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INFLUENCE OF HEAT OF HYDRATION INDUCED THERMAL HISTORY ON MECHANICAL CHARACTERISTICS AND DURABILITY OF MASSIVE CONCRETE

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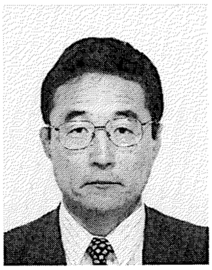
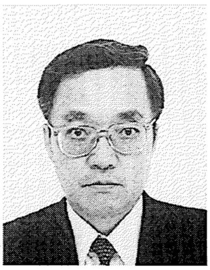
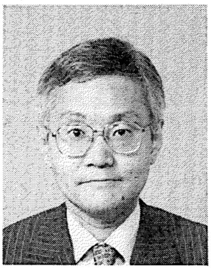
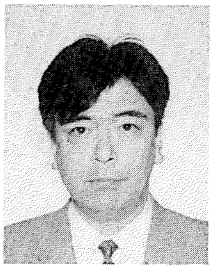
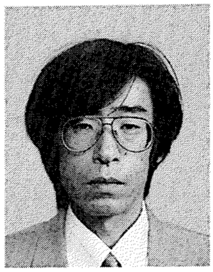

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This study investigates the characteristics of massive concrete that has experienced a thermal history induced by heat of hydration. Through a study of both mortar and concrete specimens cured under artificial heating to simulate heat of hydration, the influence of temperature history on the mechanical characteristics and durability of mortar and concrete are revealed. The specimens are blocks designed to simulate actual massive structures, and the test results indicate that chloride ion penetration depth and carbonation depth, as well as compressive strength, degrade as a result of the initial temperature history for at least 6.5 years after casting.

Key Words: massive concrete, compressive strength, chloride permeability, carbonation, microstructures, heat of hydration, durability

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1. INTRODUCTION

From the viewpoint of durability, it is very important to evaluate the characteristics of massive concrete structures subjected to high temperatures and to take countermeasures against cracks that may be induced by heat of hydration. It is known that, when high temperatures are induced in massive concrete by heat of hydration, its characteristics are poorer as compared with those of concrete cured at moderate temperatures. Investigations of the influence of curing temperature on compressive strength and microstructure[1][2][3], as well as the influence of steam curing on concrete strength[4][5], have been reported. As for high-performance concrete, which contains a high volume of cement and so suffers a more extreme thermal history, research has demonstrated the importance of controlling the rate of temperature rise as well as the maximum temperature induced by heat of hydration if adequate concrete strength is to be achieved[6][7].

This paper focuses on the influence of initial heat of hydration on the long-term characteristics of concrete. The investigation makes use of 6.5-year-old mortar specimens, 5.5-year-old concrete specimens exposed to an artificial thermal history simulating heat of hydration, and 4.5 year-old core samples taken from a massive concrete block.

2. TEST PROCEDURE

Three types of cement were used in the experiments: ordinary Portland cement (OPC), blast-furnace slag cement type B (BB), and low-heat blast-furnace slag cement type B (LBB). The LBB contains 46% low-heat Portland cement conforming to JIS R 5210 except in the amount of SO_3, and 54% ground blast-furnace slag. The chemical composition and physical properties of these cements are indicated in **Tables 1** and **2**, respectively.

(1) Test Series 1

In this series of experiments, cylindrical mortar specimens measuring $\phi 50 \times 100$ mm were used to investigate the influence of an artificial thermal history on mortar characteristics. As indicated in **Table 3**, tests were carried out for 18 cases consisting of three types of cement, three water-cement ratios, and two maximum temperatures.

Table 1 Chemical composition of cements

Type of cement	Chemical composition (%)								
	ig. loss	insol.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Total
OPC	1.0	0.4	21.8	5.8	2.6	63.4	1.5	2.2	98.7
BB	1.3	0.5	25.6	9.0	1.7	55.8	2.6	2.1	98.6
LBB	0.2	0.0	29.8	9.3	2.1	51.3	3.4	1.6	97.6

Table 2 Physical properties of cements

Type of cement	Density (kg/m^3)	Specific surface (cm^2/g)	Compressive strength (N/mm^2)			Heat of hydration (J/g)	
			7days	28days	91days	28days	91days
OPC	3150	3350	27.8	42.0	46.8	385	410
BB	3020	4090	21.1	41.2	49.0	352	378
LBB	3050	4580	11.1	31.3	48.0	193	236

Table 3 Cases investigated in Series 1

Type of cement	Temp at casting	Max. temp.	Temp. rise rate	water / cement		
				0.45	0.55	0.65
OPC	20℃	Cured in water		○		
	20℃	Cured in water			○	
	20℃	Cured in water				○
	20℃	70℃	40℃/day	○		
	20℃	70℃	40℃/day		○	
	20℃	70℃	40℃/day			○
BB	20℃	Cured in water		○		
	20℃	Cured in water			○	
	20℃	Cured in water				○
	20℃	60℃	40℃/day	○		
	20℃	60℃	40℃/day		○	
	20℃	60℃	40℃/day			○
LBB	20℃	Cured in water		○		
	20℃	Cured in water			○	
	20℃	Cured in water				○
	20℃	50℃	40℃/day	○		
	20℃	50℃	40℃/day		○	
	20℃	50℃	40℃/day			○

