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Properties of Concrete with Blast-Furnace Slag Cement Made from Clinker with Adjusted Mineral Composition

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ABSTRACT

In order to improve the properties of blast-furnace slag cement, several types of blast-furnace slag cement type A were made from clinker with high C_3S content ranging from 59 to 71 % and the properties of concrete were investigated with comparison of ordinary Portland cement. From the experimental data, the followings results were obtained. When the cement with high C_3S content was used, the water content required to obtain the specified slump was decreased by using blast-furnace slag down to the same level as that of ordinary Portland. Early-age compressive strength of concrete with blast-furnace slag cement type A was improved by increasing C_3S content more than 65%, especially at low temperature. Effects of C_3S content of blast-furnace slag cement type A on the rate of accelerated carbonation rate and shrinkage under drying condition were small, and these properties were about the same as Ordinary Portland cement.

Keywords. C_3S content, Blast-furnace slag cement, Compressive strength, Autogenous shrinkage, Drying shrinkage

INTRODUCTION

In Japan, Portland cement accounts for about 75% of all cement used, and blended cements account for about 25%. Blended cements help control CO_2 emissions because some of the ordinary Portland cement is replaced with industrial by-products, such as ground granulated blast-furnace slag and fly ash. Moreover, proactive use of blended cement will be important in the future to help control CO_2 emissions and ensure effective utilization of resources (Sakai, 2007).

Table 1 shows the calculation results for the amount of CO_2 produced when manufacturing 1t of ordinary Portland cement, blast-furnace slag cement type A (containing 20% ground granulated blast-furnace slag) and blast-furnace slag cement type B (containing 40% ground granulated blast-furnace slag). It was assumed that CO_2 emissions are 746.6 g/kg for ordinary Portland cement (Japan Society of Civil Engineers, 2005), and 40.4 g/kg for ground granulated blast-furnace slag (Japan Society of Civil Engineers, 2005). When blast-furnace slag cement type B is employed, CO_2 emissions are reduced by about 282.5 g/kg compared with ordinary Portland cement. With blast-furnace slag cement type A containing 20% ground granulated blast-furnace slag, CO_2 emissions are reduced by about 141.2 g/kg compared with ordinary Portland cement.

Table 1 CO_2 emission of blast-furnace slag cement

Type of cement	Slag content (%)	CO_2 emission (g/kg)	Difference with ordinary Portland cement(g/kg)
Ordinary Portland cement	0	746.6	0
Blast-furnace slag cement A-type	20	605.4	-141.2
Blast-furnace slag cement B-type	40	464.1	-282.5

Many blended cements in Japan are blast-furnace slag cement type B, and this type has many advantages, such as improved chemical resistance, control of salt osmosis, and control of the alkali aggregate reaction. On the other hand, it has a number of problems compared with ordinary Portland cement, including low compressive strength at early ages, large autogenous shrinkage, and rapid carbonation rate. Therefore, although blast-furnace slag cement is widely utilized in civil engineering structures, it is not often used in architectural structures. To broaden the use of blended cement, there is a need to develop blast-furnace slag cement with performance equivalent to ordinary Portland cement. Therefore, the authors have focused on blast-furnace slag cement type A, developed prototypes in which the chemical composition of the cement is adjusted with gypsum and limestone powder, and reported on the physical properties of the concrete (Miyazawa, 2011), (Fujiwara, 2011). Although it has been possible to improve shrinkage characteristics, crack control effectiveness, and carbonation characteristics, further improvement was needed in characteristics such as strength development in cold temperatures (Yatagai, 2011).

In this study, in order to further improve the performance of blast-furnace slag cement, the authors ascertained the characteristics of blast-furnace slag cement type A employing clinker with adjusted mineral composition. Experimented studies were carried out to investigate the fresh properties, carbonation characteristics, shrinkage characteristics and strength characteristics of concrete made with blast-furnace slag cement type A prototyped using clinker with high C_3S content.

EXPERIMENTS

Employed Materials. Table 2 provides an overview of the prototyped clinkers, and Table 3 shows their chemical compositions. No. 2 cement is Portland cement in which the mineral composition of clinker was adjusted and C_3S content was set to 68.6% using the Bogue formula. No.1 and No.3-No.6 are blast-furnace slag cement type A made from a base cement with C_3S content set in the range 65.9-71.1% . For comparison, ordinary Portland cement with 58.7% C_3S content (OPC) and blast-furnace slag cement type A using OPC as the base cement (BA) were also used.

