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Long-term investigation of the properties on slag and fly ash cement and the appropriate curing condition

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ABSTRACT

This study reports on the property of several types of blast furnace slag (BFS) cement concrete and those obtained by adding fly ash (FA) and curing for 45 years in water. Ca leaching around the surface area of the specimens was confirmed, but compressive strength tended to develop with an increase in the BFS ratio for long-term curing. As for the BFS cement replaced with 30% FA, the compressive strength increased after 10 years. This suggests that adding FA contributes to the improvement in the long-term compressive strength of BFS cement. On the other hand, such type of blended cement is well known that importance to maintain moisture curing condition at early age. We evaluate the appropriate curing condition on the basis of durability and compressive strength using blended cement. We found that it is necessary to extend the curing period of ordinary portland cement concrete by two days for maintaining durability.

Keywords. blast-furnace slag, fly ash, durability, curing condition, compressive strength

1.INTRODUCTION

Concretes made from blast furnace slag (BFS) and fly ash (FA) cement have shown good performance in reducing expansion due to alkali silica reactions and chloride ingress compared with ordinary portland cement (OPC). In Japan, the blast furnace slag cement type B (BB), which contains a slag of 40–45%, is most widely used for the construction of civil structures, but the quantity of FA cement consumed is less than that for BB. Adding FA to the concrete using BB is a possible method as practical use because which contributes to the sustainability of the construction industry. Increasing the quantity of cement that contains BFS and FA is not only the most effective means for reducing CO_2 gas but it also reduces the amount of lime stone and energy use. However, because the early strength of these blended cements is usually lower than that of OPC, sufficient moist curing is necessary at an early age (JSCE, 2007). To understand the importance of early-age curing of BB, the relationship between the curing condition and durability of concrete has been investigated (Dan et al., 2009). It has been confirmed that to improve the strength and material movement resistance, early-age curing for three days or more is necessary for OPC and five days or more for BB. However, studies investigating how the compressive strength of a cement will change in a long term (after 50 and 100 years) are few in number. There is a necessity for enhancing the database regarding long-term variations in the various physical properties of concrete according to the usage and purpose of the structure in order to select the appropriate blended cement.Then, a concrete in which FA was added to BB was investigated as the first stage of the experiment by using specimens that were cured in water for 45 years in order to evaluate its strength and micro structure over a long term. Then, enough moist curing was provided to the concrete, and the potential performance of the concrete sample was evaluated. Next, as the second stage of the experiment, the curing conditions of this concrete sample were changed, and the influence of the curing condition on permeability was evaluated.

2. EXPERIMENTAL METHOD

2.1 Properties of concrete cured for a long term in water

2.1.1 Materials

The binders used in this study were manufactured until 1963~64 years; these binders include OPC, blast furnace slag cement type A (BA: slag-replacement ratio is 20%), type B (BB: 50%), type C (BC: 65%), low-heat blast furnace slag cement (LBB: 50%), BA replaced with 30% FA (BAF), and BB replaced with 30% FA (BBF). The cement used is prepared by crushing clinker in a ball mill. The ground granulated BFS obtained in a similar method was mixed with this cement and it was manufactured by the so-called separate crushing method. Table 1 shows the chemical composition and physical properties of the cement and FA used. Physical testing of the cement was conducted according to JIS R 5201-1964, and the Toyoura standard sand was used for the strength test.

Table 1.The chemical composition and physical properties of cement and FA

Sample code	Chemical composition(%)						Density	Blaine	Compressive Strength (MPa)		
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	(g/cm^3)	(cm^2/g)	3d	7d	28d
N	22.52	4.92	3.26	64.74	1.5	1.85	3.18	3080	11.4	19.6	41.1
BA	22.6	7.9	2.5	59.4	2.6	1.9	3.11	3930	9.9	21	42.8
BB	27.26	11.29	2.09	52.53	2.76	1.63	3.01	3940	8.3	14.7	37.4
LBB	26.24	10.83	2.51	52.94	3.42	2.18	3.02	3480	6.3	12.7	31.7
BC	27.32	15	1.46	48	4.6	2.16	2.98	3940	8.2	17.3	38.7
FA	61.82	28.07	3.81	2.09	0.72	0.3	2.06	3430	-	-	-