Table 4 Mix proportions of mortar in Series 1

Type of cement	W/C	Unit weight (kg/m^3)				
		Cement	Water	Fine aggregate	Admixture	
					Water-reducing	Air-entraining
OPC	0.45	544	232	1345	8.07	5.44
	0.55	442	233	1452	5.65	4.42
	0.65	373	233	1516	5.51	3.73
BB	0.45	540	230	1334	8.01	5.40
	0.55	439	232	1453	6.52	4.39
	0.65	371	232	1508	5.48	3.71
LBB	0.45	541	231	1337	8.02	5.41
	0.55	440	232	1455	6.53	4.40
	0.65	370	232	1510	5.49	3.71

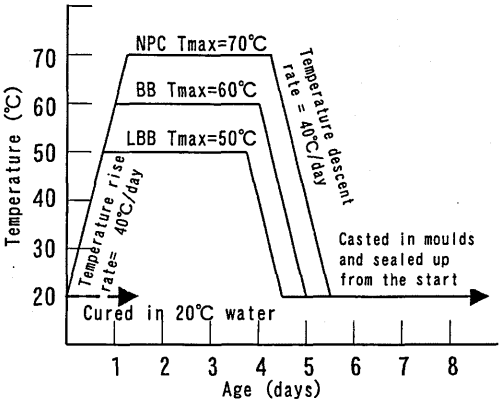


Fig. 1 Artificial thermal history in Series 1 and 2

The mortar mix proportions are shown in **Table 4.** The fine aggregate used in the test was river sand with a fineness modulus of 2.84 and a density of 2.61 g/cm^3. The mortar was mixed in a pan-type mixer of 30-liter capacity for two minutes without water and for two minutes after adding the water. As an AE admixture, ligninsulfonic acid and an alkyl-allyl sulfonate anion surface-active agent was used. After casting in steel molds, which were sealed at the top with steel plates and a sealant, the mortar specimens were cured under the thermal histories shown in **Fig. 1**[8]. These thermal histories were obtained from the adiabatic temperature rise characteristics of a typical massive concrete containing 300 kg/m^3 of cement. After experiencing these thermal histories, the specimens were kept in a room at a constant temperature of 20℃ and a constant relative humidity of 60%.

For reference, some specimens were not subjected to a thermal history. These were removed from the molds one day after casting and cured in water at 20℃ as standard cured specimens until testing.

Table 5 Mix proportion of concrete in Series 2

Type of cement	W/C	Unit weight (kg/m^3) Cement	Water	Aggregate Fine	Aggregate Coarse	Admixture Water-reducing	Admixture Air-entraining
OPC	0.55	295	162	797	1061	0.738	0.177
BB	0.55	295	162	794	1056	0.738	0.177
LBB	0.55	295	162	793	1054	0.738	0.708

Table 6 Investigated cases in Series 2

Type of cement	Temp at casting	Max. temp.	Temp. rise rate	water / cement 0.45	0.55	0.65
OPC	20℃	Cured in water		-	○	-
	20℃	70℃	40℃/day	-	○	-
BB	20℃	Cured in water		-	○	-
	20℃	60℃	40℃/day	-	○	-
LBB	20℃	Cured in water		-	○	-
	20℃	50℃	40℃/day	-	○	-

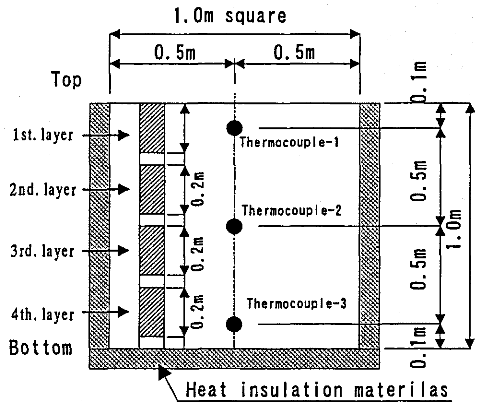


Fig. 2 Outline of concrete block

(2) Test Series 2

In this series, the same thermal histories as in Series 1 were applied to cylindrical concrete specimens measuring ϕ100×200 mm. Mix proportions and cases are shown in **Tables 5** and **6**, respectively. The fine aggregate used for these concrete specimens was river sand with a fineness modulus of 3.08 and a density of 2.62 g/cm^3, and the coarse aggregate was crushed stone with a maximum particle size of 20 mm and a fineness modulus of 6.7.

The mixing, casting, and sealing procedure was the same as in Series 1. After applying the artificial thermal history, the specimens were kept in a room at 20℃ and 60% R.H. until testing.

(3) Test Series 3

To evaluate the influence of thermal history in an actual concrete structure, a one cubic meter concrete block enclosed in heat-insulating material, as shown in **Fig. 2**, was prepared. The water-cement ratio was 0.55 and BB cement was used, as indicated in **Table 7.** The fine aggregate was river sand with a fineness modulus of 2.55 and a density of 2.59 g/m^3. As a coarse aggregate, gravel and crushed stone with fineness modulus 6.84 and 6.67 and densities of 2.59 and 2.65 g/cm^3, respectively, were equally mixed. The concrete was cured under a wet mat for 3 days after placement and was then stored outdoors.

