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LOW-HEAT HIGH-STRENGTH CONCRETE USING HIGHLY PULVERIZED BLAST-FURNACE SLAG

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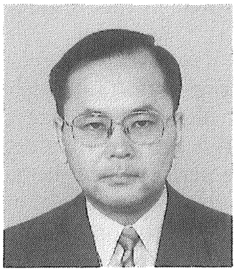

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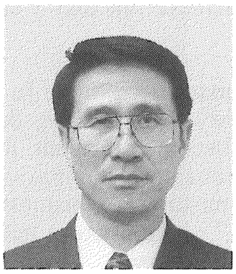

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The heat and strength properties of concrete using highly pulverized blast-furnace slag, silica fume, superplasticizer, and low-heat cement were extensively studied. The results revealed that it is possible to produce low-heat concrete of extremely high strength, even at an early age by properly exploiting the properties of the materials used. Results at low temperatures also showed that this type of concrete has much higher strength than conventional concretes. Mechanisms of the low-heat and the high-strength characteristics are comprehensively explained in terms of hydrates, pore structure, and combined water.

Keywords: *adiabatic temperature rise, admixtures, blast-furnace slag,* $Ca(OH)_2$ *,carbonation, combined water, concrete, freezing and thawing resistance, high strength, porosity, shrinkage*

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1. INTRODUCTION

Materials such as blast furnace slag, fly ash, and silica fume have been widely used as admixtures in concrete due to their latent hydraulicity and pozzolanic activity. Blast-furnace slag and fly ash are usually premixed with the cement. In some Western countries, cement mixed with silica fume is commercially available. These admixtures are industrial byproducts and effective use of such materials has been promoted to save resources and energy. With the increasing seriousness of global environmental problems, it is essential to transform industrial-waste generating societies, in which large amounts of resources are thrown away, into industrial-resource cycling societies. Various measures are being taken to achieve this and it can be said that in this respect concrete technology is ahead of other industries.

Meanwhile, the above-mentioned admixtures continue to play a more important role than ever before in developing materials that satisfy the increasing demand for high-performance concretes. Since the use of these admixtures has become prevalent, manufacturers now tend to regard them not as byproducts but as important materials which improve concrete performance. In fact, efforts continue to increase the value of such admixtures. Admixtures have long been studied, and international conferences organized by CANMET/ACI1)-5) have played a major role in accumulating information on admixtures.

The history of blast-furnace slag cement in Japan dates back to the early Taisho era6). In 1994, blast-furnace cement accounted for approximately 21% of all cement production7). The production of blast-furnace slag totaled approximately 23 million tons, of which 63% was used as silica fume in cement7). Given this background, the Japan Society of Civil Engineers drew up "Guidelines for Design and Construction of Concrete Using Blast-Furnace Slag (Draft)" 8) in 1988. A total of 532 papers were cited in the data summary, which formed the basis for the guidelines (draft). The guidelines are now being revised. In 1992, the Architectural Institute of Japan published "Status of Technology Regarding Blast-Furnace Slag." 9)

The previous studies on blast-furnace slag demonstrare that it offers the following advantages: decreased unit water content, prevention of bleeding in concrete, increased long-term concrete strength, reduced heat of hydration as the proportion of slag is increased, improved watertightness and durability, and prevention of alkali-aggregate reaction. Blast-furnace slag has a fineness approximately 4,000 cm^2/g in terms of Blaine specific surface area. The guidelines published by the Japan Society of Civil Engineers cover slag fineness of 2,750-6,000 cm^2/g.

There is an increasing demand for high-performance concrete. Concrete performance is evaluated in terms of flowability, heat generation, strength, volumetric change,and resistance to various types of deterioration. Studies of high-flowability concrete, have been particularly prevalent in recent years10). Blast-furnace slag has also been utilized. Furthermore, as structures have become larger, studies of low-heat or high-strength concretes have been become more and more common. For example, low-heat belite cement has recently been developed11). In Japan, the Ministry of Construction's Comprehensive Technology Development Project12) has produced super-high-strength concretes with a low water-binder ratio by using a high-range water-reducing (AE) agent (superplasticizer).

However, these types of concrete have their own problems. Binder content is generally large in highly-flowable concrete and in high-strength concrete with a low water-binder ratio. Therefore, more heat is generated. Furthermore, belite cement is inferior in early-age strength development. Thus, high strength and low heat seem to be incompatible: conventional concrete technology tells us that it is difficult to develop a concrete with both these properties. The authors, however, have been trying to develop a concrete which meets these conflicting demands of low heat and high strength, and have shown that it is not necessarily impossible to satisfy them13)-15). However, previous studies may not have reached the concrete's performance limits, and further studies were necessary. Furthermore, mechanisms of low heat and high strength were not fully explained.

Table 1 Physical Properties of Cement

Cement	Specific gravity	Fineness (in Blaine) (cm^2/g)	Setting			Compressive strength (kgf/cm^2)				Heat of hydration (cal/g)		
			Water content (%)	Initial (h-m)	Final (h-m)	3 days	7 days	28 days	91 days	7 days	28 days	91 days
Moderate -heat	3.21	3,310	29.2	2-30	3-50	127	172	350	430	65	75	85
Low -heat	3.24	3,450	27.6	2-54	4-05	68	105	327	561	51.5	66.2	76.0

Table 2 Chemical and Mineral Compositions of Cement

Cement	Chemical components (%)												Mineral composition (%)			
	ig·loss	insol	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	R_2O	Cl	C_3S	C_2S	C_3A	C_4AF
Moderate -heat	0.5	0.0	23.1	4.2	3.6	64.1	1.8	2.4	0.17	0.32	0.38	0.004	43	34	5	11
Low -heat	0.7	0.2	25.2	3.6	3.7	62.6	0.9	2.0	0.17	0.40	0.43	0.003	28	51	3	11

Following this earlier work, the intent of this study was to develop improved low-heat, high-strength concrete. To this end, detailed research was conducted to clarify strength and heat properties using highly pulverized blast-furnace slag, silica fume, and low- and moderate-heat portland cement. The relationship between strength development and microstructures of concrete was also studied.

2. EXPERIMENTAL DETAILS

2.1 Materials

A moderate-heat portland cement and a low-heat portland cement were used. Tables 1 and 2 show the physical properties, as well as the chemical and mineral composition of each cement.

Two types of highly pulverized blast-furnace slag with Blaine specific surface areas (hereafter referred to as "slag fineness") of 8,690 cm^2/g and 16,120 cm^2/g were used. Table 3 shows their physical properties and chemical compositions. Fig.1 shows their particle-size distributions.

Gypsum was added to provide 4% SO_3. This amount represents the total of gypsum in the cement and the added gypsum. In measuring the ettringite peak strength by X-ray diffraction, the cases of 2 and 6% SO_3 were also considered.

As for the aggregates, sea sand from Tarumae, in Tomakomai, and crushed stones from Miharashi, Otaru, were used. Tables 4 and 5 show the results of tests on the fine and coarse aggregates.

Silica fume with a fineness of 200,000 cm^2/g was used. Table 6 shows its physical properties and chemical composition.

As for a superplasticizer, prototypes made primarily from aromatic aminosulfonate high-polymer compounds were used. Furthermore, an air-entraining admixture was used to adjust the amount of entrained air. The maximum amount of superplasticizer that could be added without causing separation of the concrete was used.

2.2 Concrete production and mix proportions

To mix the concrete, a pan-type forced mixing machine with a capacity of 100 liters was used. The concrete was mixed for 1 minute following addition of binder and fine aggregate to the mixer, for 3-12 minutes following water addition, and for 3 minutes after coarse aggregate addition. The target slump and air content values were 861cm and 3.561%, respectively. The concrete was mixed at 20°C and

Table 3 Physical Properties and Chemical Composition of Blast-Furnace Slag

Fineness (in Blaine) (cm²/g)	Average particle size (μm)	Specific gravity	Chemical composition (%)								
			ig·loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	Basicity
8,690	2.8	2.90	0.2	34.2	15.0	0.6	41.7	6.2	0.9	0.3	1.84
16,120	1.6	2.87	0.3	33.9	15.1	0.8	41.4	6.2	0.9	0.3	1.85

Table 4 Results of Fine Aggregate Tests

Type	Specific gravity	Absorption (%)	Unit weight (kg/m³)	Percentage of solid volume (%)	Mass loss in washing-out (%)	Organic impurities	Mass loss in soundness test (%)	Chloride content (%)	Particle-size distribution (percentage remaining%)						Fineness modulus
									5.0	2.5	1.2	0.6	0.3	0.15	
Sea sand from Tarumae	2.68	1.17	1,780	67.1	0.37	Passed	0.3	0.000	0	6	30	56	83	92	2.67

Table 5 Results of Coarse Aggregate Tests

Type	Maximum size (mm)	Specific gravity	Absorption (%)	Unit weight (kg/m³)	Percentage of solid volume (%)	Mass loss in washing-out (%)	Mass loss due to abrasion (%)	Mass loss in soundness test (%)	Particle-size distribution (percentage remaining%)					Fineness modulus
									25	20	15	10	5	
Crushed stones from Miharashi	25	2.68	1.58	1,560	58.1	0.25	11.3	0.7	0	23	47	74	100	6.97

Table 6 Physical Properties and Chemical Composition of Silica Fume

Fineness (BET method) (cm²/g)	Average particle size (μm)	Specific gravity	Apparent density (kg/m³)	Chemical composition (%)							
				ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
200,000	0.15	2.2	300	0.37	98.7	0.30	0.01	0.14	0.01	0.09	0.01

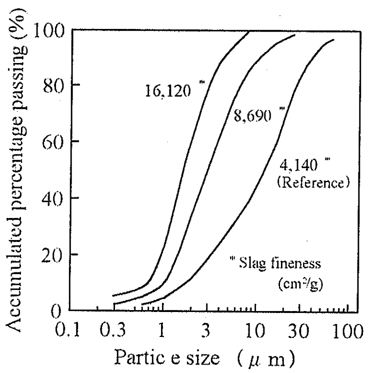


Fig. 1 Particle-Size Distribution of Slag

cured at 20℃, 5℃ and adiabatically. The concrete was sealed and cured for 1 to 2 days, immediately after production of the specimens, and then the specimens were cured in water after demolding until the testing age.