2.1.2 Concrete mixes and curing condition

The mixing proportion is shown in Table 2. Sea sand was used as the fine aggregate (specific gravity: 2.56 g/cm^3, F.M.: 2.76), and the natural river stone was used as the coarse aggregate (maximum size: 20 mm and specific gravity: 2.64 g/cm^3 and F.M.: 6.68). Water-reducing agents were not widely used, and plain concrete was used. The sand percentage is constant; the water content per unit volume of concrete is changed and adjusted to the constant slump value.

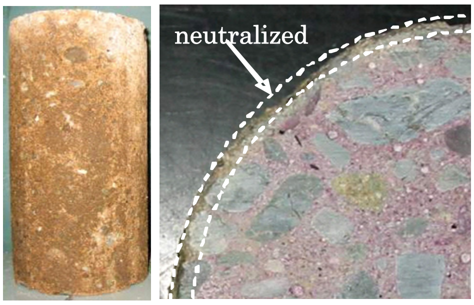
Moreover, the concrete temperature is influenced by the surrounding temperature and is in the range 9.0–23.0 °C because the temperature of the room was not constant during the experiment. The specimen was molded in the cylinders having dimensions of 5 cm × 30 cm and demolded on the next day and cured in the outdoor water tank for 45 years in the KitaKyushu City. The outdoor water tank is an environment that provides water for industrial use, and the tank is always filled.

Table 2. The concrete mix proportion

Sample code	Concrete placed date	Room Temp. (℃)	Concrete Temp. (℃)	Gmax (mm)	Slump (cm)	W/B (%)	s/a (%)	Unit weight (kg/m^3)				
								W	C	FA	S	G
N	Jan 07, 1964	13.0	12.0	20	19.0 ±1.0	63.0	42	189	300	-	753	1074
BA	Feb 27, 1964	10.5	10.5			63.0		189	300	-	753	1074
BAF	Apr 20, 1965	14.0	14.5			58.7		176	210	90	761	1077
BB	Nov 20, 1964	18.0	17.0			65.0		194	300	-	750	1067
BBF	May 22, 1965	23.0	23.0			60.7		182	210	90	756	1064
LBB	Dec 20, 1964	11.0	10.0			64.0		192	300	-	750	1069
BC	Jan 23, 1964	11.0	9.0			63.0		189	300	-	753	1074

2.1.3 Measurement of compressive strength and pore-size distribution

The compressive strength was measured according to JIS A 1108, at the ages of 7, 28, and 91 days and 1, 10, and 45 years. The specimen was discoloured to brown owing to underwater curing for 45 years, as shown in Figure 1. After spraying phenolphthalein onto the concrete cutting plane, about several mm was made a neutral from the surface of the concrete, and it was guessed that Ca was leaching for a long term. The mortar gathered from the central part of the concrete was adjusted to a practical size of 2.5–5.0 mm, a large amount of acetone was added, and hydration was stopped, then, the pore-size distribution was evaluated by mercury intrusion porosimetry.



Left: External appearance

Right: Cutting plane of the specimen to which phenolphthalein solution was applied

Photograph 1. Test piece after 45 years

2.2 Curing condition and durability on adding fly ash to slag cement

2.2.1 Materials

The material generally marketed now was used for this experiment. The density of OPC was 3.14 g/cm^3, and its Blaine fineness was 3150 cm^2/g, while the density and Blaine fineness of BFS were 2.91 g/cm^3 and 4000 cm^2/g, respectively. BB made from OPC and BFS substituted OPC by 50%. Then, 15% FA (density: 2.30 g/cm^3, blaine fineness: 3150 cm^2/g) was added to N and BB. The chemical composition of the binder is shown in Table 3. The fine aggregate has a maximum size of 5 mm. Its specific gravity, water absorption, and fineness modulus were measured to be 2.57 g/cm^3, 1.52%, and 2.68, respectively. The coarse aggregate has a maximum size of 20 mm. Its specific gravity, water absorption, and fineness modulus were measured to be 2.72 g/cm^3, 0.36%, and 6.58, respectively. The AE water-reducing agent is of the lignin type. The mix proportion and fresh properties of concrete are shown in Table 4.