Table 2 Mineral composition of clinker

Type of clinker	Mineral composition (%)			
	C_3S	C_2S	C_3A	C_4AF
A	71.1	1.8	8.6	10.3
B	68.6	3.4	8.5	10.4
C	65.9	6.2	8.6	10.3
D	58.7	14.0	8.5	10.2

For blast-furnace slag cement type A, the content of blast-furnace slag was set to 20% using ground granulated blast-furnace slag with a specific surface area of 4530 cm^2/g (indicated BS in diagrams), but this ratio was varied in the range 15-25% when C_3S content was set to 68.6%. Gypsum and limestone powder were added within the range of the JIS standard for blast-furnace slag cement type A. The specific surface area of the No.1-No.6 cements was about 4800 cm^2/g, and was set to be somewhat larger than OPC. This is because it was assumed the cement would satisfy an ISO strength class of 52.5.

In addition, as shown in Table 3, the amount of CaO in Type B clinker and Type D clinker is the same irrespective of the C_3S content. Moreover, the burning temperature of high C_3S clinker is the same as that of ordinary OPC clinker (Type D clinker). Therefore, it is presumed that emissions of CO_2 at the time of clinker production are the same irrespective of the C_3S content.

Table 4 shows the results of physical properties of the prototyped cements. In the case where ground granulated blast-furnace slag was mixed in, setting time was delayed somewhat compared to the case where it was not mixed in, irrespective of the C_3S content. At 3 days, compressive strength was 7-10 N/mm^2 greater than with OPC, due to setting specific surface area to 4800 cm^2/g and C_3S content to 65-71%. This difference in compressive strength was particularly notable when ground granulated blast-furnace slag was not mixed in. When C_3S content was set to 65-71%, compressive strength of blast-furnace slag cement type A decreased by 4-9 N/mm^2 due to the increase in the amount of ground granulated blast-furnace slag. Cement in which C_3S content was set to 65% or more satisfied the ISO strength class of 52.5. Almost no differences were evident between the compressive strength of OPC and BA. At 28 days, compressive strength when ground granulated blast-furnace slag was mixed in became greater than when it was not mixed in.

Table 3 Chemical composition and slag content of cements

Type of cement	Type of clinker	Slag content (%)	Chemical composition of cement (%)											
			ig-loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO
No.1	A	20	2.06	21.07	6.87	2.54	59.75	2.69	3.40	0.36	0.36	0.33	0.14	0.11
No.2	B	0	1.06	19.24	5.37	3.42	64.82	1.91	2.80	0.41	0.33	0.28	0.17	0.05
No.3		15	2.17	20.28	6.40	2.73	60.16	2.47	3.41	0.35	0.31	0.32	0.14	0.09
No.4		20	2.12	21.13	6.89	2.59	59.60	2.71	3.40	0.35	0.31	0.34	0.13	0.11
No.5		25	2.07	21.80	7.32	2.42	58.44	2.93	3.42	0.33	0.31	0.36	0.12	0.13
No.6	C	20	2.04	21.30	6.92	2.57	59.46	2.70	3.42	0.35	0.36	0.33	0.13	0.11
OPC	D	0	0.99	20.31	5.36	3.37	64.13	1.90	2.51	0.41	0.37	0.27	0.18	0.05
BA		20	2.07	21.86	6.86	2.54	58.99	2.70	3.40	0.34	0.34	0.33	0.14	0.11

The fine aggregate used in concrete was river sand, and the coarse aggregate used in concrete was crushed hard sandstone. An air-entraining and water-reducing admixture (ad), whose main ingredients are lignin-sulfonic acid compound and polycarboxylic acid, was used as the chemical admixture. The mixture proportions for each concrete are shown in Table 5. The water-cement ratio was fixed at 55%. The target slump was set to 18±2.5 cm and the target air content was set to 4.5±1.0 %.