The thermal history of the block was measured by thermocouples at the positions indicated in **Fig. 2**. The thermal history measurements, as shown in **Fig. 3**, confirmed that the maximum temperature rise was approximately 30℃ at the center of the block and that the rise rate was about 25℃/day. These values were less severe than the artificial thermal history adopted for BB in Test Series 1 and 2. Moreover, the maximum temperature near the block surface, as measured by thermocouple-1 in **Fig. 2**, was approximately 10℃ lower than that measured at the center or bottom of the block.

An investigation was carried out on ϕ100 mm core specimens taken from the block as shown in **Fig. 2**. Evaluations were conducted immediately after sampling except in the case of 4.5-year-old specimens, which were sampled from the block about one year after casting and stored in water till testing. The test results were evaluated in comparison with standard cured specimens.

Table 7 Mix proportions of concrete in Series 3

Type of cement	W/C	Unit weight (kg/m^3)					
		Cement	Water	Aggregate		Admixture	
				Fine	Coarse	Water-reducing	Air-entraining
BB	0.55	273	150	803	1084	0.546	0.015

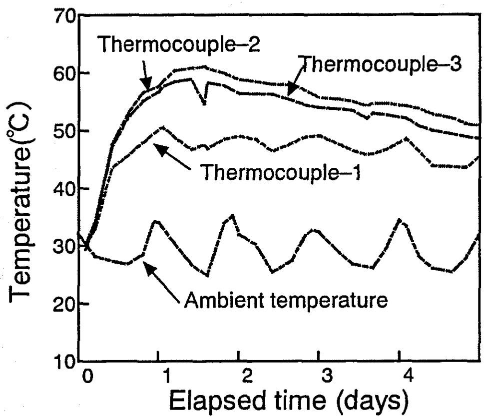


Fig. 3 Thermal history of concrete block

3. EVALUATION S AND METHODS

The evaluations used to clarify the influence of initial thermal history on the long-term characteristics of mortar and concrete are shown in **Table 8.**

(1) Compressive Strength, Tensile Strength, and Young's Modulus

The compressive strength, tensile strength, and Young's modulus of specimens were measured according to JIS A1108, JIS A1113, and JSCE G 502, respectively. The specimens in Series 1 and 2, which were subjected to the thermal history and then stored, were tested immediately after stripping from the sealed molds and polishing the upper surface. The core samples in Series 3 were taken from the block and prepared immediately before testing, except for the 4.5-year-old specimens as mentioned before.

(2) Penetration Depth of Chloride Ions

The permeability of chloride ions in the concrete was evaluated by measuring the chloride penetration depth. A 0.1% fluorescent sodium solution and 0.1 N silver nitrate solution was sprayed on the split face of a cylindrical specimen that had been immersed in sea water at a temperature of 20℃ for a specified period, and the fluorescing area was then measured. Once specimens reached the appropriate age, they were immersed in seawater

Table 8 Evaluation items adopted in each series

	1st. series				2nd. series					3rd. series			
Age	7 days	28 days	91 days	6.5 years	3 days	7 days	28 days	91 days	5.5 years	28 days	91 days	182 days	4.5 years
Compressive Strength	O	O	O	O	O	O	O	O	O	O	O	O	O
Tensile Strength					O	O	O	O	O				
Young's modulus					O	O	O	O	O	O	O	O	O
Chloride penetration depth		O	O	O			O	O	O	O			O
Carbonation depth		O	O	O			O	O	O	O	O		O
Pore size distribution			O	O						O			O
SEM observations			O	O						O			O

immediately after preparation, which entailed removal from the molds in Series 1 and 2, sampling from the block in Series 3, and removing standard cured specimens from the water. Penetration depth was measured at six points of fluoresced area from the surface where the chloride concentration can be estimated more than 0.25% by weight of oven dried mortar component [9].

(3) Carbonation Depth

Specimens were prepared as for the chloride ion penetration depth measurements and exposed in a room at a constant temperature of 20℃ and a relative humidity of 60%. Carbonation depth was measured on split specimens after exposure for the specified term at the specified age, with the average of six measurements by the phenolphthalein method being calculated.

(4) Microstructure

At the specified age, the midsections of some specimens were crushed into fragments measuring 3 to 5 mm. The fragments were immersed in acetone for 2 hours and hydration was terminated by D-dry method in preparation for testing. The pore size distribution of the samples was measured with a mercury intrusion porosimeter. The microstructure was observed with a scanning electron microscope (SEM).

4. EXPERIMENTAL RESULTS AND DISCUSSION

(1) Compressive Strength, Tensile Strength, and Young's Modulus

a) Compressive strength of mortar specimens in Series1

The measured compressive strength of mortar specimens up to the age of 6.5 years is shown in **Fig. 4**. These results indicate that the compressive strength of specimens subjected to an artificial thermal history was greater than that of standard-cured specimens up to 7 days. Thereafter, the rise in compressive strength slows and by 28 days is the same as that of standard-cured specimens, regardless of cement type. By the age of 91 days, the compressive strength of specimens subjected to the artificial thermal history was between 0.72 and 0.79 that of the standard-cured specimens for OPC, 0.57 to 0.69 for BB and 0.45 to 0.59 for LBB.