Table 3. The chemical composition of used materials

	Density	Blaine	Chemical composition (%)												
	(g/cm^3)	(cm^2/g)	ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	Na_2O	K_2O	P_2O_5	Cl
N	3.14	3150	1.58	20.9	5.4	2.8	64.5	1.5	0.29	0.13	2.18	0.27	0.32	0.19	0.012
BFS	2.91	4000	0.12	33.5	14.6	0.3	43.3	5.4	0.55	0.15	1.92	0.27	0.33	0.01	0.004
FA	2.30	3100	1.82	58.1	21.4	4.9	6.0	1.1	0.99	0.03	1.35	0.68	0.84	0.35	0.001

Table 4. The concrete mix proportion on FA addition

Sample code	W/C (%)	s/a (%)	Unit weight(kg/m^3)						Flesh property		
			W	N	BB	FA	S	G	Slump (cm)	Air (%)	Concrete Temp. (℃)
N	55	48	172	313	-	-	843	967	12.0	5.2	21.8
N+FA				266	-	47	836	959	14.0	4.5	21.8
BB				-	313	-	838	961	11.0	4.5	21.4
BB+FA				-	266	47	832	954	14.0	4.0	21.8

2.2.2 Curing condition

The concrete was casted in cylinders having dimensions of φ100 × 200 mm^2; its upper surface was covered with a film to prevent dryness resulting from evaporation of moisture. The condition and methods of curing of each concrete are shown and Table 5 and Figure 1. According to the demolding period, the curing conditions were as follows. Demolding the specimen on the next day and maintaining a constant temperature in the room is referred to as D series, and sealing the mold for the required curing period is referred to as S series; demolding the specimen on the next day after placing in water for 28 days is referred to as W series. D, S, and W indicate the curing periods when dryness began. When BB contained FA, it thought the early-age curing to have a large the amount of the mixture material use, is very necessary, it differed from other conditions, 9 and 14 day of the sealed curing was added. Curing was conducted at a temperature of 20 °C and a relative humidity of 60% in the controlled constant-temperature room.

Table 5. Curing period

Curing condition	Dry curing D	Sealed→Demold S					Water curing W
Curing days	1	3	5	7	9	14	28
N	○	○	○	○	-	-	○
N+FA	○	○	○	○	-	-	○
BB	○	○	○	○	-	-	○
BB+FA	○	○	○	○	○	○	○

○ : Conducted

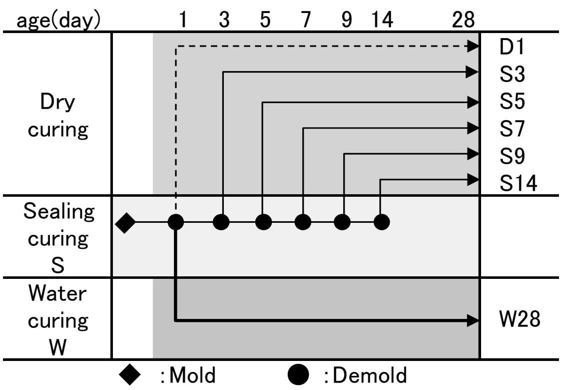


Figure 1. Curing conditions and method

2.2.3 Influence of curing conditions on compressive strength and mass transport property

(1) Measurement of compressive strength and mass loss of the concrete

The compressive strength of the specimen, which was cured under the abovementioned conditions, was evaluated as JIS A1108 at the ages of 7, 28, and 91 days. Moreover, the mass decrease rate defined the weight when the curing period ended as 100.

