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RELATIONSHIP BETWEEN STRUCTURE AND PENETRABILITY OF Na ION IN HARDENED BLENDED CEMENT PASTE, MORTAR AND CONCRETE

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1. INTRODUCTION

The penetrability of alkali ions in hardened mortar and concrete is regarded as one of the most important properties influencing the resistance to alkali-aggregate reaction(AAR). The control of ionic penetrability is absolutely essential to inhibiting AAR in the hardened specimens. Some researchers studied the relationship between the structure and the penetrability of ion including water in hardened cement paste (1)(2)(3). Since there is a wide difference in the pore and hydrated structure among hardened cement paste, mortar and concrete (4), the direct application of the experimental results of hardened paste to mortar and concrete may draw an incorrect conclusion.

In this study, the relationship between the structures and penetrability of Na ion in hardened cement paste, mortar and concrete prepared with ordinary Portland cement and several kinds of blending component with various ages and alkali contents cured at various temperatures was investigated and the factors controlling the penetrability of alkali ions in hardened cement paste, mortar and concrete and the inhibitory effect of blending component were also studied.

2. SAMPLE AND SAMPLE PREPARATION

Characters of ordinary Portland cement (ordinary cement) and blending components used for the experiment are shown in **Table 1.** Blastfurnace slag cement contains 50% of slag (slag cement)and fly ash cement contains 25% of fly ash (fly ash cement). Silica fume blended cement paste, mortar and concrete were molded in such a way that 10% of silica fume to 100% of cement was added to the mixing water and dispersed in it and then the other materials were mixed with them (silica fume cement). Characters of aggregate used and mix proportion are shown in **Table 2** and **3**, respectively. KOH was mixed with some specimens so that the total alkali (R_2O) content in cement would be 1.2%.

3. EXPERIMENTAL METHODS

3.1 Characterization of hardened specimen

The amounts of $Ca(OH)_2$ and combined water in hardened specimen were measured by the DSC and ignition loss methods. Distribution and composition of hydrates in the hardened specimens were measured by CMA/EPMA, respectively. Capillary pore structure in hardened specimens were determined by a newly developed mercury porosimetry (5).

3.2 Measurement of diffusion coefficient and diffusion route of Na ion

The diffusion coefficient was measured by the diffusion cell method (3). The volume of cell for paste and mortar was 125ml and that for concrete was 200ml. The penetrability surface for cement paste and mortar was a circle with a diameter of 2cm and that for concrete was a circle of 4cm. The thickness of test specimens of paste, mortar and concrete were 1.5, 3 and 4mm, respectively.

Table 1 Character of cement and blending component

sample	chemical composition (%) CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	Total	Bl*1 (cm^2/g)	density (g/cm^3)	mineral*2 phase(%)
cement	64.4	22.0	5.4	3.0	1.5	2.0	0.2	0.6	99.1	3,300	3.15	
blastfurnace slag	42.9	33.9	15.1	0.4	6.3	0.9	0.2	0.6	100.3	3,950	2.71	Me: 1.1
fly ash	4.5	60.3	17.9	10.1	1.5	0.2	0.7	0.9	96.1	3,420	2.50	Q: 15, M: 17
silica fume	1.5	83.7	1.7	2.1	1.0	0.3	0.8	1.1	92.2	-	2.6	Q: 2.5

*1; Blaine specific surface area, *2; Me: melilite, Q: quartz, M: mullite

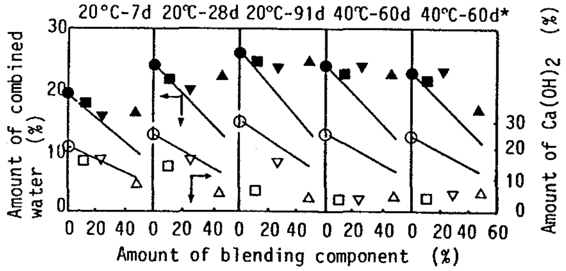
Table 2 Character of aggregate

aggregate	kind (rock facies)	density (g/cm^3)	fine modulas	range of size(mm)	use
fine sand	pit sand	2.59	2.78	5>	mortar, concrete
coarse aggregate	crushed stone (hard sand stone)	2.68	6.22	5-13	concrete