It was observed that a gradual increase in compressive strength of specimens subjected to the thermal history took place up to 6.5 years. At this age, the compressive strength exceeded the 28-day strength of the standard-cured specimens, which is usually adopted as the design strength of OPC and BB, by a sufficient margin. However, the compressive strength of LBB at 6.5 years did not reach the 91-day strength of standard-cured specimens, which is usually adopted as the design strength for low-heat cement.

The reduced rise in compressive strength observed in specimens subjected to an artificial thermal history might result from a shortage of water during sealed curing. To confirm the influence of curing conditions on strength, some of the specimens subjected to an artificial thermal history and stored in sealed molds were cured in water

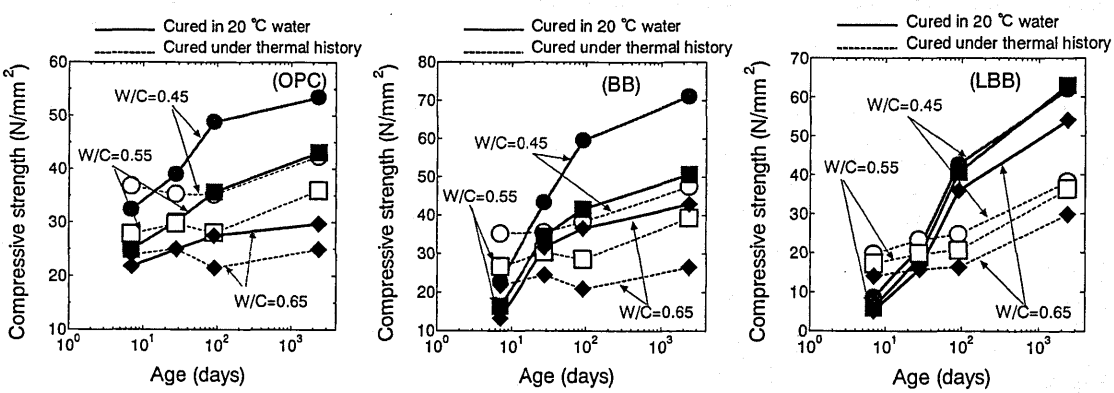


Fig. 4 Changes in compressive strength of mortar specimens in series 1

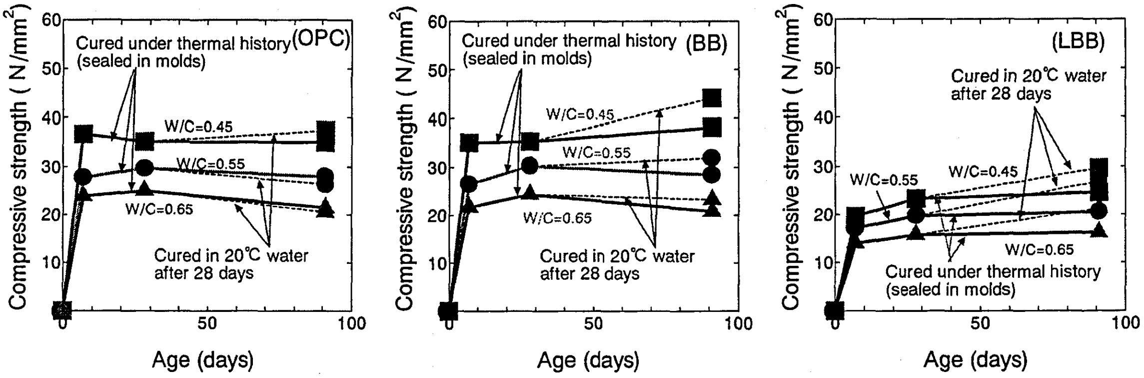


Fig. 5 Differences in strength development after 28 days between water curing and sealed curing