(2) Air permeability test

The concrete specimen was cut in into slabs having a thickness of 50 mm at 28 days, as shown in Figure 2, and set up the side in the testing condition that was able to hold constant pressure after having spread epoxy resin. The outline of the equipment is shown in Figure 3. The gas used for the air permeability test was exhausted using chokedamp so that the hydration product does not affect the concrete sample inside. The velocity of air permeability was requested from the amount of the gas that had been exhausted by applying a constant pressure of 4 kg/cm^2 from the upper surface of the specimen and collecting the chokedamp from the lower side of the concrete in water for a fixed period. The air permeability coefficient was calculated from the value obtained from the d'Alcy method.

(3) Water-absorption test in vacuum

The outline of the equipment is shown in Figure 4. Water was poured on to the specimen after the air permeability test ended so that half of the height of the specimen may be soaked in the container; it put on the vacuum chamber, and it absorbed. After absorption in the pump for one hour, vacuum maintenance was conducted for three hours; the concrete specimen was split and the absorbed area was confirmed to the specimen. The area ratio at which water rose to the sectional area (50 × 100 mm^2) of the entire specimen was calculated by image analysis, and it was defined as the ratio of water-absorption area in vacuum.

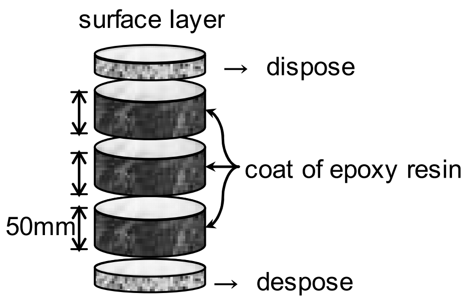


Figure 2. Pretreatment of specimen

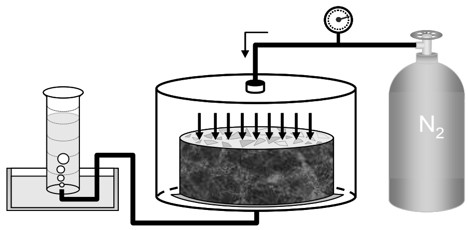


Figure 3. Gas permeability test

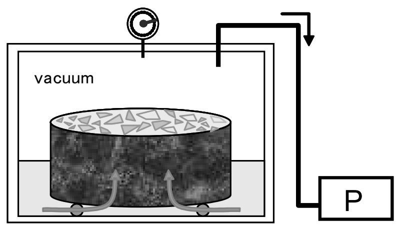


Figure 4. Water absorption test in vacuum

3. RESULTS AND DISCUSSION

3.1 Properties of concrete that was under water for long term curing

3.1.1 Compressive strength

The results of compressive strength measurement are shown in Figure 5. The water to cement ratio of each concrete is plotted in the figure, and these correspond to the values indicated on the right-side axis. Because concrete cured under outdoor conditions after demolding in winter, the strength is less than 10 N/mm^2 at 7 days; at 28 days, the strength tends to decrease with slag content owing to the addition of BB, LBB, and BC. The strength of BA at 91 days is larger than that of N; this is possibly because the specific surface area of BA is larger than that of N, as shown in Table 1. Moreover, the strength after one year is large because of an increase in the slag-replacement ratio.

As for BAF and BBF to which FA is added, because the unit volume of water is low even though the same slump is obtained because of FA addition, as shown in Table 2, W/B is about 5%. Thus, the compressive strength at 91 days was defined as 100 because W/B and the curing temperature are different according to the specimen; then, long-term strength was evaluated. This result is shown in Figure 6. The strength ratio of one year from the 91 days improved as the slag-replacement ratio increased. The strength of BC improves significantly from 1 to 10 years. On the other hand, the concrete to which FA was added showed a considerable improvement in strength after 10 years and is believed to be due to the extension of the hydration reaction over a long term. According to past research (Yoda, 2002), various slag cement concrete specimens were exposed to outdoor and indoor conditions for 40 years; it was shown that the increase in long-term compressive strength followed the order BC > BB > BA, and it was similar to the test result.

