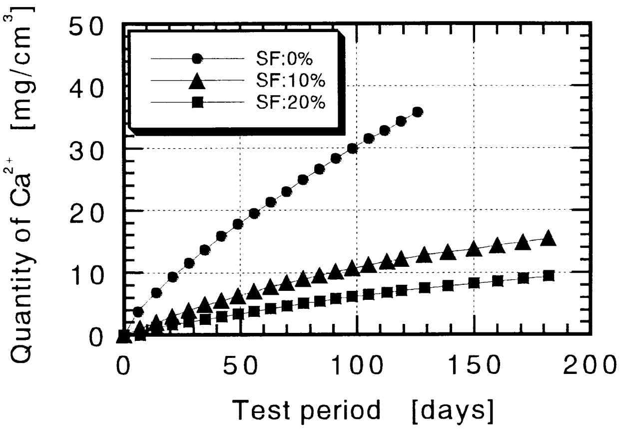

Fig. 8. Cumulative quantity of dissolved Ca^{2+} (4).

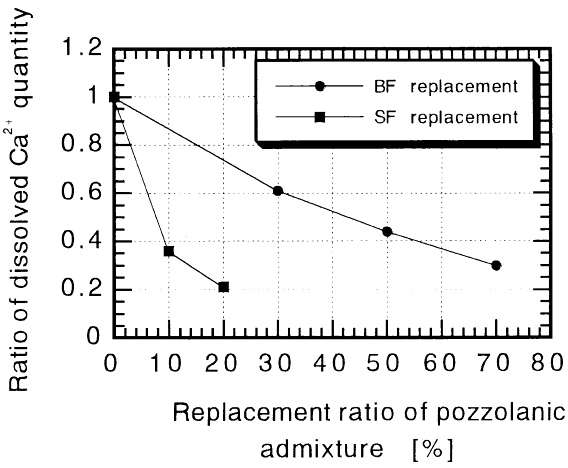

Fig. 9. Relationship between replacement ratio of admixture and dissolved Ca^{2+} ratio.

6. Degradation of specimen

The degraded region could be clearly distinguished visually in most specimens, because they were coarser than the undegraded regions. Table 6 shows the degradation thickness of the mortar, the length from cathode side surface to degradation boundary, and the quantity of dissolved Ca^{2+} ions. The degradation thickness corresponds well with the quantity of dissolved Ca^{2+} ions, and it shows a linear relation [8].

Based on the results obtained by X-ray diffraction and TG–DTA, the main minerals were confirmed to be $Ca(OH)_2$, C–S–H, and monosulfate in the undegraded region, as they were prior to the test, but only C–S–H in the degraded region.

Table 6
Degradation thickness

		Degradation thickness [mm]	Quantity of dissolved Ca^{2+} [mg]	Remarks
Sand content	No. 1	14.4	1258	S/C = 1.62
	No. 2	15.2	1757	S/C = 1.0
	No. 3	15.5	2034	S/C = 0.57
	No. 4	15.8	2303	S/C = 0.25
Water/cement ratio	No. 5	11.2	1449	W/C = 0.32
	No. 6	15.5	1925	W/C = 0.41
	No. 7	21.3	2130	W/C = 0.5
	No. 8	22.1	2128	W/C = 0.6
Admixture replacement	No. 9	15	1207	BF = 30
	No. 10	11	829	BF = 50
	No. 11	9	575	BF = 70
	No. 12	9	760	SF = 10
	No. 13	8	460	SF = 20