Table 3 Mix proportion of test specimens

specimens	weight % W	C	S	A	volume % paste	S+A
paste	33.3	66.7	0	0	100	0
mortar	14.3	28.5	57.1	0	51.9	48.1
concrete	6.4	12.9	28.7	52.0	25.4	74.5

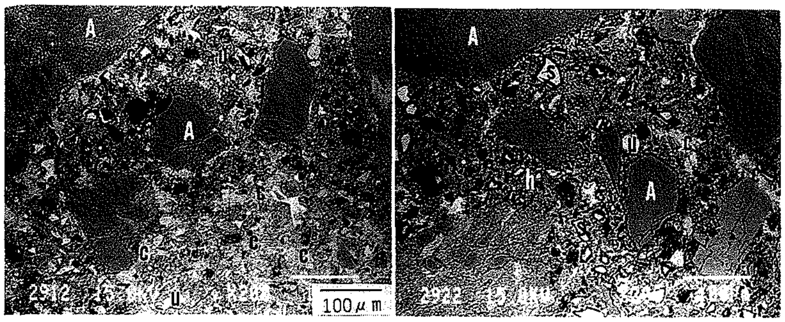
W: water, C: cement, S: sand, A:aggregate



○●: ordinary Portland cement,
△▲: blastfurnace slag cemet containg 50% of slag (slag cement)
▽▼: fly ash cement containing 25% of fly ash (fly ash cement)
□■: silica fume blended cement containg 10% of silica fume (silica fume cement)
*: KOH added as 1.2% of R_2O

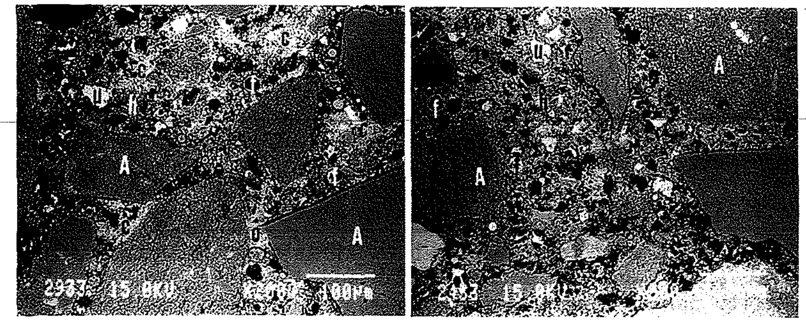
Fig. 1

Amount of combined water and $Ca(OH)_2$ in hydrated cement paste (W/C=0.5)



Ordinary Portland cement concrete(20℃, 91days)

Slag cement concrete (20°C, 91days)



Fly ash cement concrete (20℃, 91days)

Fly ash cement concrete (40℃, 60days)

A: aggregate, c: $Ca(OH)_2$, f: fly ash, h: C-S-H phase, s: slag, u: unhydrated cement particle

Fig. 2

Back scattered elecron image on the polished surface of hardened concrete (W/C=0.5)

The diffusion coefficient was calculated by Fick's diffusion formula 1):

$$D = 1/A \times L/C_0 \times dQ/dT \quad \text{---------} \quad 1)$$

where D is diffusion coefficient of ion, A is area of penetrability, L is thickness of test specimen, Co is concentration of diffusion solvent, and dQ/dt is rate of penetration. The measurement was made after confirming that the measurements did not vary according to the sample size. 1N NaOH solution was used as the diffusion solvent. The rate of penetration was calculated by measuring the concentration of Na in the pure water cell at a specified interval by flame photometry. The distribution of Na on the vertical surface in the hardened specimens used for the penetration test were measured by CMA/EPMA.