3.1.2 Pore-size distribution

The surface of the specimen aged 45 years increases compressive strength with the age though was observed the leaching. Then, mortar was gathered from the central portion of the specimen, pore-size distribution was measured, and its relationship with compressive strength was investigated. The pore distribution of the specimen using various blended cements is shown in Figure 7. It was confirmed that the number of fine pores having sizes of 20–1000 nm decreased with an increase in the slag-replacement ratio, and the number of fine

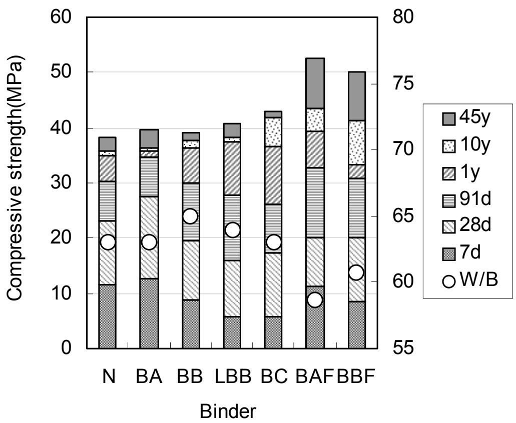


Figure 5. Compressive strength of concrete with each binder

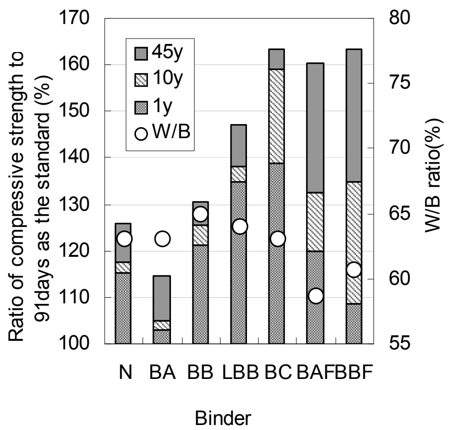


Figure 6. Ratio of compressive strength to 91 days as the standard

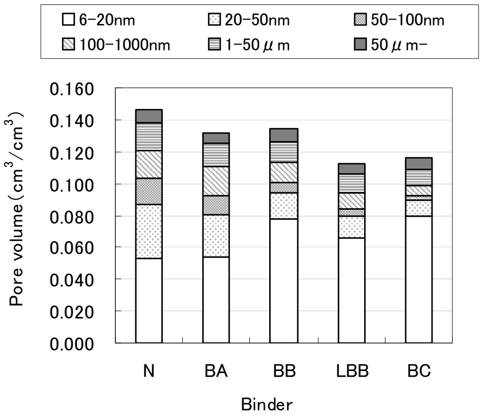


Figure 7. Micropore distribution: the central portion of concrete

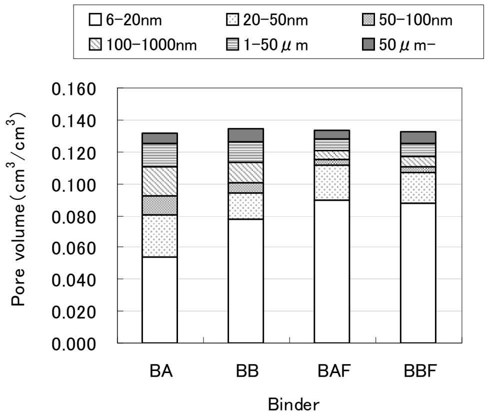


Figure 8. Micropore distribution: the central portion of concrete added FA

pores having sizes of 6–20 nm increased. According to past research (Nagao et al., 1990), it was reported that the slag-replacement ratio obtained from the evaluation of the pore-size distribution in the central portion of the outdoor specimen that was cured for 35 years by using BB was large, and the high slag content cement (slag-replacement ratio 83%) shifted to small pores diameter, and was a tendency similar to this result.