Table 4 Physical properties of cements (JIS R 5201)

Type of cement	Density (g/cm^3)	Specific Surface area (cm^2/g)	Water content (%)	Setting time		Bending strength (N/mm^2)			Compressive strength (N/mm^2)		
				Initial (h:m)	Final (h:m)	3d	7d	28d	3d	7d	28d
No.1	3.08	4840	30.5	1:50	2:50	6.5	8.1	9.3	37.5	49.7	66.5
No.2	3.15	4780	31.1	1:20	2:00	7.9	8.5	8.7	44.4	56.1	64.5
No.3	3.09	4820	31.0	2:05	3:05	6.6	8.2	9.6	40.4	52.5	68.0
No.4	3.08	4850	30.6	1:55	3:10	6.8	8.1	9.7	37.6	51.1	69.3
No.5	3.06	4830	31.0	2:10	3:15	6.6	7.9	9.6	35.5	49.2	67.0
No.6	3.06	4670	30.8	2:20	3:20	7.0	8.5	10.1	39.0	51.1	67.6
OPC	3.15	3460	28.8	1:40	3:05	5.9	8.1	8.4	31.2	46.9	58.3
BA	3.08	3860	28.3	2:20	3:30	5.3	7.8	9.8	30.0	43.4	62.1

Table 5 Mix proportion of concretes

Type of cement	Target slump (cm)	Target air content (%)	W/C (%)	s/a (%)	Unit content (kg/m^3)				ad (×C%)
					W	C	S	G	
No.1	18±2.5	4.5±1.0	55	45.6	180	327	806	953	1.0
No.2					185	336	799	945	
No.3					180	327	806	954	
No.4					180	327	806	953	
No.5					180	327	805	952	
No.6					180	327	805	952	
OPC					180	327	809	957	
BA					175	318	816	965	

Test Methods. The cement specific surface area, setting time, and compressive strength were tested based on JIS R 5201 "Physical testing methods for cement." In slump testing of concrete, measurement was performed according to JIS A 1101 after 0, 30, 60 and 90 minutes. Air content testing was performed according to JIS A 1128. Testing of concrete setting time was performed according to JIS A 1147.

Concrete compressive strength testing was performed according to JIS A 1108. Curing was done underwater in an environment at 10℃ and 20℃, and testing was done after 7, 28 and 91 days. Curing temperature for cements No. 1, No. 2, No. 4, and No. 6, and OPC and BA, was 20℃, and testing was done after 1, 3 and 7 days.

Autogenous shrinkage testing was performed by referring to Technical Committee Report on Autogenous Shrinkage (Japan Concrete Institute, 2002). An embedded strain gauge (static modulus of elasticity: 40 N/mm^2) was used for strain measurement. Autogenous Shrinkage was determined by subtracting thermal strain from the observed strain ,where the coefficient of thermal expansion of concrete was taken to be $10x10^{-6}/℃$.

In drying shrinkage testing, 100x100x400 mm concrete specimens were cured under water up to 7 days, and then measurement was performed by placing the specimen in a room set to a temperature of 20Cº and a relative humidity of 60%. Measurement of the change in length was performed according to JIS A 1129-2. Accelerated carbonation testing was performed according to JIS A 1153.

RESULTS AND DISCUSSION

Slump and Setting Time Tests. As shown in Table 5, among the mixture proportions satisfying the target slump, the quantity of water per unit volume of concrete was the smallest in the case when BA was used. When No. 2 cement, with C_3S content set to 68.6%, was used, the quantity of water per unit volume of concrete increased by 5 kg/m^3 compared to OPC. However, blast-furnace slag cement type A, in which ground granulated blast-furnace slag was mixed into base cement with C_3S content of 66% or more, had the same quantity of water per unit volume of concrete as OPC. It was found that the quantity of water per unit volume of concrete could be reduced by mixing in ground granulated blast-furnace slag, and that there are no major differences when the slag content from 15 to 25%.

Variation over time in slump is shown in Fig. 1 and Fig. 2. Fig. 1 shows that slump retention performance of blast-furnace slag cement type A with a C_3S content of 68.6% is equivalent to or better than OPC or BA. Fig. 2 shows that, in the C_3S content range of 66-71%, C_3S content did not have an effect on slump retention performance of blast-furnace slag cement type A.