4. RESULTS AND DISCUSSIONS

4.1 Structure of hardened specimens

4.1.1 Amounts of $Ca(OH)_2$ and combined water

Although hydrates such as C-S-H, monosulfate hydrate and $Ca(OH)_2$ were found in hardened cement paste, mortar and concrete, ettringite was hardly observed. The amounts of $Ca(OH)_2$ and combined water in hydrated cement pastes are shown in **Fig. 1.** The amount of combined water is an index of hydration degree and that of $Ca(OH)_2$ is an index of the degree of pozzolanic reaction. The straight lines shows the amounts of combined water and $Ca(OH)_2$ produced from the portion of Portland cement contained in each cement and deviation from the line shows the consumption of $Ca(OH)_2$ by the pozzolanic reaction with the blending component.

The pozzolanic reaction took place at 7days in slag cement, at 7 to 28days in silica fume cement and at 28 to 91days in fly ash cement cured at 20°C. The degree of pozzolanic reaction at 91days in both silica fume and slag cements were high, while that in fly ash cement was much lower than those in both cements. The pozzolanic reaction proceeded rapidly at 40°C for 60 days in fly ash cement. The pozzolanic reaction, however, did not proceed so rapidly in slag cement. Accordingly the difference in the dependence of curing temperature upon the pozzolanic reaction between the blending components was clarified. The addition of K_2O to cement, especially to slag cement, depressed the hydration. The phenomenon was similar to the effect of alkali on ordinary cement(6).

The hydration reaction was temporally accelerated sometimes in hardened mortar and concrete up to 7days because the precipitation site is increased by the aggregate(7). However, the amounts of combined water and $Ca(OH)_2$ of the paste parts in hardened specimens cured for 7days are almost the same as those in cement paste. The same results were obtained in those of blended cements.

4.1.2 Structure in hardened specimens and composition of C-S-H

Although there is no intrinsic difference in structure of paste parts between hardened specimens, a characteristic structure is formed on the interface between the paste and the aggregate in mortar and concrete as called transition zone(5). **Fig. 2** reveals that transition zone was increasingly filled with hydrate as the age advanced and the precipitation of $Ca(OH)_2$ in this region depended upon the type of cement. A large amount of $Ca(OH)_2$ was produced on the transition zone in ordinary and fly ash cement concretes cured at 20°C for 91 days, which only a small amount of $Ca(OH)_2$ was produced there in slag cement concretes because of high addition and high pozzolanic reactivity. Silica fume cement concrete showed the same tendency. The layer of $Ca(OH)_2$ formed on the surface of aggregate is thinner and the structure was denser in fly ash cement concrete cured at 40°C for 60days than those in slag cement concrete cured at 20°C for 91days. Unhydrated cement particles were increased by adding K_2O.

Table 4 shows the mean composition of C-S-H in hardened concrete. Many researches on cement paste have been reported (8)(9)(10). According to these reports, the molar ratio of Ca/Si in C-S-H produced in ordinary, slag, fly ash and silica fume cement pastes were 2.0 to 1.6, 1.8 to 1.5, 1.4 to 1.1 and 1.5 to 1.2, respectively. The average molar ratio of Ca/Si in C-S-H in those hardened concretes cured at 20°C for 91days were 1.8, 1.5, 1.7 and 1.3, respectively. Although the ratio of fly ash cement concrete was unexpectedly high because the pozzolanic reaction did not so proceed at 20°C, the ratio in concrete cured at 40°C for 60days sharply decreased to 1.2. The amount of alkali in C-S-H increases with the decreases of the Ca/Si ratio in C-S-H.

4.1.3 Pore structure in hardened specimens

The water void in hardened cement paste includes capillary pore space and gel pore space. The models of capillary and gel pore assumed as a cylinder had diameters of 6nm or more and below that, respectively (5). The cumulative pore size distribution of paste cured are shown in **Fig. 3.** The capillary pore volume in ordinary cement paste cured at 20°C for 7days was the lowest and the maximum pore diameter was the smallest as much as 100nm. Hardened fly ash cement paste was most porous. Each cement paste cured for 91days became so dense that there was little difference between pore structure. Although the total pore volume in cement paste cured at 40°C for 60 days was similar to that cured at 20°C for 91 days, pore size distribution largely depended upon the type of cement. The production of fine hydrates was increased and the maximum pore diameter was decreased in fly ash cement cured at to 40°C. In the other pastes, however, the capillary pore with diameters from 10 to 30nm were increased. The differences in pore structure among the types of cement were also increased by adding an alkali. Especially in slag cement paste, the capillary pore volume was markedly increased and the maximum pore diameter was shifted to the larger side by adding an alkali, while the structure of silica fume cement paste was densified.