Table 7 shows the concrete mixture proportions and curing temperatures. Water-binder ratios (W/B) were 0.20, 0.25, 0.30, and 0.35. Blast-furnace slag content was 50% or 60%. Silica fume content was 10%.

2.3 Items examined

a) Unit water content

The effects of slag fineness and type of cement on unit water content were investigated.

b) Compressive strength

Compressive strengh tests were conducted at the ages of3, 7, 28, and 91days with specimens of φ 100×200mm.

In the adiabatically cured specimens, curing was controlled in water immediately after the concrete was placed using equipment able to simulate the temperatures measured in adiabatic temperature rise tests.

Table 7 Mixture Proportions and Curing Temperatures

Water binder ratio	Air (%)	Cement	Slag fineness (cm^2/g)	Slag cont. (%)	Gypsum addition (%)	Silica fume cont. (%)	Superplasticizer (%)	Sand percentage s/a (%)	Unit quantity (kg/m^3)						Curing
									Water W	Binder B	Fine aggre. S	Coarse aggre. G	Superplasticizer (kg)	AE (ml)	
0.35	3.5	Moderate-heat	8,690	60	4	0	1.9	42	113	323	833	1,158	6.14	29.1	20℃
				50		10	1.9		115	329	828	1,144	6.25	52.6	20℃, 5℃
			16,120				2.5		117	334	822	1,139	8.35	66.8	20℃
		Low-heat	8,690				1.9		117	334	822	1,142	6.35	53.4	
			16,120				2.5		117	334	822	1,139	8.35	66.8	
0.30	3.0	Moderate-heat	8,690	60		0	2.2	41	108	360	812	1,171	7.92	43.2	
				50		10	2.2		108	360	809	1,166	7.92	36.0	20℃ ,5℃ ,Adiabatic
			16,120				2.8		109	363	806	1,163	10.16	72.6	20℃ ,Adiabatic
		Low-heat	8,690				2.2		109	363	806	1,166	7.99	36.3	20℃ ,5℃
			16,120				2.8		108	360	809	1,166	10.08	72.0	20℃ ,Adiabatic
0.25	2.5	Moderate-heat	8,690	60		0	2.3	40	107	428	774	1,163	9.84	85.6	20℃
				50		10	2.3		106	424	772	1,163	9.75	84.8	20℃, 5℃
			16,120				3.0		107	428	769	1,158	12.84	85.6	20℃
		Low-heat	8,690				2.3		104	416	780	1,171	9.57	70.7	
			16,120				3.0		105	420	774	1,168	12.60	84.0	
0.20	2.0	Moderate-heat	8,690				2.5	39	99	495	740	1,163	12.38	49.5	20℃, 5℃
		Low-heat					2.5		101	505	734	1,155	12.63	50.5	20℃

c) Adiabatic temperature rise
The dimensions of specimens used for the adiabatic temperature rise tests were ϕ440×290 mm. Air-circulating test equipment was used. The ultimate adiabatic temperature rise was the temperature rise measured at the age of 7 days.

d) Simplified adiabatic temperature rise of mortar
The mortar mix was the same as concrete mix proportion but excluding the coarse aggregate. The mortar was mixed in a mortar mixer with a capacity of 20 liters. Mixing time was 3 minutes after all materials was added, with rotation at low speed (160 rpm) and high speed (216 rpm). In the simplified adiabatic temperature rise tests, precise thermometers (accuracy: 0.01 ℃) as well as platinum thermo-resistors (accuracy: 0.03 ℃) were used. Both were set in the center of mortar placed in an insulated container (ϕ 22 × 20cm). Measurements were conducted at 1-minute intervals. An accuracy of 0.03 ℃ was achieved with the platinum thermo-resistors as a result of various techniques, including annealing of the platinum elements, use of gold-plated wire terminals, and use of 4-wire connections.

e) Pore structure
The pore-diameter distribution in the hardened cement paste in the concrete was measured with a mercury intrusion porosimeter. The process for preparing specimens used for these measurements was as follows. Concrete inside a specimen on which a compressive strength test had been conducted was crushed and sieved into pieces 2.5-5.0 mm in diameter. After stirring and washing in an acetone solution for 20 minutes, the pieces were dried in a vacuum for 3 days.

f) Combined water
The combined water of hardened cement paste in the concrete was measured by thermogravimetric analysis (changes in mass at temperatures of 110℃ and 700℃).

g) $Ca(OH)_2$
The $Ca(OH)_2$ content of hardened cement paste in the concrete was measured by differential thermal analysis (measurement of DTA endothermic peak area at approximately 450℃).

h) Semi-quantitative analysis of ettringite by X-ray diffraction
Semi-quantitative analysis of ettringite was conducted on hardened cement in the concrete by X-ray diffraction$^{16)}$.

i) SEM observations and quantitative analysis of chemical constituents by EDS
SEM observations of hardened binder in the concrete and quantitative analysis of chemical constituents by EDS were carried out. For EDS analysis, mortar was prepared in accordance with the basic concrete mix proportion, but without the coarse aggregate.

j) Drying shrinkage strain
Concrete strain caused by drying shrinkage was measured by a comparator with specimens of 10 × 10 × 40 cm at 20℃ and at a relative humidity of 60%.

k) Freezing and thawing resistance
At the age of 28 days, freezing and thawing resistance tests were conducted on the concrete with specimens of 10 × 10 × 40 cm.

l) Carbonation
At the age of 28 days, accelerated carbonation tests were conducted on the concrete with specimens of $\phi 10 \times 20$ cm at 30℃, at a relative humidity of 60%, and at the CO_2 concentration of 10%. The carbonation depth was measured using a phenolphthalein solution 2, 4, 8, 13, and 28 weeks after the start of the tests. Furthermore, microscope observations were conducted by the transmission method.

3. RESULTS AND DISCUSSION

3.1 Unit water content

Figures 2 and 3 show the relationship between unit water content and water-binder ratio. As water-binder ratio decreased, the amount of superplasticizer which could be added to the concrete increased. As a result, the unit water content greatly decreased. Table 7 shows that the largest difference in unit water content with binder ratios of 0.35 and 0.2 was reached at approximately 16 kg/m^3. However, slag fineness, the presence of silica fume, and the type of cement had relatively little effect on unit water content. The largest difference in unit water content was reached at several kg/m^3. It can be presumed that when the water-binder ratio was 0.25, silica fume contributed to a slight decrease in unit water content. Actually, the use of silica fume improved the properties of the fresh concrete. Mixing times were 8 minutes 15 seconds and 14 minutes 30 seconds, respectively, for concrete with silica fume and without silica fume.

3.2 Compressive strength

Figures 4 and 5 show the relationship between compressive strength and age of concrete with moderate- and low-heat portland cement, respectively, using slag fineness and water-binder ratio as variables. In both cases, as slag fineness increased or water-binder ratio decreased, compressive strength increased. The maximum compressive strength at the age of 3 days was 83.8 N/mm^2.

Figure 6 shows the relationship between compressive strength and age of concrete using water-binder ratio and type of cement as variables, when the slag fineness was 8,690 cm^2/g. For any water-binder ratio, the strength development of concrete using moderate-temperature portland cement was larger than that for concrete using low-temperature portland cement. As shown in Fig.7, the relationship when slag fineness was 16,120 cm^2/g is also the same. The maximum compressive strength at the age of 91 days was 119 N/mm^2 when the water-binder ratio was 0.2.