Table 7
Pore volume after test

		Degraded region		Undegraded region		
		PV [cm^3/cm^3]	PV/V_p [cm^3/cm^3]	PV [cm^3/cm^3]	PV/Vp [cm^3/cm^3]	Remarks
Sand content	No. 1	0.274	0.505	0.142	0.261	S/C = 1.62
	No. 2	0.317	0.482	0.139	0.212	S/C = 1.0
	No. 3	0.357	0.463	0.166	0.215	S/C = 0.57
	No. 4	0.417	0.471	0.185	0.209	S/C = 0.25
Water/cement ratio	No. 5	0.311	0.435	0.123	0.173	W/C = 0.32
	No. 6	0.338	0.474	0.150	0.210	W/C = 0.41
	No. 7	0.384	0.537	0.210	0.295	W/C = 0.5
	No. 8	0.444	0.622	0.244	0.341	W/C = 0.6
Admixture replacement	No. 9	0.226	0.344	0.148	0.225	BF = 30
	No. 10	0.193	0.293	0.123	0.186	BF = 50
	No. 11	0.201	0.305	0.147	0.224	BF = 70
	No. 12	0.261	0.397	0.171	0.260	SF = 10
	No. 13	0.221	0.336	0.155	0.235	SF = 20

The pore volumes and distributions obtained after the acceleration test are shown in Table 7 and Figs. 10–12, respectively. The pore volumes in the undegraded region were 5% to 18% less than those obtained at the beginning of the acceleration test. This shows that the cement hydrate structure became tighter during the 4- to 6-month test period. However, there was little change in the pore distribution. Comparing the undegraded and the degraded regions, the pore volume increased by about two times in the no-pozzolanic-admixture-replacement test. This shows that the cement hydrate structure became coarser with leaching. The pore volume increased markedly, not only for pores under 5 nm and in the range of 500 nm to 1 μm in diameter, but also in the range of 50 to 500 nm in diameter.

The pore volume increased by 40% to 50% in the pozzolanic admixture replacement test. This also shows that the cement hydrate structure became coarser with leaching. However, the rate of increase is smaller than that for the no-replacement test. Based on the results, the loss in strength and the increase in water permeability due to leaching are controlled by pozzolanic admixture replacement, because of the soluble small $Ca(OH)_2$ content. Pore distribution increased over whole range.

7. Relationship between water permeability and pore volume

The water permeability of the region degraded by leaching will increase with pore volume, because the cement hydrate structure becomes coarser. We adopt a new ratio, K_w/V_p (water permeability to cement paste volume). Fig. 13 shows the relationship between K_w/V_p and pore volume per cement paste volume (PV/V_p). K_w/V_p is shown in logarithmic scale. They show good correlation independent of pozzolanic admixture replacement: log K_w/V_p increases almost proportionally with PV/V_p. Based on this result, dissolution of cement hydrate causes an increase in water permeability due to an increase the porosity of the cement hydrate structure. Therefore, an increase in water permeability could be expected from an increase in pore volume in cement hydrate structure. It is thus necessary to relate the quantity of dissolved Ca^{2+}

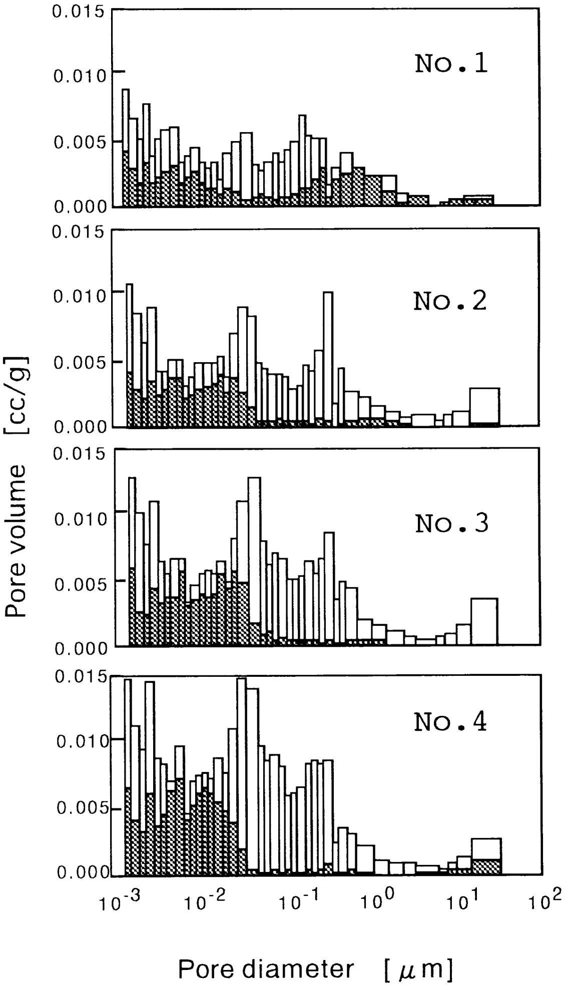

Fig. 10. Pore size distribution (S/C) (hatched: undegraded; unhatched: degraded).