The relationships between setting time (initial and final setting) and C_3S content

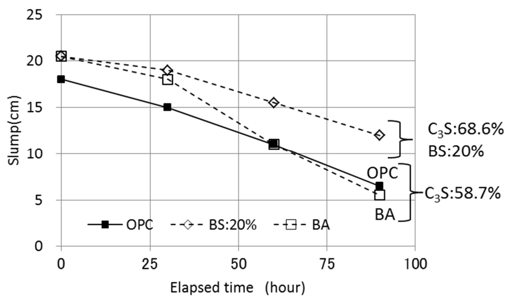

Fig.1 Change in slump with time

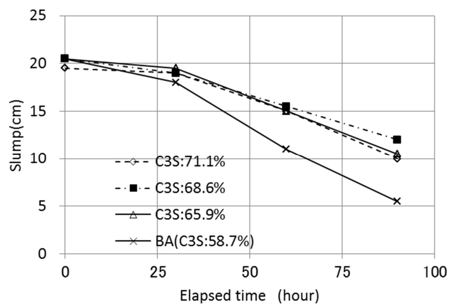

Fig.2 Change in slump with time (BS：20%)

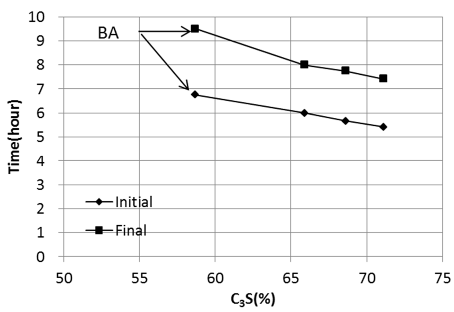

Fig.3 Relationship between C_3S content and setting time (BS：20%)

are shown in Fig. 3. The initial and final setting time both occurred sooner as C_3S content increased.

Compressive Strength Test. The relationships between compressive strength and C_3S content are shown in Fig. 4, Fig. 5, and Fig. 6. The concrete lot in Fig. 4 differs from that in Fig. 5 and Fig. 6. Fig. 4 and Fig. 5 show that, from 1 day to 28 days, compressive strength of blast-furnace slag cement type A with C_3S content of 66% or more was equivalent to or better than OPC. This increase in strength was particularly evident at very early ages of 1 to 3 days. With a C_3S content of 66% or more, compressive strength of blast-furnace slag cement type A was almost the same irrespective of the C_3S content.

Fig. 6 shows the results for a curing temperature of $10C^{o}$. Compressive strength of blast-furnace slag cement type A with C_3S content of 65% or more became greater than that of BA on 7 days. This trend was more notable than in the case of curing at $20C^{o}$. The compressive strength on 91 days became almost fixed irrespective of the C_3S content and curing temperature ($10C^{o}$ or $20C^{o}$).

The relationships of compressive strength and

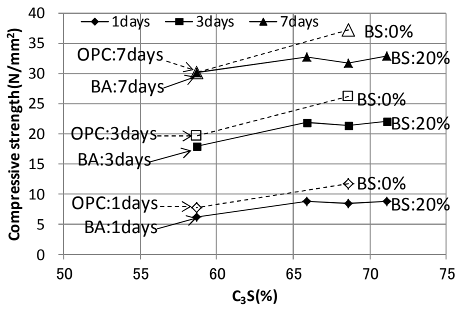

Fig.4 Relationship between C_3S content and compressive strength (20℃)

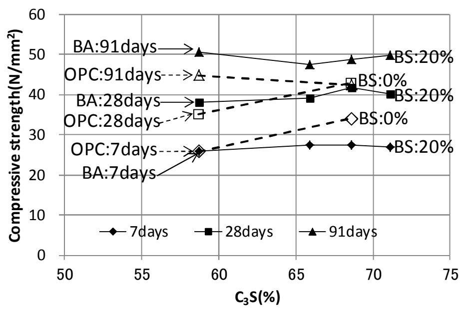

Fig.5 Relationship between C_3S content and compressive strength (BS: 20% ,20℃)

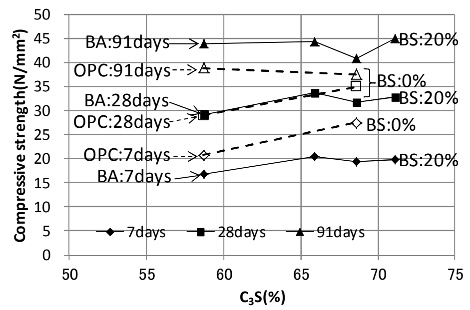

Fig.6 Relationship between C_3S content and compressive strength (BS: 20%,10℃)