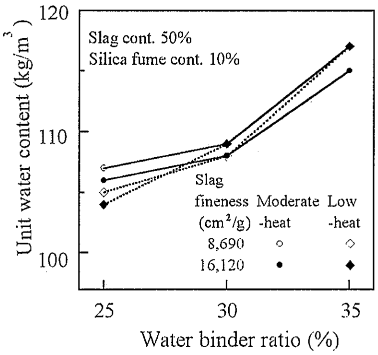


Fig. 2 Relationship between Unit Water Content and Water Binder Ratio

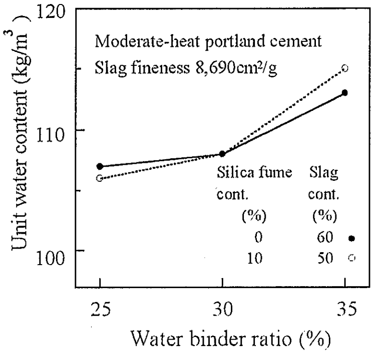


Fig. 3 Effect of Silica Fume Content on Unit Water Content

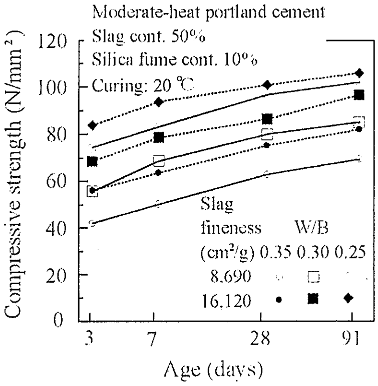


Fig. 4 Effect of Slag Fineness on Compressive Strength

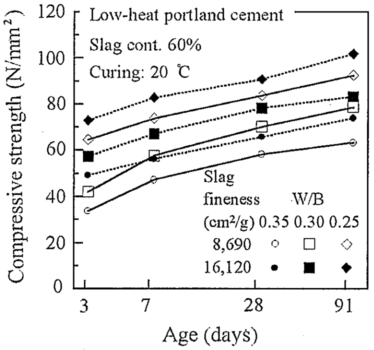


Fig. 5 Effect of Slag Fineness on Compressive Strength

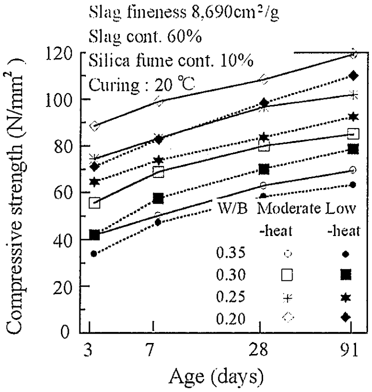


Fig. 6 Effect of Water-Binder Ratio on Compressive Strength

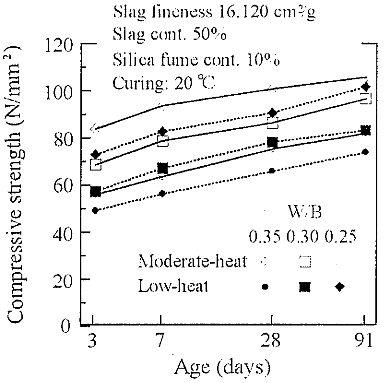


Fig. 7 Effect of Type of Cement on Compressive Strength

The features of compressive strength obtained from the test results are that early strength development is remarkably high and strength developed almost linearly with age. The mechanisms behind this strength development behavior will be discussed later.

Figure 8 shows the effects of silica fume on compressive strength using water-binder ratio as a variable. The compressive strength of concrete with silica fume was smaller than that of concrete without silica fume. However, it is obvious that as the water-binder ratio decreased, the difference in compressive strength decreased.

Figure 9 shows the effects of curing temperatures on the compressive strength of concrete using moderate-heat portland cement. At the age of 3 days, the compressive strength of concrete cured at 5℃ was much lower than that of concrete cured at 20℃. However, the compressive strength of the former had recovered greatly by the age of 7 days, and at 91 days, was almost the same as that of concrete cured at 20℃. This tendency became more notable as the water-binder ratio decreased. At the age of 3 days, the compressive strength of concrete cured at 5℃ was 14.5 N/mm^2 and 35.2 N/mm^2, respectively, for water-binder ratios of 0.35 and 0.20. This means that this concrete is much stronger than conventional types of concrete. Fig.10 shows comparisons of the effects of curing temperature on compressive strength for concretes using low- and moderate-heat portland cement.

Figure 11 shows the relationship between compressive strength and accumulated temperature using water-binder ratio and curing temperature as variables. From the figure, it is clear that compressive strength can be evaluated from the accumulated temperature. Fig.12 shows the relationship between

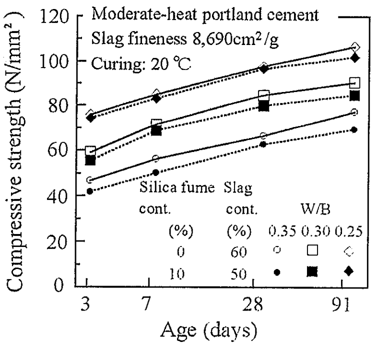


Fig. 8 Effect of Silica Fume Content on Compressive Strength

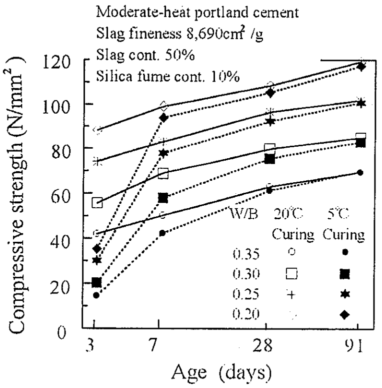


Fig. 9 Effect of Curing Temperature on Compressive Strength

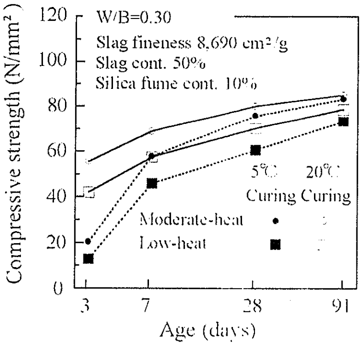


Fig. 10 Effect of Curing Temperature on Compressive Strength

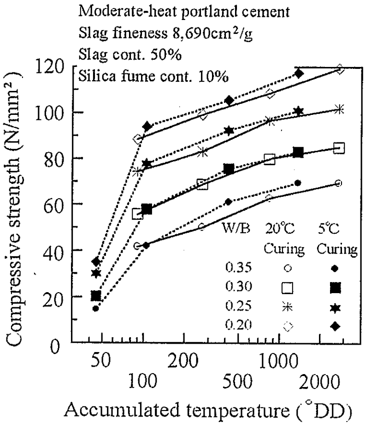


Fig. 11 Relationship between Compressive Strength and Accumulated Temperature

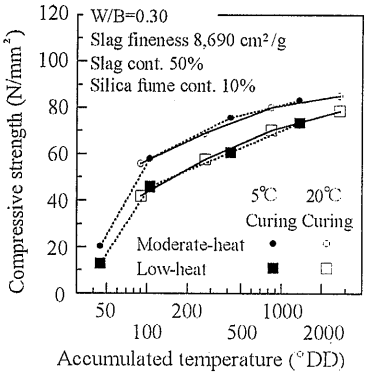


Fig. 12 Relationship between Compressive Strength and Accumulated Temperature according to Type of Cement

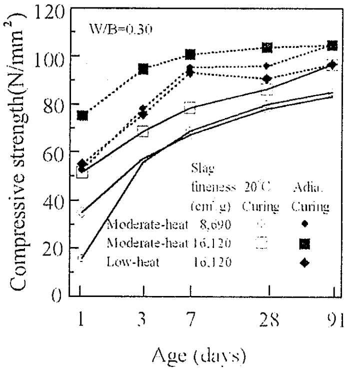


Fig. 13 Relationship between Compressive Strength and Age under Adiabatic Curing

compressive strength and accumulated temperature according to type of cement. It is obvious that although the properties differ depending on cement type, the compressive strength can be calculated in terms of accumulated temperatures.

Figure 13 shows a comparison of compressive strength of concrete cured at adiabatic temperatures and that cured at 20℃. The compressive strength of concrete cured adiabatically was significantly greater than that of concrete cured at 20℃. However, in the case of adiabatic curing, compressive strength just about peaked by the age of 7 days, with no significant increase later.

3.3 Adiabatic temperature rise

Figure 14 shows examples of the effects of slag fineness and type of cement on adiabatic temperature rise. It can be seen that with greater slag fineness, the adiabatic temperature rise was slightly higher. In cases of other water-binder ratios, a similar tendency was observed. Fig.15 shows the effects of silica fume on adiabatic temperature rise. From the start of the test to approximately the first day, the adiabatic temperature rise of concrete with silica fume was larger than that of concrete without silica fume. This means that silica fume promoted hydration at the early stages. However, the final adiabatic temperature rise of concrete with silica fume was slightly less than that of concrete without silica fume. Figs.16 and 17 show the effects of water-binder ratio on adiabatic temperature

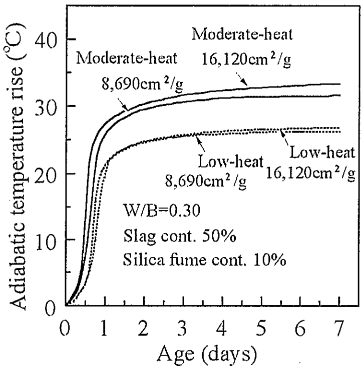


Fig. 14 Effect of Slag Fineness and Cement Type on Adiabatic Temperature Rise

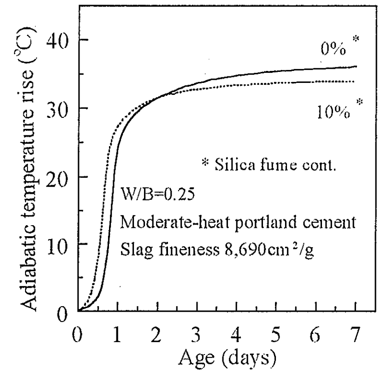


Fig. 15 Effect of Silica Fume Content on Adiabatic Temperature Rise

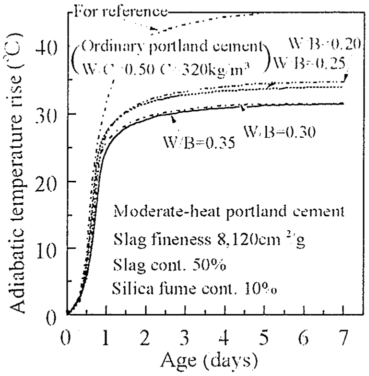


Fig. 16 Effect of Water-Binder Ratio on Adiabatic Temperature Rise

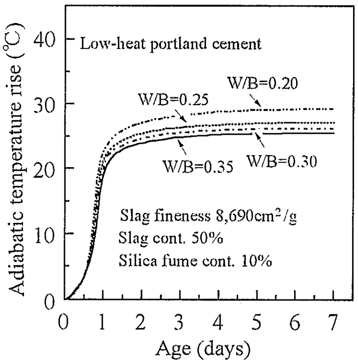


Fig. 17 Effect of Water-Binder Ratio on AdiabaticTemperature Rise

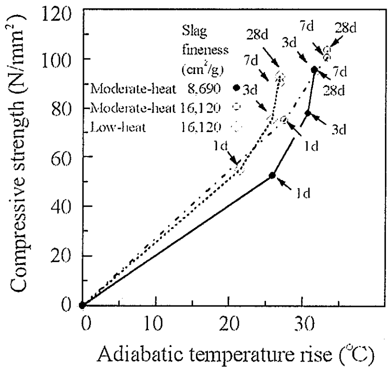


Fig. 18 Relationship between Compressive Strength and Adiabatic Temperature Rise

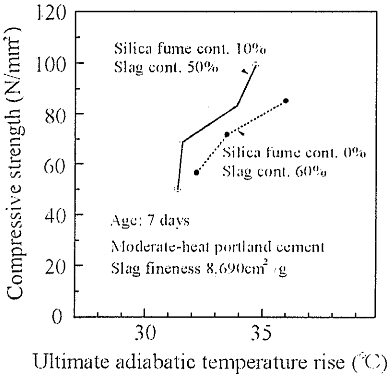


Fig. 19 Effect of Silica Fume on Relationship between Compressive Strength and Ultimate Adiabatic Temperature Rise

rise for concretes using moderate- and low-heat portland cement, respectively. When the water-binder ratio was changed from 0.35 to 0.20, the binder content increased by approximately 170 kg/m³. Nevertheless, the temperature rise was only approximately 3 or 4℃.