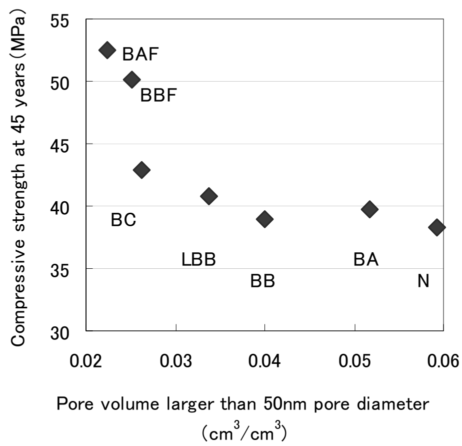


Figure 9. Relationship between pore volume larger than 50-nm pore diameter and compressive strength

The pore-size distribution of the concrete to which FA was added is shown in Figure 8. The pore volume of the 6–20 nm pores increased when FA was added to BA and BB, while the pore volume of the 20–1000 nm pores decreased. According to past research (Uchikawa et al., 1990), the pore size distribution of the concrete with a slag of 50% suggests that the pore volume of more 20-nm pores decreases remarkably compared with that in OPC, and the compressive strength of the blended cement shows that the pore volume of the 50-nm pores increases.

The relationship between a pore diameter of more than 50 nm and concrete compressive strength is shown in Figure 9. The pore volume of the 50-nm pores decreases as the replacement ratio of slag and FA increases, and the compressive strength increases. Especially, the compressive strength increases significantly in BAF and BBF as the pore volume of 50-nm pores decreases to less than 0.025 (cm^3/cm^3), and it is thought that the pozzolanic reaction of FA progressed over a long term.

3.2 Concrete curing condition and durability by adding fly ash to slag cement

3.2.1 Compressive strength

We were able to confirm that the strength of the BB specimen BB to which FA was added increased remarkably by curing in water for a long period. Then, the relationship between