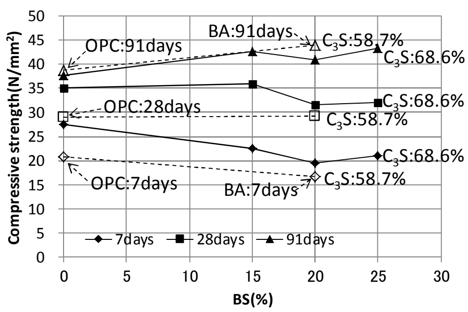

Fig.7 Relationship between BS content and compressive strength (10℃)

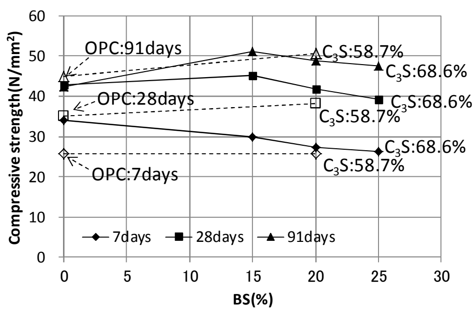

Fig.8 Relationship between BS content and compressive strength (20℃)

the content of ground granulated blast-furnace slag, when C_3S content is set to 58.7% and 68.6%, are shown in Fig.7 and Fig.8. Compressive strength decreased in 7 days due to the increase in the content of ground granulated blast-furnace slag. However, since blast-furnace slag cement type A exhibited a larger increase in strength after 7 days, strength at 28 days became equivalent to that of concrete without ground granulated blast-furnace slag when the content was 15% (10Cº) or 20% (20Cº) or less, and strength at 91 days, exceeded that of concrete without ground granulated blast furnace slag up to the content of 25%.

Autogenous Shrinkage Test. Variation over time in autogenous shrinkage is shown in Fig. 9-Fig. 12. Fig.9 shows that ground granulated blast-furnace slag, an expansion strain of about $10x10^{-6}$ appeared in concrete without at an early age, irrespective of C_3S content. In 182 days, shrinkage strain of No. 2 cement, with C_3S content set to 68.6%, increased by about $40x10^{-6}$ compared to OPC. Fig. 10 shows that, when the content of ground granulated blast-furnace slag was 20%, an expansion strain of about $20x10^{-6}$ to $30x10^{-6}$ appeared at an early age, irrespective of C_3S content. In 182 days, shrinkage strain of blast-furnace slag cement type A, with C_3S content set to 65% or more, increased by about $35x10^{-6}$ compared with BA.

Fig. 11 shows that, when C_3S content was 58.7%, the expansion strain at an early age was somewhat larger with BA than with OPC. Although shrinking behavior was the same up to about 7 days, after that the shrinkage strain of BA increased, and at 182 days the shrinkage strain of BA was about $70x10^{-6}$ larger than that of OPC. Fig. 12 shows that, when C_3S content was 68.6%, expansion strain at an early age was somewhat larger in concrete with ground granulated blast-furnace slag than concrete without it. Up to about 7 days, the same

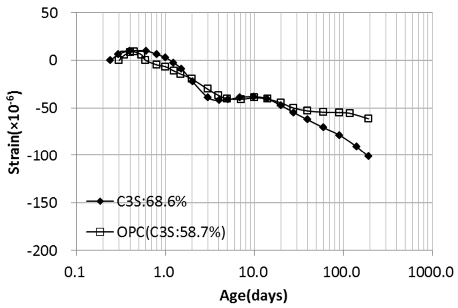

Fig.9 Test results of autogenous shrinkage (BS: 0%)

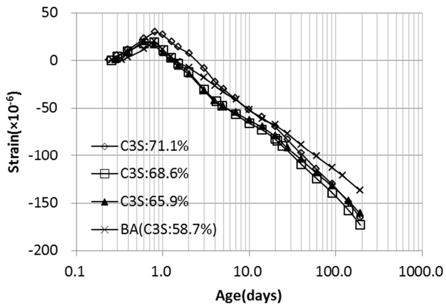

Fig.10 Test results of autogenous shrinkage (BS:20%)