Thus, the adiabatic temperature rise of the concretes used in this study was much smaller than that of conventional high-strength concretes, which had a small water-binder ratio.

3.4 Relationship between compressive strength and adiabatic temperature rise

Figure 18 shows the relationship between compressive strength and adiabatic temperature rise. The compressive strength values are those obtained from test specimens cured under adiabatic conditions. Values for adiabatic temperature rise at the age of 7 days were used for those at the age of 28 days. It is obvious that, although the compressive strength per unit adiabatic temperature rise differed according to the type of cement and slag fineness, the values were extremely large after a certain age. Fig.19 shows the effects of silica fume on the relationship between compressive strength and ultimate adiabatic temperature rise. It can be said that silica fume reduced the ultimate adiabatic temperature rise necessary to develop an equivalent compressive strength. Fig.20 shows the relationship between compressive strength and ultimate adiabatic temperature rise according to the type of cement.

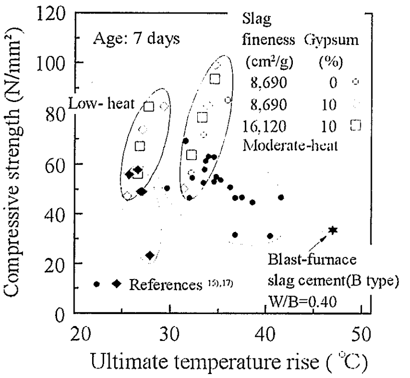


Fig. 20 Relationship between Compressive Strength and Ultimate Adiabatic Temperature Rise

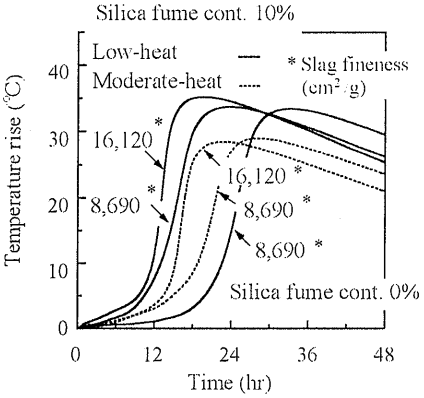


Fig. 21 Simplified Adiabatic Temperature Rise in Mortar

The figure also includes the results for various mix proportions at water-binder ratios of 0.35 and 0.40, as obtained in a separate series of tests[15)17)]. These results demonstrate that it is possible to increase compressive strength and at the same time reduce the ultimate adiabatic temperature rise by choosing the materials and their form. The results for smaller water-binder ratios show that the ultimate adiabatic temperature tends to increase again. However, it is clear that the concrete developed in this study is superior to conventional concrete as regards low-heat and high-strength properties.

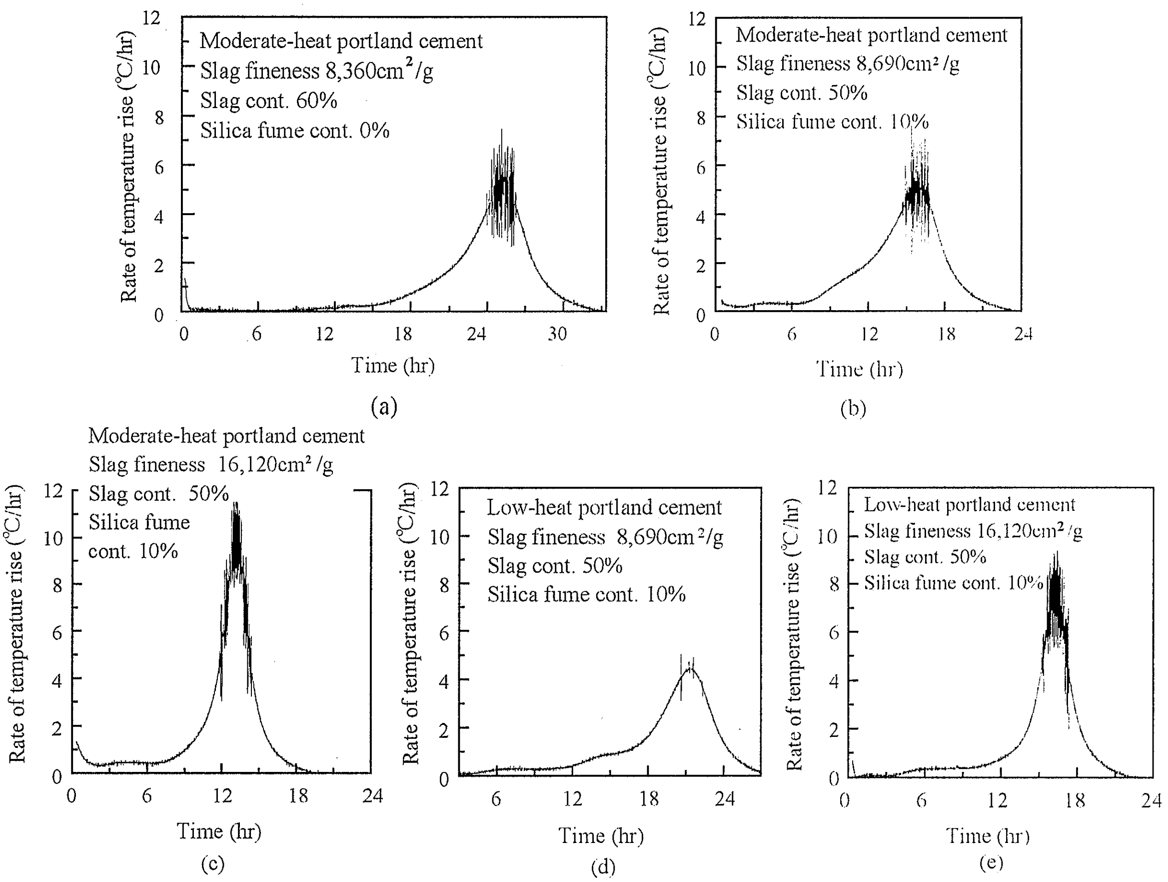
3.5 Simplified adiabatic temperature rise of mortar

Figure 21 shows the results of the simplified adiabatic temperature rise mortar tests. The results are basically the same as those of the concrete adiabatic temperature rise tests. To obtain the initial degree of hydration, the rate of temperature rise was calculated by dividing the change in measured temperature by the measurement interval. Fig.22 shows the results of these calculations. The rate of temperature rise peaked earlier for mortar using moderate-heat portland cement with silica fume than for that without. As slag fineness increased, the rate of temperature rise increased. When mortars using low- and moderate-heat portland cement are compared, the rate of temperature rise of the former is seeen to peak later than that of the latter. Figs.23 (a) and (b) are magnifications of Figs. 22 (c) and (d). The rate of temperature rise changed greatly in the former, meaning that active hydration reactions occurred. Thus, it is shown that the rate of temperature rise is an effective way to evaluate hydration reaction.

3.6 Pore structure

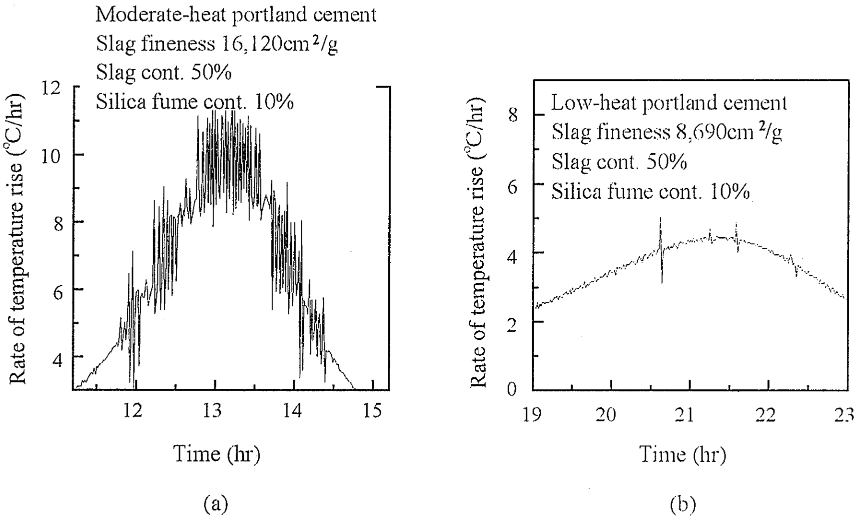
The pore structure of concrete directly affects its strength. Uchikawa et al.[18)] Indicated that a certain range of pore volume significantly affects compressive strength. They suggested that pore diameter of 20 nm is the limit up to which the compressive strength of ordinary concrete using blast-furnace slag is affected. In this study, extensive examinations were conducted so as to divide the pore-diameter range of 3 nm to 2 mm into several sub-ranges according to their effect on compressive strength. Figs.24 (a), (b) and (c) show the relationship between compressive strength and pore volume for pore-diameter ranges of 3 nm to 2 mm, 5 nm to 2mm and 20 nm to 2 mm, respectively. It can be seen from these figures that pore volume and compressive strength are more strongly related in the pore-diameter range 5 nm to 2 mm than in the range 3 nm to 2 mm, and that in the pore-diameter range 20 nm to 2 mm, high-strength data is widely dispersed. Given these results, this study focused on, the relationship between pore volume and compressive strength according to these pore-diameter ranges of 3 nm to 2 mm, 5 nm to 2 mm, and 20 nm to 2 mm. All data for ages 3 and 28 days were used in Fig. 24.