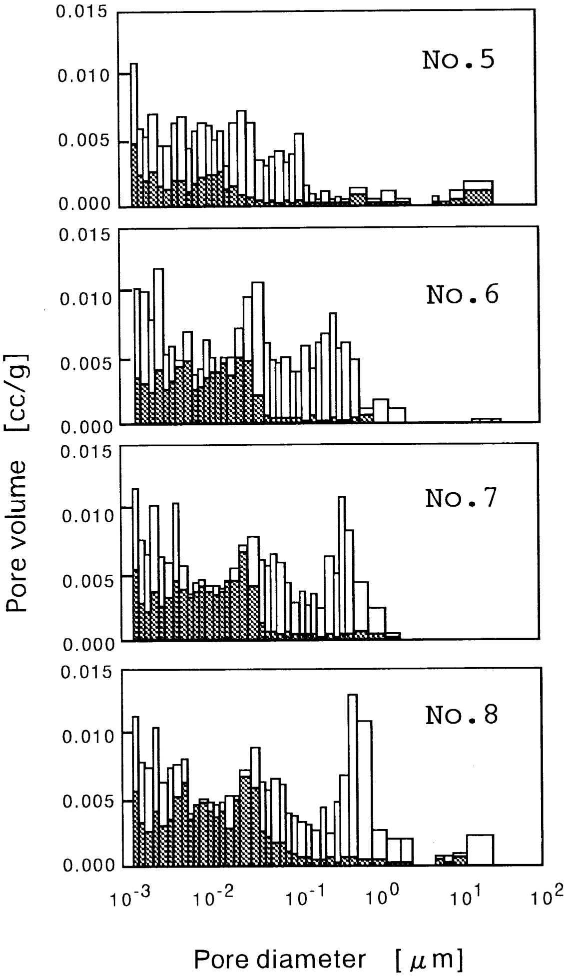

Fig. 11. Pore size distribution (W/C) (hatched: undegraded; unhatched: degraded).

ions to the pore volume in the cement hydrate structure. That is a task for the future. Comparing replacement with non-replacement of pozzolanic admixture, it is especially noteworthy that water permeability in the degraded region increased by about two orders of magnitude in the non-replacement test, but by one order of magnitude in the replacement test, while water permeability in the undegraded region in both tests were the same: 10^{-13} [m/sec]. This is because of the small increase in pore volume due to dissolution of the cement hydrate, as described in Section 6. Therefore, it is judged that replacement of pozzolanic admixture controls the increase in water permeability after degradation due to leaching.

8. Relationship between compressive strength and pore volume

Fig. 14 shows the relationship between compressive strength and pore volume. The compressive strength of the degraded specimens was 20% to 60% that of the undegraded specimens. It was clarified that compressive strength decreased greatly with dissolution of the cement hydrate. It is clearly seen that the compressive strength decreases as the pore volume increases. Thus, the loss of strength is caused mainly by a change in the cement hydrate structure to a porous structure due to dissolution of hydrates. From the viewpoint of pozzolanic admixture replacement, the loss of strength can also be explained by increase in pore volume. Thus, the loss is smaller than for non-replacement. This is due to the small increase in pore volume due to dissolution of the cement hydrate, as described in Section 6. Therefore, it is judged that replacement of pozzolanic admixture also controls the loss of compressive strength after degradation due to leaching.