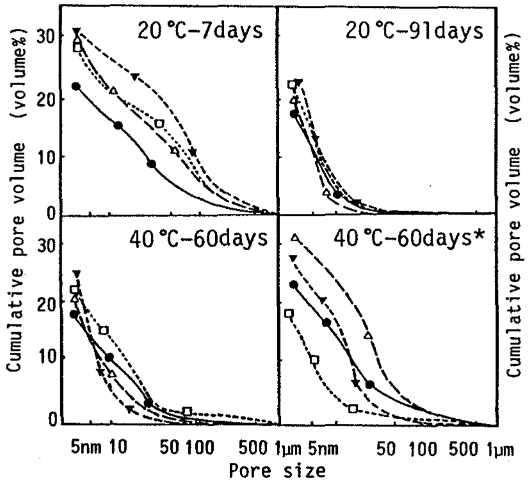
The cumulative pore size distribution in hardened specimens are shown in **Fig. 4.** The maximum pore diameter hardly decreased in mortar and concrete, compared with that in paste, though the capillary pore volume decreases with age. The pores 10 to 200nm in diameter in cement paste, those 30 to 500nm in mortar and those 50nm to 1μm in concrete markedly decreased with age. Since a large volume of coarse pore still remained in mortar and concrete even at advanced age, the transition zone between the aggregate and the paste was hardly densified. The capillary pore volume in slag cement paste, mortar and concrete cured at 20°C decreased at advanced age and the maximum pore diameter shifted to smaller, while pore 20 to 300nm in diameter in fly ash and silica fume cement concretes cured at 40°C markedly decreased. These phenomena are probably caused by the reason why the pore in the transition zone were filled with hydrates formed by the pozzolanic reaction of blending components.

4.2 Diffusion coefficient of Na ion in hardened specimens and diffusion route

The relationship between the diffusion coefficient of Na ion in hardened specimens is shown in **Fig. 5.** The diffusion coefficient of Na ion in cement paste was 0.2 to 20cm^2/s, decreasing with age. Among the diffusion coefficients in cement paste cured at 20°C, that in fly ash cement paste was the highest and that in slag cement paste were the lowest. Those in ordinary and silica fume cement paste were intermediate. The diffusion coefficient in cement paste cured at 40°C did not vary so much according to the type of cement. The diffusion coefficient of Na ion in mortar varied within the same range as that in cement paste. The effect of the type of cement on the diffusion coefficient in mortar was also almost the same as that in cement paste. Although the diffusion coefficient in concrete cured at 20°C was similar to that in cement paste, the effect of the type of cement on the diffusion coefficient in concrete was much different from the others. The diffusion coefficient in ordinary and fly ash cement concretes were the highest and almost the same as each other. That in silica fume cement concrete was the next highest and that in slag cement concrete was the lowest. However, the order of the diffusion coefficient in

Table 4 Composition of C-S-H in hardened concrete (W/C=0.5, 20℃, 91days)