Figure 25 shows the effect of slag fineness on pore-diameter distribution in concrete using low-heat portland cement, as well as the relationship between pore volume and compressive strength. When



(a) (b) (c) (d) (e)

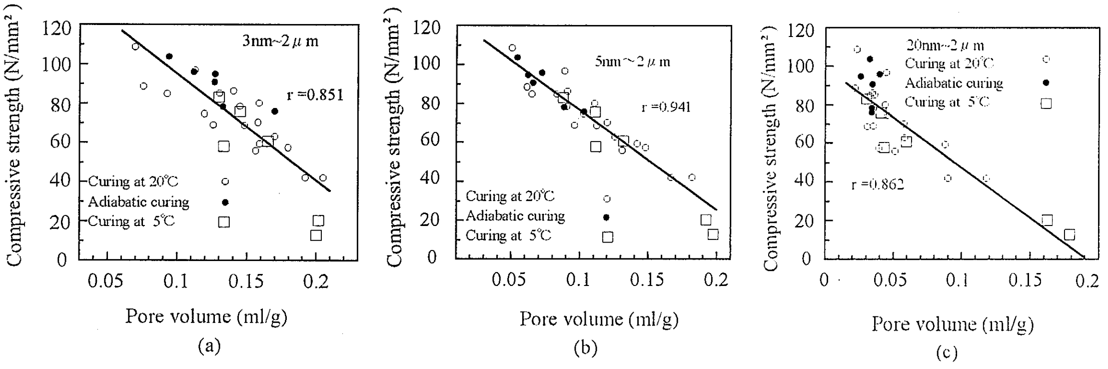
Fig. 22 Rate of Temperature Rise



(a) (b)

Fig. 23 Magnification of Simplified Adiabatic Temperature Rise Rate in Mortar

slag fineness increased, the pore-diameter distribution shifted toward smaller pore diameters. At the age of 28 days, the volume of small pores was considerably higher. Fig.25 (c) shows that, at the age of 3 days, as slag fineness increased, compressive strength also increased. It can be said that this increase in compressive strength corresponds to the pore volume in the pore-diameter range of 2nm



(a) (b) (c)

Fig.24 Relationship Between Compressive Strength and Pore Volume

to 20mm. It can also be seen that the pore volume increased in the pore-diameter range of 5 to 20 nm and 3 to 5 nm, and therefore, these pores did not affect compressive strength. At the age of 28 days, however, pore volume contributed to an increase in compressive strength in the pore-diameter ranges of 5 to 20 nm and 20 nm to 2 mm. Fig.26 shows the results for concrete using moderate-heat portland cement. The results are basically the same as in Fig.25. Fig.27 shows the effects of silica fume content. It turned out that, at the age of 3 days, the relationships between pore-diameter distribution and compressive strength and between pore volume and compressive strength are not obvious. However, when silica fume was used, pore volume increased in all pore-diameter ranges at the age of 28 days, thus decreasing compressive strength.

Figure 28 shows the effect of water-binder ratio on pore-diameter distribution. As the water-binder ratio decreased, the distribution shifted toward smaller pore diameters. Fig.29 shows the changes in pore-diameter distribution with aging. Fig.30 shows the effect of curing temperature on pore-diameter distribution. At the age of 3 days, the pore-diameter distribution varied greatly according to the curing temperature. However, by the age of 28 days, concretes cured at 20℃ and 5℃ had almost the same pore-diameter distributions. In the case of adiabatic curing, the pore diameter tended to be smaller pore diameters. It is obvious that compressive strength development reflects the pore-diameter distribution.

3.7 Combined water

Figure 31 shows the relationship between compressive strength and combined water content. As the age increased, the combined water content became larger. However, with lower water-binder ratios, there was a tendency for compressive strength to increase significantly, while the combined water content decreased. This may be explained as follows. When the water-binder ratio decreased, the unit binder content increased, reducing the space between binder particles, which is what makes hydration possible, and lowering hydration, i.e. combined water content, to a degree. Despite the limited hydration, compressive strength increased because the amount of redundant water was very small. This is confirmed in Fig.32, which shows the relationship between pore volume and combined water content. In other words, when the water-binder ratio is reduced, the combined water content and pore volume also decrease. Thus, a decrease in pore volume means an increase in compressive strength.

Figure 33 shows the effect of slag fineness on the relationship between compressive strength and combined water content. There is a tendency for concrete with finer slag to contain less combined water. In other words, to obtain a certain level of strength, concrete with finer slag requires relatively less hydration.

A smaller water-binder ratio results in a larger unit binder volume. However, if hydration is relatively low, heat generation is suppressed. It is believed that this is the mechanism causing the high- strength and low-heat characteristics of this concrete.

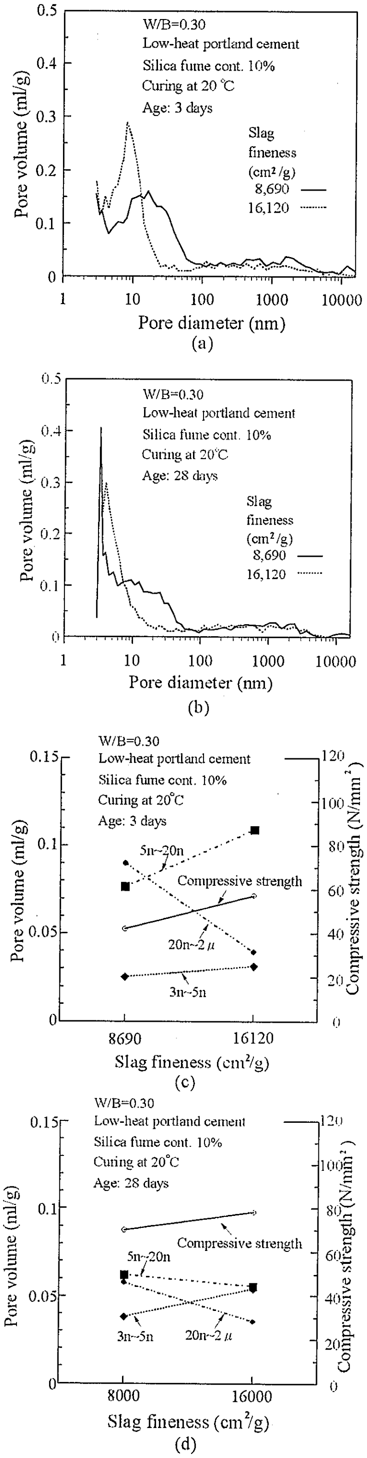


Fig. 25 Effects of Slag Fineness on Pore-Diameter Distribution and Relationship between Pore Volume and Compressive Strength

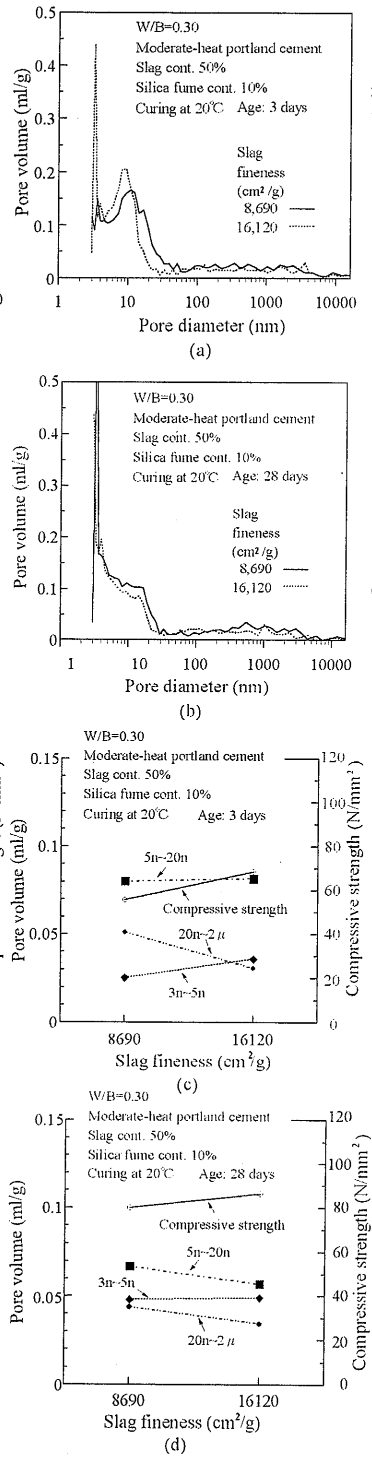


Fig. 26 Effects of Slag Fineness on Pore-Diameter Distribution and Relationship between Pore Volume and Compressive Strength