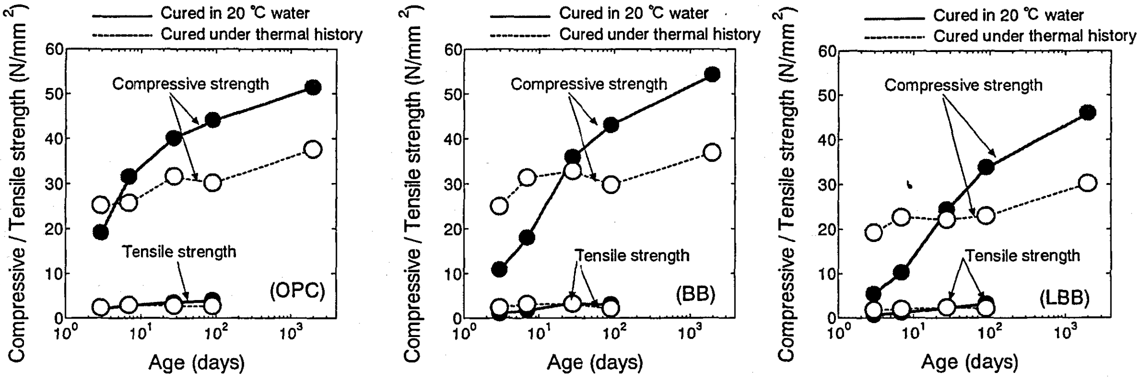


Fig. 6 Changes in compressive/tensile strength of concrete in Series 2

from 28 days to 91 days. As shown in **Fig. 5**, no rise in compressive strength of these specimens was obvious in the case of OPC specimens, while slight and significant increases were observed in the case of BB and LBB. These results indicate that the hydration of ground blast-furnace slag dominated the increase in compressive strength of BB and LBB specimens during water curing, while the reduced compressive strength resulting from saturation of the specimens prevailed in the case of OPC[10][11]. A comparison of Figs. 4 and 5 indicates that the development of compressive strength in specimens that experience an initial thermal history is poor regardless of the curing conditions when compared with that of standard-cured specimens.

b) Compressive strength of concrete specimens in Series 2

The compressive strength of concrete specimens subjected to an artificial thermal history is similar to that of mortar specimens, as shown in **Fig. 6**. At 5.5 years, the compressive strength of specimens subjected to the thermal history was comparably less than that of standard-cured specimens, with ratios of 0.73 for OPC, 0.68 for BB, and 0.66 for LBB.

c) Compressive strength of block specimens in Series 3

It has been reported that an artificial thermal history has a different influence on concrete characteristics from an actual heat of hydration history[12]. The changes in compressive strength of core specimens taken from the block and of standard-cured specimens are shown in **Fig. 7**. This confirms that the rise in compressive strength in cores taken from the block surface is less than that in the standard-cured specimens used in Series 1 and 2. No such tendency was obvious in cores taken from the center or lower part of the block. **Figure 8** shows the compressive strength of each core and its location; the compressive strength increases with distance from the block surface. In these test results, not only the thermal history but also bleeding and/or surface drying of the concrete block during curing [13] and consolidation by self-weight [7] influenced the test results.

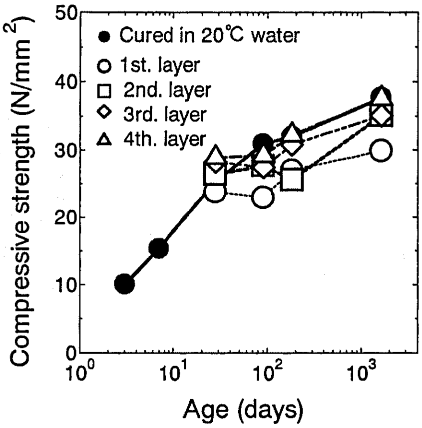


Fig. 7 Changes in compressive strength of core specimens in Series 3

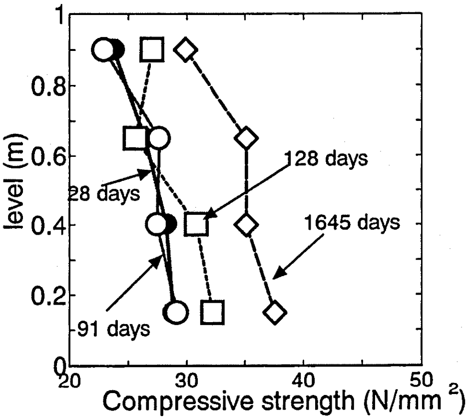


Fig. 8 Distribution of compressive strength of block

It has previously been reported that the compressive strength of concrete is affected by curing temperature rather than the temperature of the fresh concrete at casting [14][15], and these test results fit these findings.

d) Tensile strength and Young's modulus in Series 2

The influence of heat of hydration on the tensile strength of concrete is shown in **Fig. 6**. The changes in tensile strength of concrete specimens subjected to the artificial thermal history are similar to those in compressive strength; i.e. there is greater tensile strength at an early age, but the rate of increase is lower. The relationship between compressive strength and tensile strength, which is shown in **Fig. 9**, shows no obvious influence of thermal history. The correlation between compressive strength and Young's modulus for Series 2, as shown in **Fig. 10**, indicates good agreement with the dotted line, which is the relationship for common concrete as given in the JSCE concrete standard, and the effects of the thermal history are not significant.

(2) Penetration Depth of Chloride Ions

a) Penetration chloride ions in Series 1 mortar specimens

The chloride penetration depth into mortar specimens immersed in seawater for two months after the specified age is shown in **Fig. 11**. This figure shows that the penetration depth was greater in the case of OPC and BB specimens subjected to the initial thermal history up until the age of 6.5 years. On the other hand, the chloride

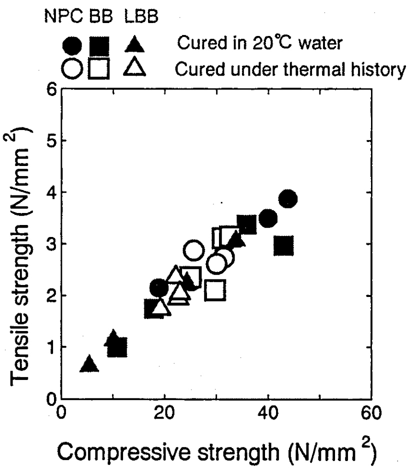


Fig. 9 Relationship between compressive strength and tensile strength in Series 2