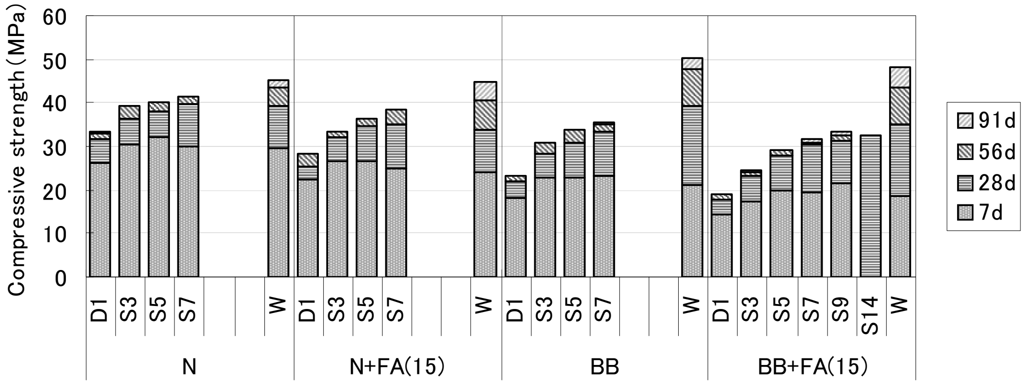


Figure 10. Compressive strength of concrete under different curing conditions

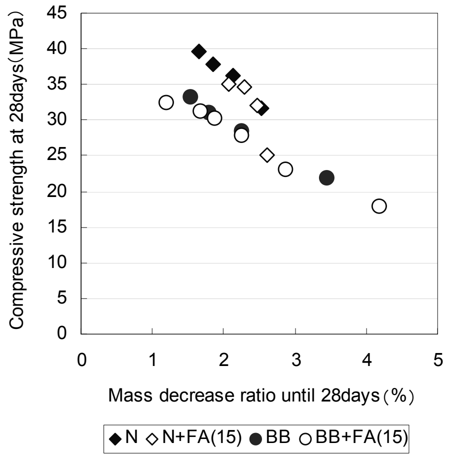


Figure 11. The relation between mass decrease ratio and compressive strength

the moist cure period and compressive strength was investigated referring to the curing condition at an actual construction site. The relationship between the curing condition and compressive strength is shown in Figure 10. In the condition of W, 91 days strength of BB and BB+FA that the amount of the mineral admixture is large improve compared with N and N+FA. Thus, blended cement is excellent in the long-term strength appearance, and Figure 5 shows a result that is similar to the result obtained under the curing condition in which enough water is provided. According to the relationship between the curing period and compressive strength, the strength of N and N+FA at 28 days obtained by conducting sealing and curing for five days or more is almost equal to W28. On the other hand, BB and BB+FA under S7 conditions show a strength of about 85% compared with W28, although the strength at 28 days improved as the curing period increased. Moreover, the strength of BB and BB+FA for D1 for the shortest curing period is about 50% compared with W28, and the strength changes remarkably from the initial curing condition compared with N and N+FA. The relationship between the mass decrease rate and the 28 days' compressive strength of the specimen under each curing condition is shown in Figure 11. The strength at 28 days tends to decrease in the specimen with a high mass decrease rate, and the amount of moisture evaporation and strength has implications. Moreover, the strength decreases because the amount of moisture evaporation in BB+FA is larger than that in BB. On the other hand, the mass decrease rate of N and N+FA is lower than that of BB and BB+FA, and the mass decrease rate is about 2.5%, even if it is maximum. Because the strength of a specimen that contains a lot of mineral admixture shows a low value owing to the influence of dryness, it is important to conduct sufficient moist curing in the first stage.

3.2.2 Mass-transport property

The relationship between the curing condition and air permeability coefficient is shown in Figure 12. The air permeability coefficient of N and N+FA shows a low value, since S3 though the air permeability coefficient of each binder shows high permeability in D1. The air permeability coefficient of BB and BB+FA gradually decreases from S3 to S5 and shows the same degree of air permeability as that shown by N and N+FA with S7. The air permeability coefficient of the specimen to which FA was added can be equal to the one to which FA was not added, and the durability can be secured by curing for five days or more, even if FA is mixed with BB.

The relationship between the curing condition and the ratio of water-absorption area in vacuum is shown in Figure 13. The ratio of water-absorption area in vacuum decreases as the initial curing term becomes long. This ratio contains a lot of mineral admixtures like BB and BB+FA decreases rapidly from D1 to S3 and it is gradually small over S3. Especially, when it exceeds S5, BB+FA indicates the same degree of value as BB, although this ratio is large in D1. It was confirmed that cement that contained a lot of mineral admixtures showed a mass transport property almost equal to that of N owing to the lengthening of the initial curing period as well as the air permeability coefficient.

The pore-size distribution of mortar in a concrete surface part and the central portion was investigated because the curing period was thought to influence the quality of the concrete surface part, and

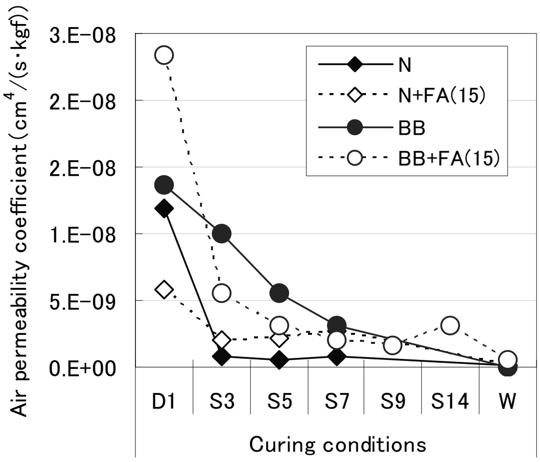


Figure 12. The relation between curing conditions and Air permeability coefficient