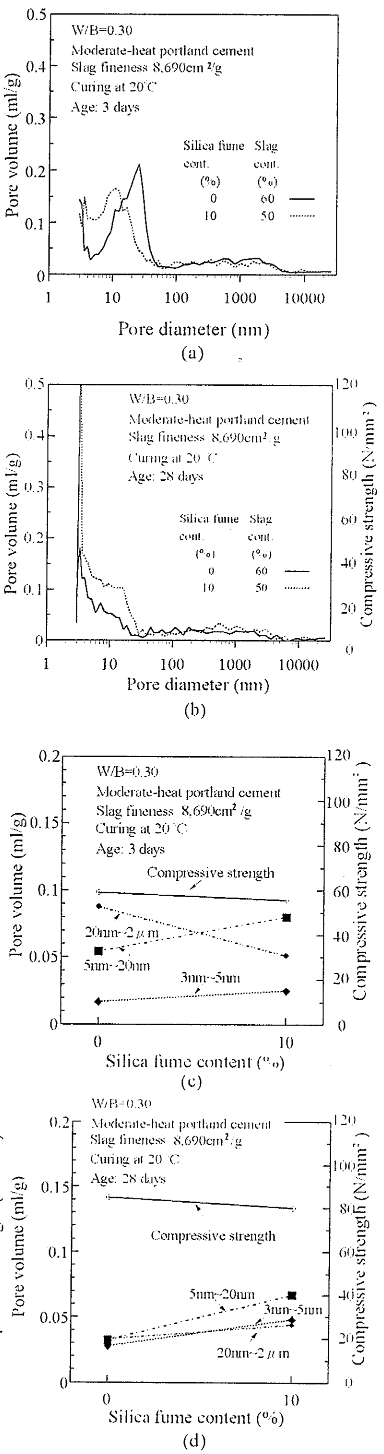
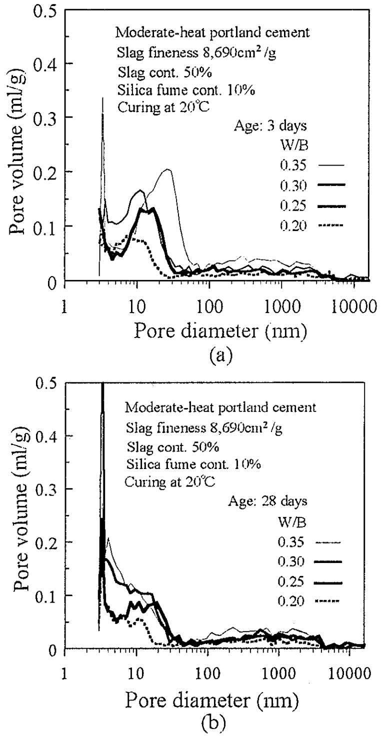
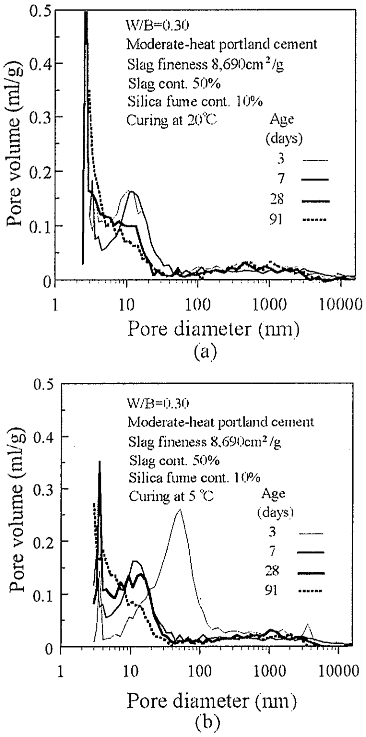


Fig. 27 Effects of Silica Fume Content on Pore-Diameter Distribution and Relationship between Pore Volume and Compressive Strength





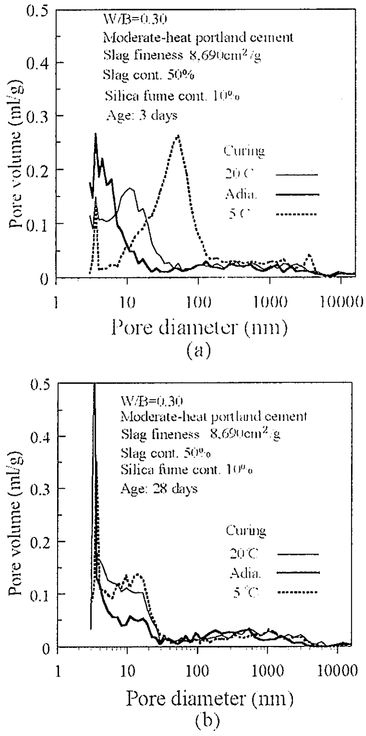
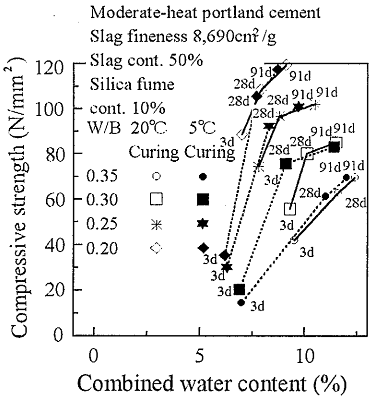
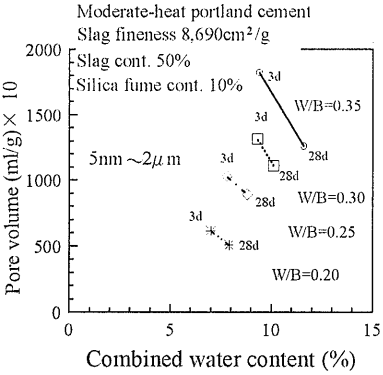


Fig. 28 Effect of Water-Binder Ratio on Pore-Diameter Distribution

Fig. 29 Change in Pore-Diameter Distribution over Time

Fig. 30 Effects of Curing TemperatureonPore-Diameter Distribution





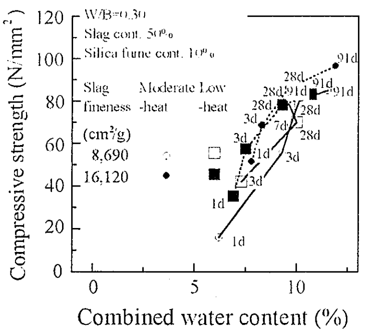


Fig. 31 Relationship between Compressive Strength and Combined Water Content

Fig. 32 RelationshipbetweenPore Volume and Combined Water Content

Fig. 33 EffectsofSlagFinenesson the Relationship between Compressive Strength and Combined Water Content

3.8 Ca(OH)$_2$

Figure 34 shows changes in Ca(OH)$_2$ content with age. In the case of slag with a fineness of 16,120cm^2/g, Ca (OH)$_2$ was barely detected because only a small amount of Ca(OH)$_2$ was produced and it reacted with the slag. However, in the case of slag with a fineness of 8,690 cm^2/g,

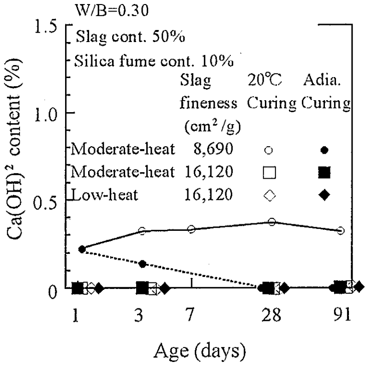


Fig. 34 Ca(OH)2 Content

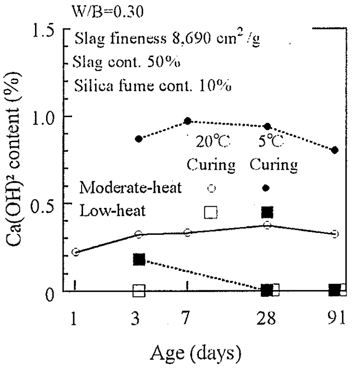


Fig. 35 Effects of Low Temperature on Ca(OH)2Content

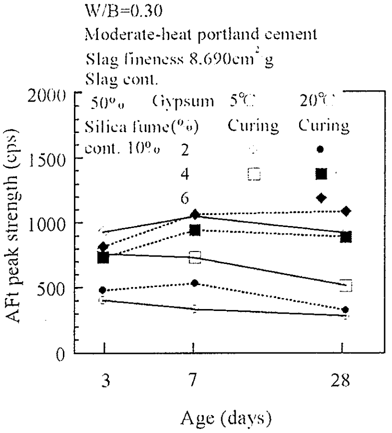


Fig. 36 Peak Strength of Ettringite by X-ray Diffraction

it can be assumed that the supply and consumption of $Ca(OH)_2$ were almost equal. It can be assumed that, in the case of adiabatic curing, hydration of the slag greatly reduced the $Ca(OH)_2$ content. Fig.35 shows the effect of low temperature on the $Ca(OH)_2$ content. It can be deduced that when moderate-heat portland cement was used, the low curing temperature inhibited the consumption of $Ca(OH)_2$ and so ettringite formation was predominant. This led to a large $Ca(OH)_2$ content, whereas, in the case of curing at 20℃, a certain amount of $Ca(OH)_2$ was consumed. In the case of low-heat portland cement, the amount of $Ca(OH)_2$ formed was small.

Figure 36 shows the relationship between age and peak ettringite strength by X-ray diffraction. From the figure, it can be seen that when the concrete was cured at low temperature, the formation of ettringite was generally more active than C-S-H formation. This explains the relatively large amount of remaining $Ca(OH)_2$ in the above-mentioned case of low-temperature curing.