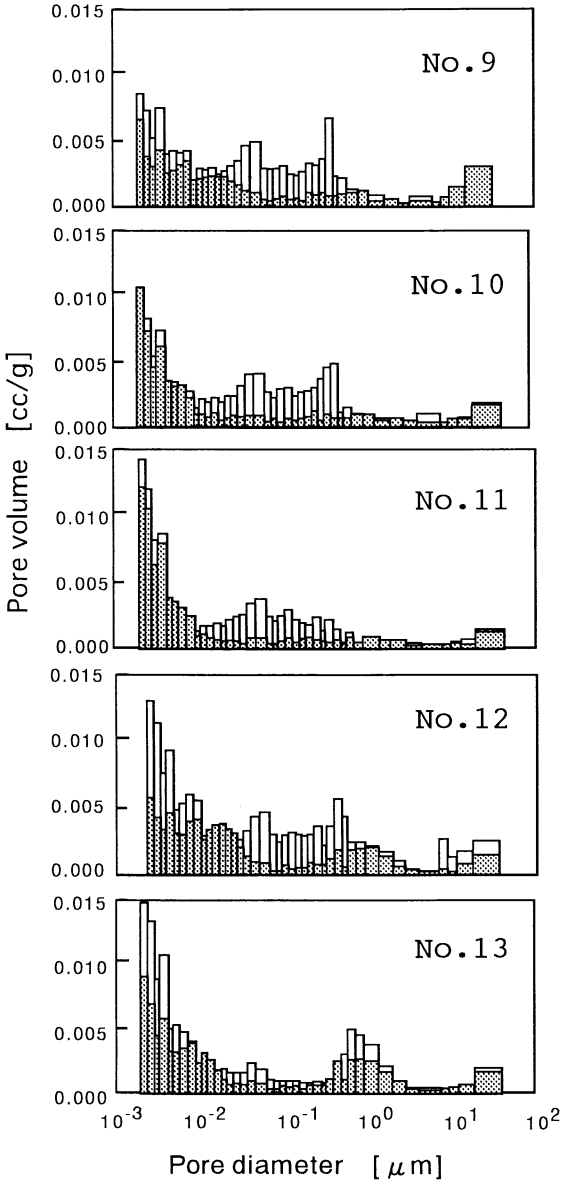

Fig. 12. Pore size distribution (BF, SF) (hatched: undegraded; unhatched: degraded).

9. Conclusions

Leaching tests were carried out on different mortars using an electrochemical method that accelerates the dissolution of cement hydrate from mortar in contact with water, by applying a potential gradient across the specimen. Sand cement tests were carried out to determine differences in the quantity of cement hydrate. Tests were carried out on water/cement ratio and pozzolanic admixture (BF and SF) replacement of part of the cement tests to determine differences in the quality of cement hydrate. The differences in Ca^{2+} ion dissolving speed and the changes in water permeability and compressive strength due to dissolution of the cement hydrate were discussed. The results are the following.

(1) The characteristics of the cement hydrate structure reflect differences in mix proportions and pozzolanic admixture. In particular, pozzolanic admixture replacement decreases $Ca(OH)_2$ content to from a tight cement hydrate structure.

(2) The amount of Ca^{2+} ions entering the water varied with the mix proportions. It decreased with sand content, but increased with water/cement ratio. It also varied with the kind of pozzolanic admixture and replacement ratio. It decreased as the replacement ratio increased, and it was 20% to 40% that for non-replacement. It is judged that these results reflect differences in the quantity and quality of the cement hydrate structure.

(3) In the sand content tests and water/cement ratio tests, pore volume of degraded specimens increased by 1.6 to 2 times. In the pozzolanic admixture replacement test, it increased by 40% to 60% that of the undegraded samples. The rate of increase was smaller than that for non-replacement. These results indicate that pozzolanic admixture replacement decreased $Ca(OH)_2$ content.