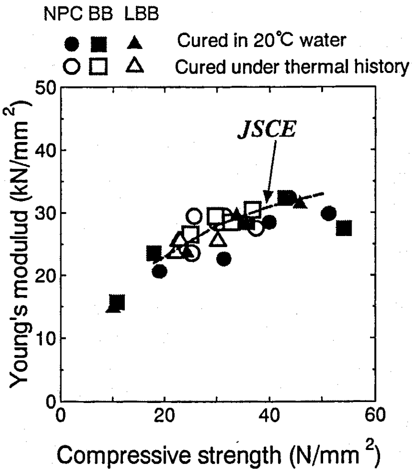


Fig. 10 Relationship between compressive strength and Young's modulus in Series 2

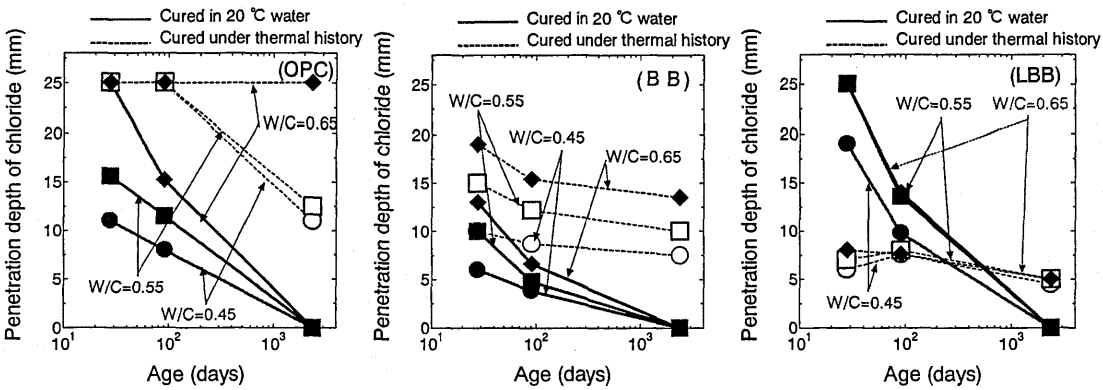


Fig. 11 Chloride penetration depth of mortar in Series 1 (Horizontal axis indicates age of specimens at start of two months immersion)

penetration depth in LBB specimens was less up to the age of 91 days, possibly because the accelerated cement hydration prevailed over the formation of defects as a result of the thermal history when compared with standard-cured specimens. However, defects formed during the initial heat of hydration tend to affect the long-term characteristics, and the penetration depth at the age of 6.5 years was greater than that of standard-cured specimens.

The time-dependent reduction in chloride penetration depth was less in specimens that experienced an artificial thermal history than that of standard-cured specimens. These test results demonstrate that the initial thermal history affects the chloride ion permeability in mortar until the age of 6.5 years.

b) Penetration depth of chloride ions in Series 2 concrete specimens

Figure 12 shows the chloride penetration depth of concrete specimens subjected to the artificial thermal history as well as that of standard-cured specimens after two months' immersion in seawater beyond the specified age. In the specimens subjected to the thermal history, the penetration depth is greater and depth reduction with age is smaller than for the standard-cured specimens. These results are similar to those for the mortar specimens. However, in contrast with the mortar specimens, the penetration depth of chloride ions at a younger age was smaller and changes in depth with age were not obvious. It is inferred that the coarse aggregate obstructs the permeation of chloride ions when the concrete is younger, while interfacial zones and/or other defects related to the coarse aggregate affect the long-term permeability[16]. Secondary ettringite formation in the interfacial zone, which may increase the penetration depth[17], was not observed in the EPMA investigation.

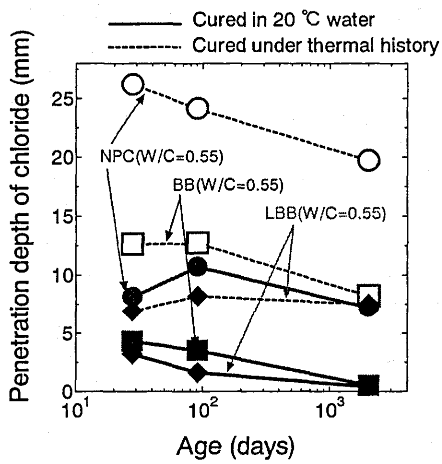


Fig.12 Penetration depth of chloride ions in concrete specimens in Series 2 (Horizontal axis indicates age of specimens at start of two months immersion