3.9 SEM observations and quantitative analysis of chemical constituents by EDS

Photo 1 shows SEM photos of the hardened binders. At the age of 3 days, the structure of a hardened binder specimen cured at 5℃ was coarser than that cured at any other temperature. A specimen cured under adiabatic conditions had the finest structure. The photo also shows that, at the age of 91 days, the structure of a hardened binder cured at 20℃was almost the same as that cured at 5℃. In this case, the hydrate was granular, while when cured under adiabatic conditions, it became plate-like. Photo 2 shows the difference in form according to water-binder ratio. When the water-binder ratio was 0.35, the result was granular. When the water-binder ratio was 0.20, the result was plate-like. The form of hydrates corresponds fully with the above-mentioned measurement results regarding pore structure and compressive strength.

Photo3 shows SEM photos of hardened binder samples cured at 20℃and under adiabatic conditions at the age of 3 days. Table 8 shows the results of EDS analysis of the points numbered in the photo. From these results, it can be seen that C-S-H with Al_2O_3 and MgO were formed. The molecular ratio of CaO to SiO_2 was 0.9-1.9. The molecular ratio of CaO to SiO_2 was generally smaller than that of the hardened binder when ordinary portland cement was used. This seems to be a result of using cement containing much C_2S, highly pulverized blast-furnace slag, and silica fume.

3.10 Comprehensive discussion of strength development and heat-generation properties

The basic properties of the concrete considered in this study are low heat and high strength. The development of early strength and of strength at low temperatures is particularly notable.

The strength of blast-furnace cement concrete derives from the hydration of cement clinker and of blast-furnace slag. The possible hydration processes of blast-furnace slag are as follows[19] :

Table 8 Results of EDS Quantitative Analysis of Chemical Composition

Specimen condition	Analytical results (%)					CaO / SiO_2 Molecular ratio	Notes
	No	SiO_2	Al_2O_3	CaO	MgO		
Curing at 20°C	1	34.4	13.9	42.8	5.7	1.3	Slag
	2	36.0	7.2	43.3	1.2	1.3	C-S-H
	3	31.7	7.4	44.4	1.9	1.5	C-S-H
	4	46.1	6.2	36.3	1.6	0.9	C-S-H
	5	33.6	14.0	42.1	5.7	1.3	Slag
Adiabatic curing	1	32.1	13.3	44.8	5.4	1.5	Slag
	2	41.1	6.4	44.0	1.9	1.1	C-S-H
	3	37.5	6.4	47.3	2.5	1.4	C-S-H
	4	31.6	7.1	53.3	2.9	1.8	C-S-H
	5	34.0	4.0	52.3	1.1	1.6	C-S-H
	6	30.6	5.2	55.2	1.7	1.9	C-S-H

Moderate-heat cement, slag fineness: 8,690cm^2/g; age: 3 days

$$\begin{aligned}&5CaO\cdot 3SiO_2\cdot Al_2O_3 + 2CaO + 16H_2O\\ &\qquad\rightarrow 5CaO\cdot 3SiO_2\cdot Al_2O_3 + 2Ca(OH)_2 + 14H_2O\\ &\qquad\rightarrow 4CaO\cdot Al_2O_3\cdot 13H_2O + 3(CaO\cdot SiO_2\cdot H_2O) \qquad (1)\end{aligned}$$

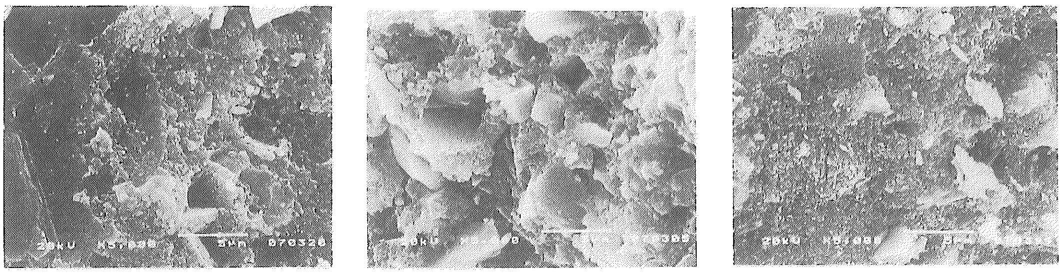
$$\begin{aligned}&5CaO\cdot 3SiO_2\cdot Al_2O_3 + 2CaSO_3 + 76/3\cdot H_2O\\ &\qquad\rightarrow 3(CaO\cdot SiO_2\cdot H_2O) + 2/3\cdot 3CaO\cdot Al_2O_3\cdot 3CaO_4\cdot 32H_2O + 2/3\cdot Al(OH)_3 \qquad (2)\end{aligned}$$

Equation (1) describes the hydration of blast-furnace slag and $Ca(OH)_2$. Equation (2) describes the formation of ettringite by the reaction of blast-furnace slag with gypsum.

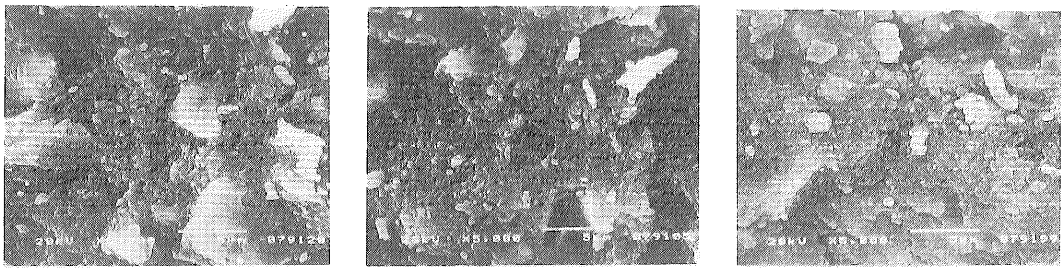
As shown in Figs. 4-10, significant strength developed at the age of 3 days. It is known from Fig.36 that a higher gypsum content results in increased ettringite formation. The gypsum used in this study was 4% SO_3. The peak strength of ettringite in hardened paste, at the age of 3 days, was almost the same whether cured at 5 ℃ or 20 ℃ .Therefore, it can be said that strength development up to the age of 3 days in the case of 5℃ curing is primarily attributable to ettringite, while the difference between compressive strengths in concrete cured at 20℃ and 5℃ is due to hydrated products other than ettringite. Fig.37 shows the effect of type of cement and slag fineness on the peak strength of ettringite. The effects of the individual factors are not clear. However, the trends indicated in the figure are that the peak strength of ettringite is much greater than that of conventional concrete[20)] and that ettringite does not change into monosulfate over time.

Figure 38 is a schematic model of concrete strength development factors based on the above understanding of the hydration of blast-furnace slag and the properties of the cement used. The influence of these factors on compressive strength differs depending on the materials used and the mix proportion. Since the concrete in this study is a high-strength concrete, the formation of C-S-H by slag and alkali water was ignored.

It can be said that the low heat of concrete in this study results from the low C_3S content in the cement, the low unit cement content, taking into account the water-binder ratio, and the reduced degree of hydration compared with conventional concrete. It is known that the formation of ettringite is usually accompanied by high heat generation. However, it is believed that at early age, the formation of ettringite did not greatly affect the ultimate adiabatic temperature since heat generation by cement clinker was limited by the properties of the cement used. Exothermic activity generally tended to be higher at early ages. However, it can be assumed that at these early ages, the adiabatic temperature rise of the concrete in this study was approximately the same as that of conventional concrete using ordinary portland cement.

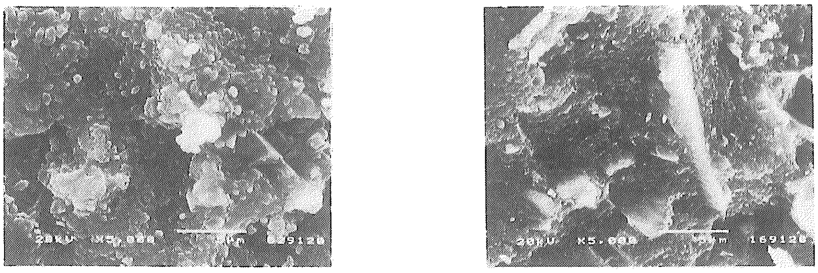


(a) 20℃ Curing (3 days)　(c) 5 ℃ Curing (3 days)　(e) Adiabatic Curing (3 days)



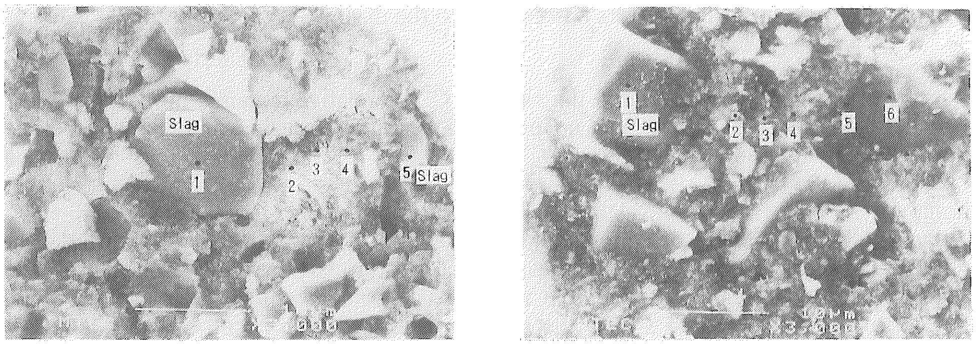
(b) 20℃ Curing (91 days)　(d) 5 ℃ Curing (91 days)　(f) Adiabatic Curing (91 days)