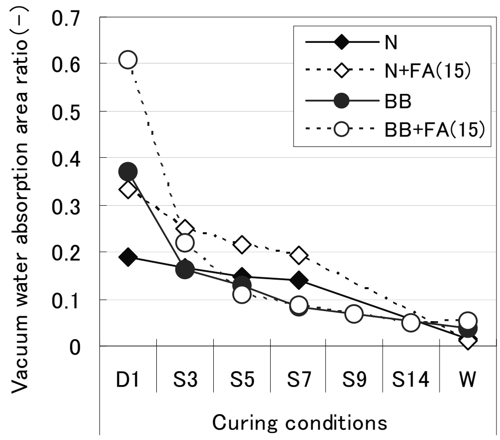


Figure 13. The relation between curing conditions and vacuum water absorption

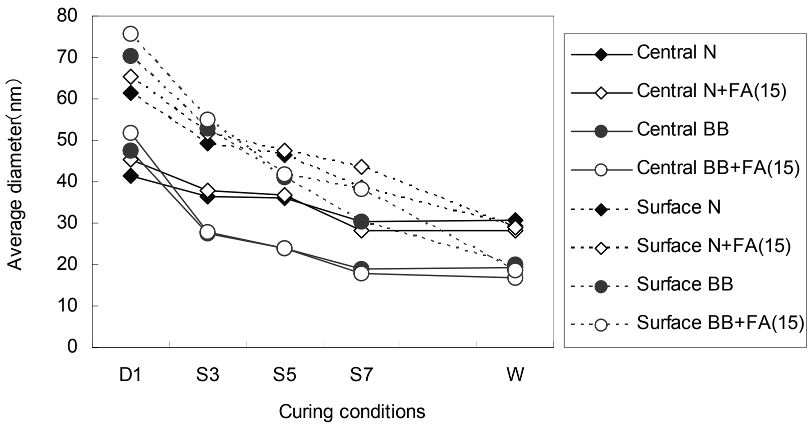


Figure 14. Effect of curing conditions on average diameter of pore

this is related to the mass-transport property (Okazaki et al., 2007). Figure 14 shows the average diameter of pores that change the curing condition at 28 days. As for the average diameter of the pores of BB and BB+FA at the center of the specimen, it shows almost same value, and adding FA does not influence the quality of a concrete. The average diameter of the pores decreases as the curing period becomes long on the surface area of specimen. The binder contains many mineral admixtures, the supply of water to the surface part becomes important for curing to improve the mass-transport property.

4. CONCLUSIONS

1) Concrete that is made from various cements was confirmed to show an improvement in the long-term strength because of an increase in its slag-replacement ratio resulting from outdoor water curing for 45 years. The compressive strength ratio of 45 years at 91 days about 120% for N, about 140% for LBB, and about 160% for BC. The strength of the concrete in which FA is substituted by BA and BB by 30% is improved by 50% until 10–45 years at 91 days, and hydration progresses to FA in an enough moist environment for the long term.
2) As for the BB specimen to which FA is added, the pore volume of 20–1000 nm pores decreases, and the pore volume of 6–20 nm pores tends to increase, and this specimen becomes a remarkably dense structure if water curing is conducted for a long term.
3) As for the relationship between concrete curing condition and durability that substitutes FA for BB by 15%, the strength at 28 days is improved as the curing period becomes long, and it is more effective to conduct sealing and curing for at least 5 days. The binder that contains a lot of mineral admixtures supplies enough water in the initial stage, and thus, the strength is improved.
4) The binder contains many mineral admixtures, the supply of water to the surface part becomes important for curing to influence the durability of concrete.

REFFERENCES

Dan H,Iyoda T,Ohtsuka Y,Sagawa Y and Hamada H." The relationship between curing condition and durability on concrete using blast-furnace slag cement" Journal of materials,concrete structures and pavements,JSCE 65(4):431-441.

Japan Society of Civil Engineer(JSCE).(2007).Standard specifications for concrete structures.

Nagao Y,Chikada T,Tomisawa T" Property of concrete having high blast-furnace slag cement by 35 years " Procceding of the Japan Concrete Institute 12(1):633-638

Okazaki S,Yagi T,Kishi T and Yajima T.(2007)" Difference of sensitive due to curing condition on strength and permeability" Cement and concrete technology 60:227-234

Uchkawa H,Hanehara S and Sawaki D.(1990)." Effect of hardend structure of blended cement mortal and concrete on their strength" CAJ proceedings of cement and concrete 44:330-335

Yoda A.(2002)" Carbonations of Portland blast-furnace slag cement concrete by 40 years natural aging and preventive effect of finishing materials" Cement science and concrete technology 56:449-454