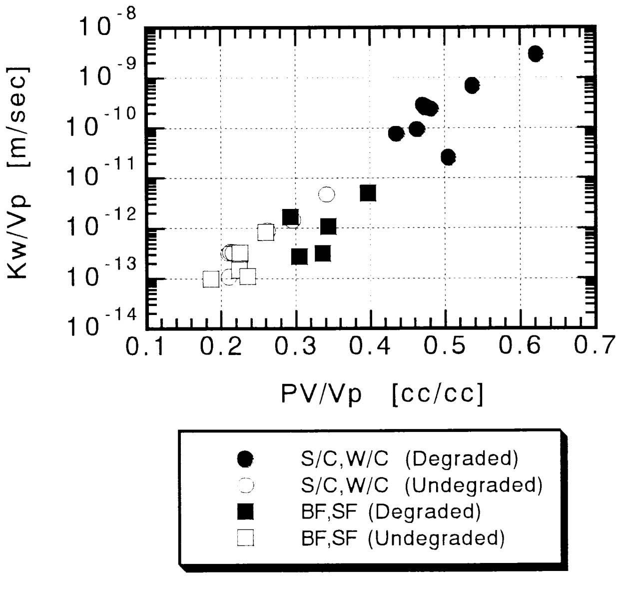

Fig. 13. Relationship between PV/V_p and K_w/V_p.

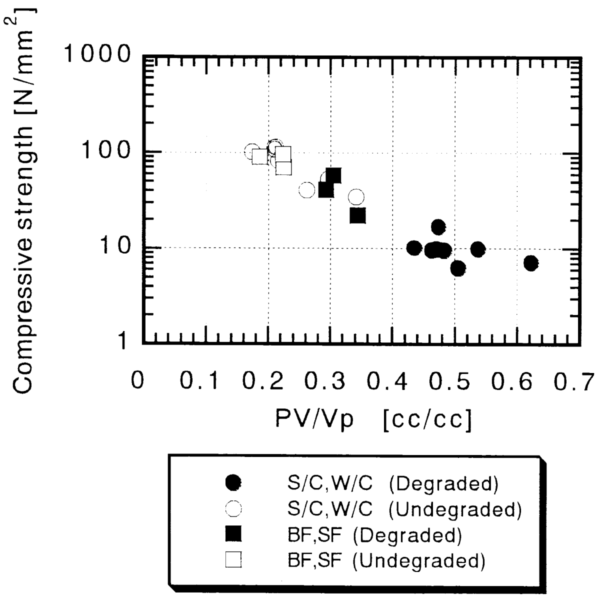

Fig. 14. Relationship between PV/V_p and compressive strength.

(4) The water permeability of the mortar specimen increased by about one to two orders of magnitude due to leaching degradation. There was good correspondence with the increase in water permeability and that of pore volume due to leaching degradation.

(5) The compressive strength of degraded mortar specimens decreased by 20% to 60% that of undegraded specimens. There was good correspondence with compressive strength and pore volume. Thus, the loss of compressive strength was determined from the increase in pore volume due to leaching.

(6) Pozzolanic admixture replacement for a part of the cement is very useful for mix proportion design of a durable concrete that resists leaching and shows small loss of performances after leaching.

References

[1] M. Roessler, I. Odler, Investigations on the relationship between porosity, structure and strength of hydrated portland cement pastes: 1. Effect of porosity, Cem Concr Res 15 (2) (1985) 320–330.

[2] J.F. Young, A review of the pore structure of cement paste and concrete and its influence on permeability, Permebility of Concrete, 1988, pp. 1–18 (ACI SP-108).

[3] H. Saito, S. Nakane, Comparison between diffusion test and electrochemical acceleration test for leaching degradation of cement hydration products, ACI Mater J 96 (2) (1999) 208–211.

[4] P. Faucon, B. Gerard, J.F. Jacquinot, J. March, Water attack of cement paste: Towards an improved accelerated test? Adv Cem Res 10 (2) (1998) 67–73.

[5] P.W. Brown, J.R. Clifton, Mechanism of deterioration in cement-

based materials and in lime mortar, Durability Build Mater 5 (1988) 409–420.

[6] T. Nishikawa, K. Suzuki, Chemical conversion of C–S–H in concrete, Cem Concr Res 24 (1) (1994) 176–182.

[7] J.A. Larbi, Microstructure of the interfacial zone around aggregate particles in concrete, HERON 38 (1) (1993) 37–39.

[8] H. Saito, S. Nakane, Y. Tsuji, A. Fujiwara, Effect of different cements and mix proportions on results obtained with accelerated electrochemical leaching test, Concr Libr JSCE 31 (1998) 255–273.