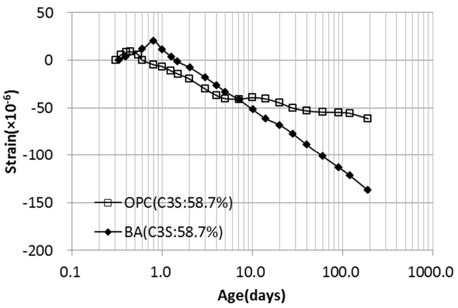

Fig.11 Test results of autogenous shrinkage

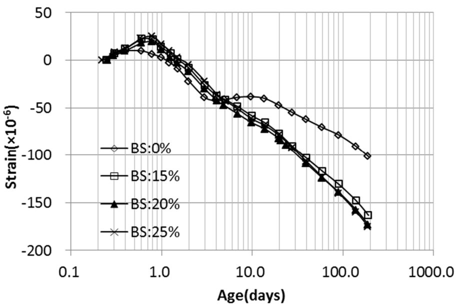

Fig.12 Test results of autogenous shrinkage (C_3S: 68.6%)

strain behavior was exhibited, irrespective of the amount of ground granulated blast-furnace slag. Shrinkage strain at 182 days was about 75×10^{-6} greater in concrete with ground granulated blast-furnace slag than concrete without it. There were no major differences in shrinkage strain when the content of ground granulated blast-furnace slag was in the range from 15 to 25%.

As mentioned above, although blast-furnace slag cement type A with C_3S content of 65% or more has greater long-term autogenous shrinkage than OPC, in the case of members subjected to drying, consideration must be given to the total strain, including drying shrinkage, as described in Section Drying shrinkage test.

Drying Shrinkage Test. Variation in drying shrinkage strain over time is shown in Fig. 13-Fig. 16. Fig. 13 shows that the shrinkage strain of No. 2 cement with a C_3S content of 68.6% , in which ground granulated blast-furnace slag was not blended, was about 50×10^{-6} larger than that of OPC. Fig. 14 shows that, when the content of ground granulated blast-furnace slag is 20%, the shrinkage strain of blast-furnace slag cement type A with C_3S content of 65% or more was about 50×10^{-6} larger than that of BA.

Fig. 15 shows that shrinkage strain of BA was about 50×10^{-6} smaller than that of OPC when C_3S content was set to 58.7%. Fig.16 shows that the shrinkage strain of cement with ground granulated blast-furnace slag was about 50×10^{-6} larger than cement without slag mixed in, in the case when C_3S content was set to 68.6%. Moreover, when the content of ground granulated blast-furnace slag was in the range of 15 to 25%, the content of slag was not

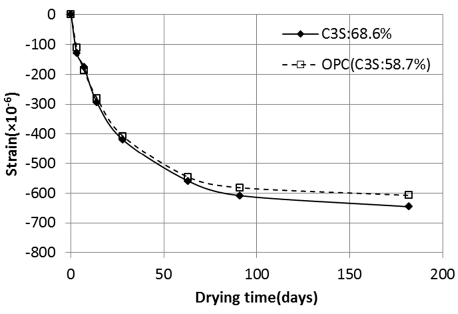

Fig.13 Test results of drying shrinkage (BS: 0%)

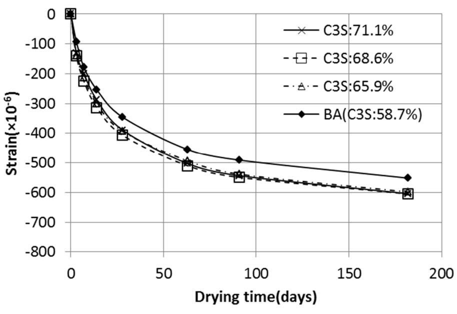

Fig.14 Test results of drying shrinkage (BS: 20%)

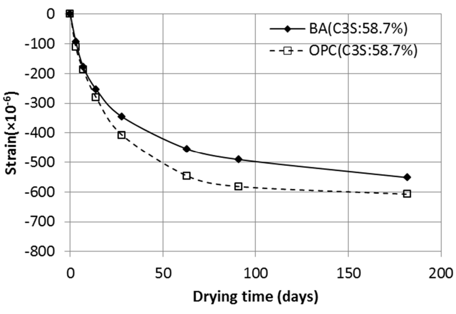

Fig.15 Test results of drying shrinkage (C_3S:58.7%)