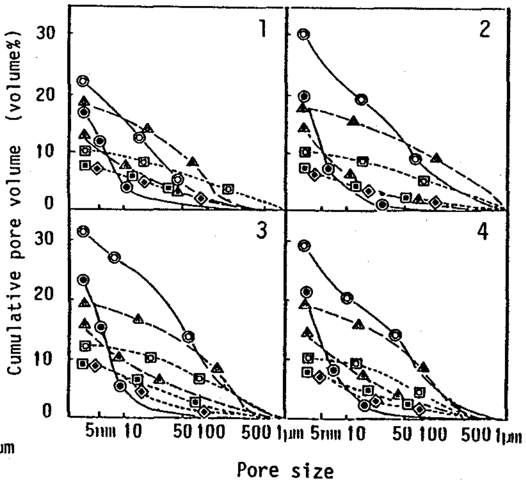
specimens	Ca/Si molar ratio	content(%) Na₂O	K₂O
ordinary Portland cement	1.8	0.03	0.10
blastfurnace slag cement containing 50% of slag	1.5	0.07	0.15
fly ash cement containing 25% of fly ash	1.7	0.05	0.12
ibid. 40℃, 60days	1.2	0.10	0.18
silica fume cement containing 10% of silica fume	1.3	0.10	0.25



●: ordinary Portland cement, △: slag cement
▼: fly ash cement, □: silica fume cement
*: KOH added as 1.2% of R₂O (detail in Fig. 1)

Fig. 3

Cumulative pore size distribution of hardened cement paste (W/C=0.5)



1: ordinary Portland cement, 2: slag cement
3: fly ash cement, 4: silica fume cement
*: KOH added as 1.2% of R₂O (detail in Fig.1)

	20℃-7d	20℃-91d	40℃-60d
cement paste	◎	◉	
mortar	△	▲	
concrete	⊡	▣	◈

Fig. 4

Cumulative pore size distribution of hardened cement paste, mortar and concrete (W/C=0.5)

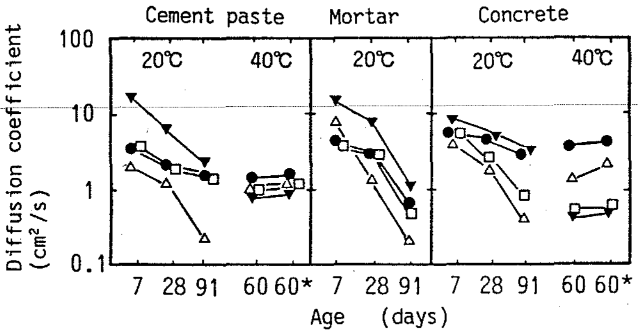


Fig. 5

Apparent diffusion coefficient of Na ion in hardened cement paste, mortar and concrete (W/C=0.5)
(same notation as in Fig. 3)

concretes cured at 40℃ was ordinary cement > slag cement > fly ash cement = silica fume cement concretes. The diffusion coefficient was hardly changed by the addition of K_2O. As later mentioned, diffusion of Na ion seems to be affected by structure of hardened specimen as well as the pore structure.

Fig. 6 shows back scattered electron image of hardened ordinary and slag cement concrete used for the penetrability test. Although Na was unevenly distributed in the vicinity of the aggregate where $Ca(OH)_2$ was produced in hardened ordinary cement concrete, it was scarcely distributed in the phase of C-S-H. Meanwhile, Na was more distributed in the phase of C-S-H, though it was not markedly distributed in the vicinity of the aggregate in slag cement concrete. The amount of Na distributed in the phase of C-S-H was 0.2% in concrete of ordinary cement and 0.4% in that of slag cement. Comparing those values with those of hardened concrete not used for the penetrability test, Na was proved to be fixed or adsorbed on the phase of C-S-H more abundantly in slag cement concrete. The same tendency was observed in paste and mortar. These results indicate that an alkali ion moved through the coarser region where $Ca(OH)_2$ is precipitated and the coarser capillary pores in hardened cement paste, while it moved mainly through the transition zone around the aggregate in hardened concrete. Although radius of K ion is different from that of Na ion, K ion is considered to diffuse in hardened specimens in the same manner of Na ion.