Photo 1 SEM Photo(W/B=30%;moderate-heat portland cement;slag fineness:8,690cm^2/g; slag content:50%;silica fume content: 10%)



(a) W/B=35%　(b) W/B=20%

Photo 2 SEM Photo(Moderate-heat portland cement;slag fineness:8,690cm^2/g;slag content: 50%; silica fume content; 10%;curing at 20℃;age:91 days)



(a) 20℃ Curing　(b) Adiabatic Curing

Photo 3 SEM Photo(W/B=30%;moderate-heat portland cement;slag fineness:8,690cm^2/g; slag content:50%;silica fume content: 10%;age:3 days)

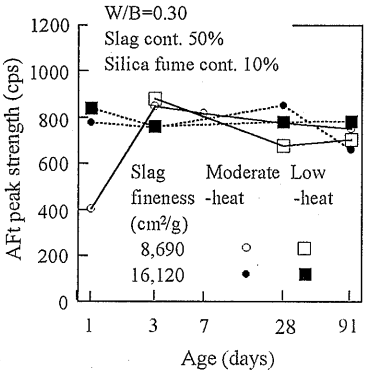


Fig. 37 Effects of Type of Cement and Slag Fineness on Peak Strength of Ettringite

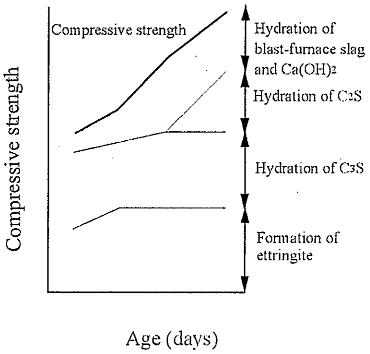


Fig. 38 Strength Development Factors

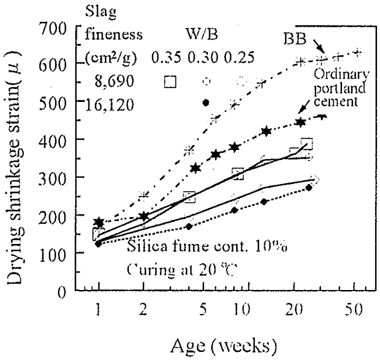


Fig. 39 Change in Drying Shrinkage Strain over Time

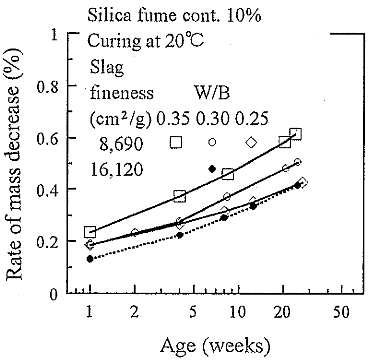


Fig. 40 Change in Rate of Mass Decrease

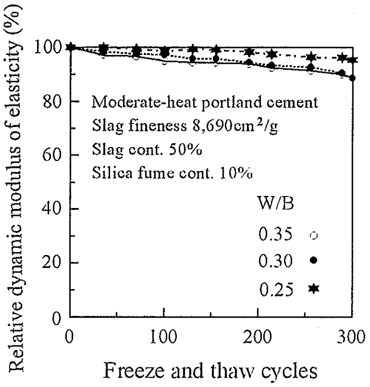


Fig. 41 Relative Dynamic Modulus of Elasticity in Freezing and Thawing Tests

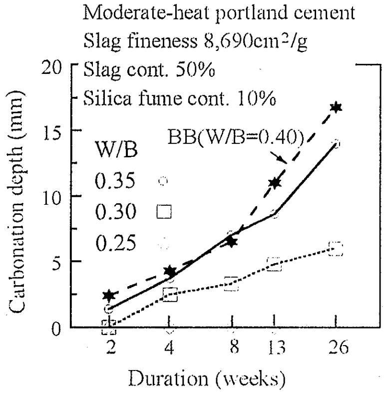


Fig. 42 Effects of Water-Binder Ratio on Carbonation Depth

3.11 Drying shrinkage strain

Figure 39 shows the drying shrinkage strain over time. As the water-binder ratio decreased or the slag fineness increased, drying shrinkage strain tended to decrease. For comparison, the figure shows a case in which the water-binder ratio was 50% and blast-furnace cement (BB) was used, and another case in which the water-binder ratio was 25% and ordinary portland cement was used. The drying shrinkage strain of concrete used in this study was smaller than that of these cases. Fig.40 shows changes in mass loss over time. The results correspond to the drying shrinkage strain.

3.12 Freezing and thawing resistance

Figure 41 shows the results of freezing and thawing tests. The relative dynamic modulus of elasticity was more than 90%, therefore, there was no problem regarding freezing and thawing resistance. The mass hardly changed at all.

3.13 Carbonation

Figures 42 and 43 show the effect of water-binder ratio and slag fineness on carbonation depth. As the water-binder ratio decreased or slag fineness increased, the carbonation depth decreased. For reference, Fig.42 shows the results of a case in which blast-furnace cement (BB) was used and the water-binder ratio was 40%. Fig.44 shows the effects of silica fume on carbonation depth. When silica fume was used, the carbonation depth increased. This corresponds to the pore-diameter distribution shown in Fig.27. As shown in Fig.34, when the slag fineness was large, $Ca(OH)_2$ was barely detected. However, Fig.43 shows that the carbonation depth was small because the concrete had a finestructure,

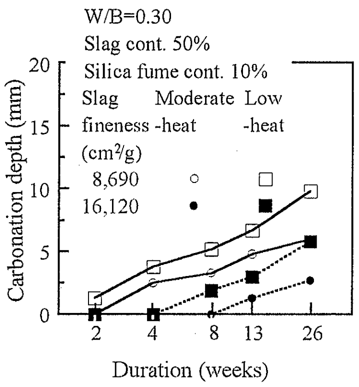


Fig. 43 Effects of Slag Fineness on Carbonation Depth

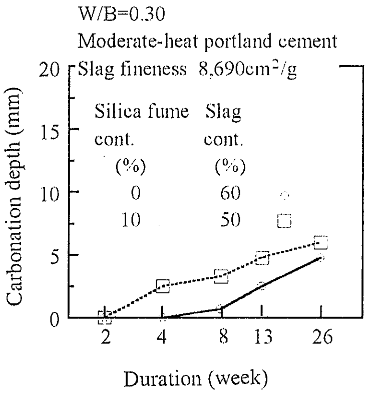


Fig. 44 Effects of Silica Fume on Carbonation Depth

as shown in Figs.25 and 26. The carbonation depth observed under a microscope was almost identical to that measured by the phenolphthalein method.

4. CONCLUSIONS

In this study, the basic heat and strength properties of concrete using highly pulverized blast-furnace slag, silica fume, and low-heat cement were studied. The results lead to a new low-heat high-strength concrete which is quite different from conventional types of concrete. From the results of this study, the following conclusions can be drawn:

(1) As the water-binder ratio decreased, the superplasticizer used in this study achieved better binder dispersion, including improved dispersion of the highly pulverized blast-furnace slag, thus greatly decreasing the unit water content and consequently the unit binder content.

(2) With increasing slag fineness or decreasing of water-binder ratio, the compressive strength increased. At the age of 3 and 91 days, the maximum compressive strengths were 83.8 N/mm^2 and 119 N/mm^2, respectively. This high compressive strength development at an early age was due to the ettringite formed by the reaction of blast-furnace slag and gypsum.

(3) The use of silica fume improved the properties of the fresh concrete. However, the compressive strength of concrete with silica fume tended to be less than that without silica fume.

(4) Concrete cured adiabatically developed the greatest strength. At the age of 3days, the maximum strength of concrete cured at 5°C was 35.2 N/mm^2.

(5) Compressive strength is related to pore volume when categorized according to pore diameters of 3 nm to 5 nm, 5 nm to 20 nm, and 20 nm to 2 mm.

(6) With aging, the combined water content increases. As the water-binder ratio decreases, the combined water content tends to decrease. Thus, concrete strength development mechanisms can be inferred by evaluating the combined water content.

(7) The adiabatic temperature rise of the concrete used in this study was much smaller than that of conventional concrete, primarily because low-heat cement was used, the cement content was small, and the hydration was relatively low due to good dispersion of the binder particles.

(8) The rate of temperature rise in simplified adiabatic temperature rise mortar tests, as measured using platinum thermo-resistor, gives an effective evaluation of the conditions under which the hydration reaction takes place.

(9) The amount of remaining $Ca(OH)_2$ is smaller than that in conventional concrete.

(10) There are no particular problems regarding drying shrinkage strain and resistance to freezing and thawing and carbonation.

5. AFTERWORD AND ACKNOWLEDGMENTS

It has been little more than 100 years since cement production technology was introduced to Japan. Since then, concrete technology has experienced several major turning points. Recent years have seen particularly daunting challenges in the development of various types of high-performance concrete; there are usually many obstacles to the practical utilization of these new types of concrete. The greatest of these obstacles is cost performance. Extreme concrete capabilities satisfy users in terms of cost performance, and the development of materials that emphasize this aspect must be promoted. To this end, it is essential to conduct basic studies aiming at the ultimate performance.

The aim of this study was to develop a low-heat, high-strength concrete. It has long been believed that these qualities are mutually exclusive in conventional concrete. The authors fully realize that there still remain areas to be dealt with and we intend to further develop our study.

In promoting this study, the authors had valuable opportunities to exchange opinions with members (representativs from 11 manufacturers of cement and admixtures) of the LHCL (Low-Heat High-Strength Concrete in Low-Temperature Environments) research group, which was led by the first author of this paper. The authors wish to thank Mr. Shinichi Wakasugi, R&D Division, Nittetsu Cement Co., Ltd. for his cooperation in conducting the various tests.

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