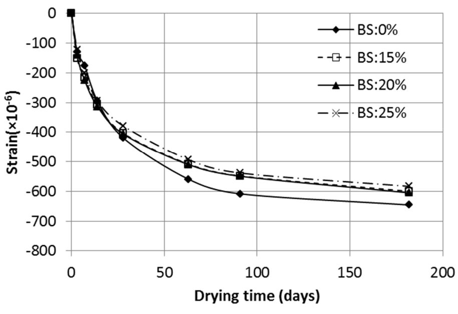

Fig.16 Test results of drying shrinkage (C_3S:68.6%)

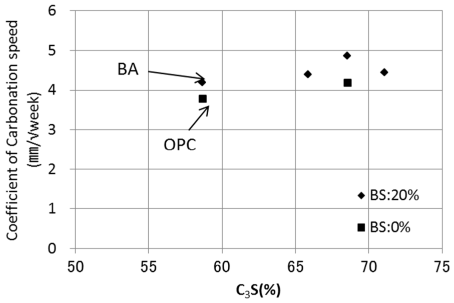

Fig.17 Relationship between C_3S content and coefficient of carbonation speed

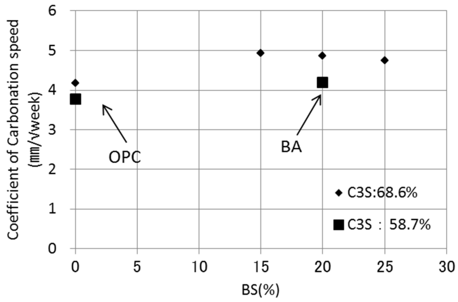

Fig.18 Relationship between BS content and coefficient of carbonation speed

found to have any effect on drying shrinkage strain. The drying shrinkage strain of blast-furnace slag cement type A, with C_3S content set to 65% or more, was the same as OPC, about $600x10^{-6}$ at 182 days.

In the case of members subjected to drying, the total strain – made up of autogenous shrinkage before the start of drying (before form removal) and shrinkage after the start of drying – has an effect on the occurrence of cracking. Thus, if the autogenous shrinkage strain before 7 days (Section Autogenous shrinkage test) is added to the strain obtained as a result of drying shrinkage testing, it is found that the total strain of concrete with blast-furnace slag cement type A with C_3S content of 65% or more is similar to that with OPC.

Accelerated Carbonation Tests. Fig. 17 shows the relationship between the carbonation rate coefficient and C_3S content. In the case of the cements without ground granulated blast-furnace slag was not mixed in, the carbonation rate coefficient was 3.8 (mm/sqr (week)) for OPC, and 4.2 (mm/sqr (week)) for No. 2 cement with C_3S content of 68.6%. When the content of ground granulated blast-furnace slag was 20%, the carbonation rate coefficient was 4.2 (mm/sqr (week)) for BA, and 4.4-4.9 (mm/sqr (week)) for blast-furnace slag cement type A with C_3S content of 65% or more. No improvement in the carbonation rate due to increasing C_3S content was found as a result of this research.

Fig. 18 shows the relationship between the carbonation rate coefficient and the content of ground granulated blast-furnace slag. The carbonation rate coefficient increased with increasing the contents of ground granulated blast-furnace slag, irrespective of C_3S content. Moreover, no major differences in carbonation rate coefficients were found for blast-furnace slag cement type A with C_3S content of 65% or more, when the content of ground granulated blast-furnace slag was in the range 15-25%.

CONCLUSION

In order to improve the performance of blast-furnace slag cement, various properties of concrete with blast-furnace slag cement type A, made from high C_3S clinker were experimentally investigated. The following conclusions were obtained within the scope of this research.

Slump retention performance of blast-furnace slag cement type A with C_3S content of 65% or more was equivalent to or better than OPC or BA.

Compressive strength of blast-furnace slag cement type A with C_3S content of 65% or more satisfied the ISO strength class of 52.5. The compressive strength of blast-furnace slag cement type A with C_3S content of 65% or more was improved compared to BA and equivalent to or better than OPC. This improvement effect was large at an early age, and was particularly notable in a low-temperature environment.
When blast-furnace slag cement with high C_3S content was used, Long-term autogenous shrinkage was the contents of somewhat. However, before 7 days, shrinkage behaviour was the same irrespective of the contents of C_3S larger than OPC, and ground granulated blast-furnace slag.
Drying shrinkage strain of blast-furnace slag cement type A with C_3S content of 65% or more was equivalent to OPC.
There was not found to be any improvement in carbonation rate due to increasing C_3S content.

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