4.3 Factors affecting diffusion coefficient of Na ion

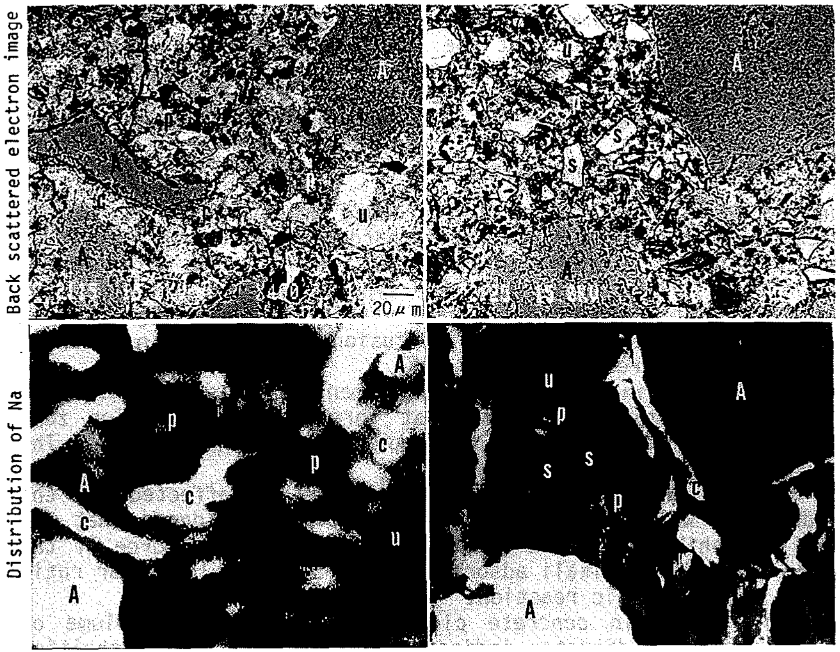
4.3.1 Effect of pore structure

Ions penetrate the hardened specimen either moving through the pore accompanied with liquid or diffusing through the solid phase or liquid phase staying in the closed pore. The former penetration is much more than the latter one (5). The relationship between the cumulative pore volume with a larger diameter to a smaller one (1μm-100nm, -50nm, -20nm, -10nm, -6nm and -3nm) and the diffusion coefficient of Na was analyzed and pore volume with diameters of 50nm or more had the closest relation with diffusion coefficient in hardened cement paste, mortar and concrete as shown in **Fig. 7.** The relationship was roughly expressed by a straight line for concrete independently of the type of cement, while it was roughly expressed by separate two lines for mortar and paste. Hardened specimen with slag, silica fume and fly ash cement cured at 40℃ with high pozzolanic reaction degree were expressed by the one line and those of ordinary and fly ash cement cured at 20℃ were expressed by the other one. The diffusion coefficient in the former was twice as high as that in the latter at the same pore volume. These results indicate that the diffusion of Na ion was affected by the composition of hydrate as well as pore structure in hardened specimens and it was affected by capillary pore volume of 50nm or more in diameter indicating the denseness of transition zone in hardened concrete.

4.3.2 Effect of structure of hardened specimens

Even at the same pore volume, the diffusion of Na was less in the hardened specimens in which the pozzolanic reaction proceeded than in that without pozzolanic reaction. It is considered that the pozzolanic reaction has two inhibitory effects. The one is to adsorb extraneous ions as well as a small amount of alkali contained in cement using C-S-H with low molar ratio of Ca/Si produced by this reaction. Since the surface of C-S-H is positively charged, so the alkali ion is repelled, the diffusion of it is inhibited. Meanwhile, the structure of hardened mortar and concrete with coarser pores is more densified as this reaction proceeds. Since the porous structure of $Ca(OH)_2$ phase in the transition zone abundant in coarser capillary pores 50nm or more in diameter is extinguished by the pozzolanic reaction and the transition zone is filled by fine C-S-H formed, Na ion hardly move in hardened mortar and concrete.