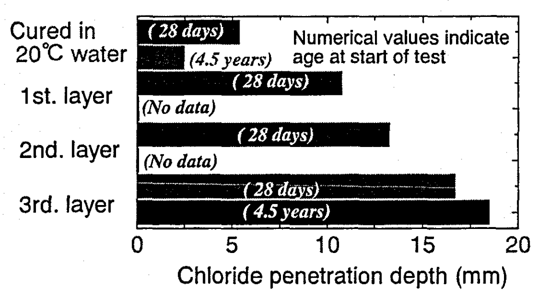


Fig. 13 Penetration depth of chloride ions in core samples in series 3

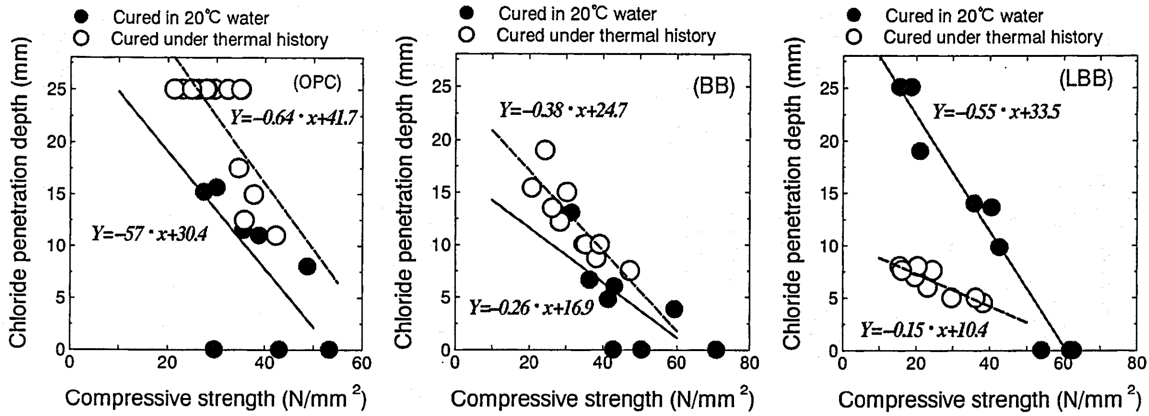


Fig. 14 Relationship between chloride ion penetration depth and compressive strength in Series 1

c) Penetration depth of chloride in block specimens in series 3
The chloride penetration depth in cored samples removed from the block specimen and in standard-cured specimens immersed in seawater for three months from the age of 28 days and from 4.5 years is shown in **Fig. 13**. These results show that the penetration depth of chloride ions in the core samples was greater than that in standard-cured specimens of both ages.

The core taken from the block surface indicates twice the chloride penetration depth seen in the standard-cured specimens, and the penetration depth increases with distance from the block surface. It is clear from these results that the heat of hydration affects the penetration depth of chloride ions. This influence of hydration heat on chloride penetration depth is clearly visible at the age of 4.5 years.

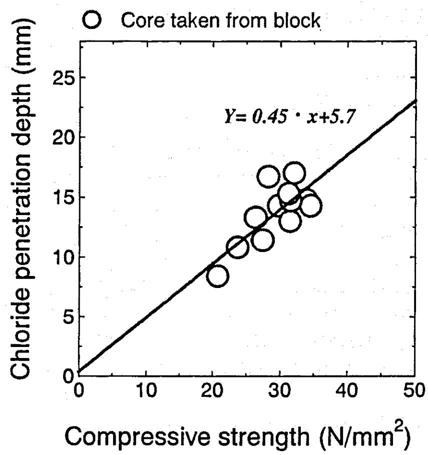


Fig. 15 Relationship between chloride penetration depth and compressive strength of core specimens taken from the block at the age of 28 days

d) Relationship between compressive strength and chloride ion penetration depth
Figure 14 shows the inverse relationship between compressive strength and chloride ion penetration depth. The correlation is different according to the cement type and the curing conditions. The relation obtained for core samples taken at the age of 28 days was different from that given by the mortar specimens, as shown in **Fig. 15**. In the mortar specimens, the increase in compressive strength was dominated by cement hydration, which closely affected chlorine permeability. On the other hand, the compressive strength and chlorine ion permeability in core samples taken from different locations in the block are likely to be affected by the thermal history, consolidation, bleeding, etc. The magnitude of these influences on chlorine permeability and strength are considered to be various, and these test results demonstrate the difficulty in evaluating chlorine permeability from the compressive strength of concrete.

(3) Carbonation Depth

a) Carbonation depth of mortar specimens in Series 1
The carbonation depth recorded in mortar specimens exposed for two months in a controlled room once the specified age was reached are shown in **Fig. 16**. The carbonation depth of those specimens subjected to the artificial thermal history is greater than that of standard-cured specimens up to the age of 6.5 years, regardless of the type of cement. However, carbonation depth does vary according to cement type, with LBB showing the