The standard test method for potential alkali reactivity of cement-



A: aggregate, c: $Ca(OH)_2$, p: C-S-H phase, s: slag, u: unhydrated cement particle

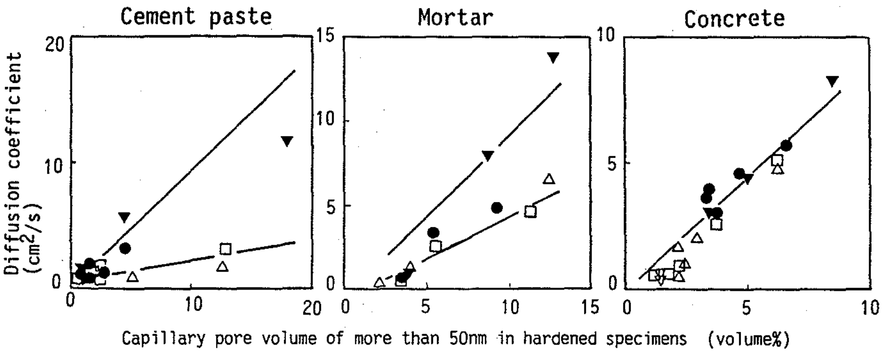
(Na is rich in white part)

Ordinary Portland cement concrete

Slag cement concrete with 50% of slag

Fig. 6

Back scattered electron image and x-ray image map of Na distribution on the polished surface of concrete (W/C=0.5, 20℃, 28days)



Note;

	20℃	40℃
ordinary Portland cement :	●	●
blastfurnace slag cement containing 50% of slag :	△	△
fly ash cement containing 25% of fly ash :	▼	▽
silica fume cement containing 10% of silica fume:	□	□

Fig. 7

Relationship between capillary pore volume of more than 50nm and apparent diffusion coefficient of Na ion in hardened specimens (W/C=0.5) aggregate combinations (mortar-bar method) specified in ASTM C227 is widely used for AAR. The test methods provides that the curing temperature is 37.8±1.7°C and practically used cement containing 0.6% or more of alkali as Na_2O. Those results indicate that mortar-bar method may underestimate the inhibitory effect by the addition of slag and overestimate the effect by that of fly ash.

5. CONCLUSIONS

1) The diffusion coefficient of Na ion in hardened cement paste is 0.2 to $20cm^2/s$. It depends upon the types of cement in hardened cement paste cured at 20°C and decreases with age. The diffusion coefficient in paste sufficiently cured at 40°C does not so largely depend upon the type of cement. The diffusion coefficient in hardened mortar and concrete vary within the same range as that in paste. However, the differences in the diffusion coefficient in concrete between the types of cement increase cured at 40°C.
2) The penetration of alkali in the hardened specimen includes the diffusion through capillary pore in cement paste and that through the transition zone between the paste and the aggregate. The latter predominates in concrete. The penetraion of alkali in mortar is intermediate.
3) The diffusion of Na ion in hardened cement paste is affected by the composition of hydrate as well as pore structure. It is considered that the diffusion of alkali is inhibited by the electromagnetic repulsion force of the positive charge generated by the alkali adsorption of C-S-H with low molar ratio of Ca/Si produced by the pozzolanic reaction.
4) The diffusion of alkali in concrete closely relates to the volume of capillary pore 50nm or more in diameter indicating the denseness of transition zone. The higher the pore volume, the larger the diffusion coefficient is.
5) Since the coarser pores, especially those 50nm or more in diameter, in concrete are also extinguished by the pozzolanic reaction, the movement of alkali ion through the coarser pores in the transition zone is inhibited. The diffusion and movement of alkali ion in hardened fly ash cement concrete cured at 20°C for 91 days are sometimes similar to those in ordinary portland cement because the pozzolanic reaction does not so proceed. The diffusion and movement of alkali ion are remarkably inhibited as the curing temperature is raised in fly ash concrete. The behavior in silica fume-blended cement concrete is similar to that in blastfurnace slag cement concrete when the curing temperature is low and that in fly ash cement concrete when it is high. Although the addition of K_2O loweres the reaction rate of hydration to coarsen the structure of hardened specimen, the diffusion coefficient of Na ion is not so affected when the pozzolanic reaction sufficiently proceeds.
6) Standard test method for potential alkali reactivity of cement-aggregate combinations (mortar-bar method) specified in ASTM C227 may underestimate the inhibitory effect of alkaline aggregate reaction by the addition of blastfurnace slag and overestimate thai inhibitory effect by the addition of fly ash at normal curing temperature.

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