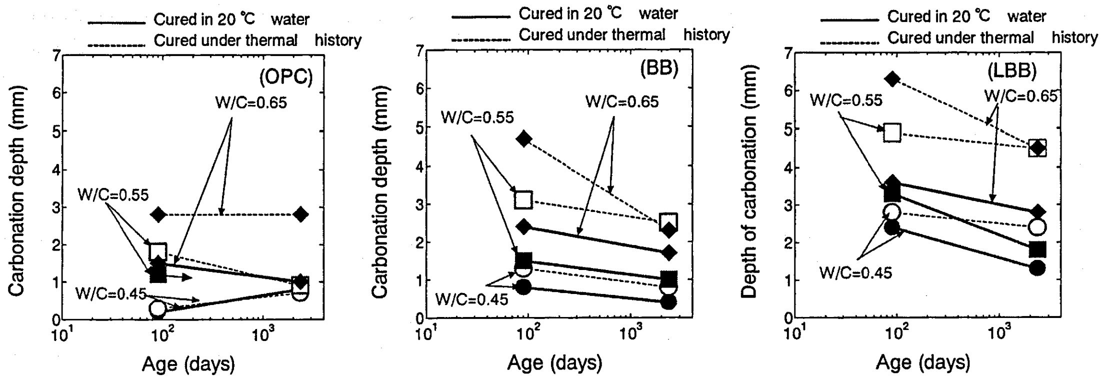


Fig. 16 Changes in carbonation depth of mortar specimens in Series 1 (Horizontal axis indicates age at start of test)

greatest depth, OPC the least, and BB in between for a given water-cement ratio. For one particular type of cement, the carbonation depth falls with a decrease in water-cement ratio. Another observation is that the carbonation depth differs according to age at which exposure begins, but the progress of carbonation depth with age is not as obvious as the rise in chloride penetration depth.

b) Carbonation depth of concrete specimens in Series 2

The influence of thermal history on concrete carbonation depth after two months of exposure is shown in **Fig. 17.** The test results show that carbonation depth is greater up to the age of 5.5 years in the case of specimens that experience the initial thermal history.

c) Relationship between carbonation depth and compressive strength

As shown in **Fig. 18,** the relationship between carbonation depth and compressive strength of mortar specimens is similar to that between chloride penetration depth and

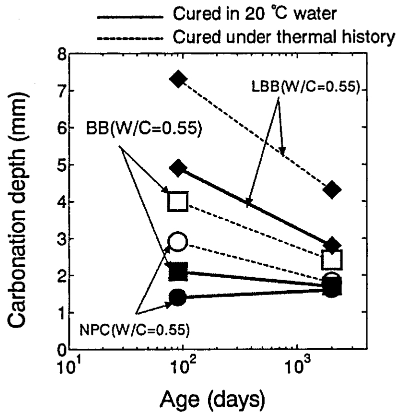


Fig. 17 Carbonation depth of concrete specimens in Series 2

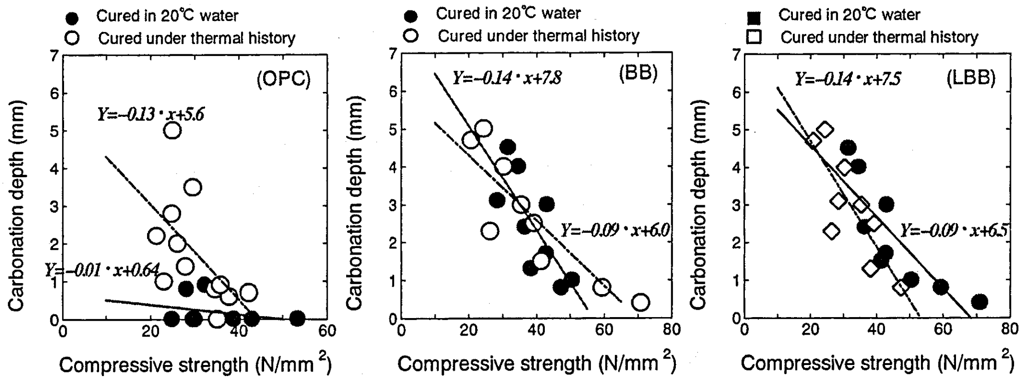


Fig. 18 Relationship between carbonation depth and compressive strength

compressive strength. However, the correlation is not as strong and is affected by the type of cement. From these results, it can be concluded that variations in the carbonation depth of mortar specimens subjected to a thermal history may arise not only from differences in microstructure but also the quantity of calcium hydrate generated[18]

(4) Pore Size Distribution

a) Mortar specimens in Series 1

Pore size distributions of mortar specimens are shown in **Figs. 19-21.** At 91 days, pores in the range 0.3-10 µm in specimens that experienced the artificial thermal history were more numerous than in specimens subjected to

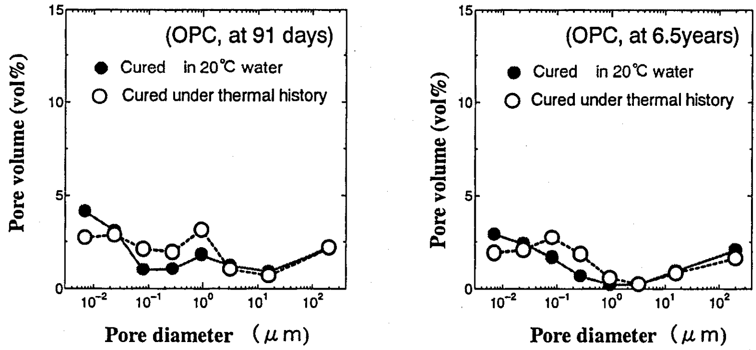


Fig. 19 Pore size distribution of OPC mortar

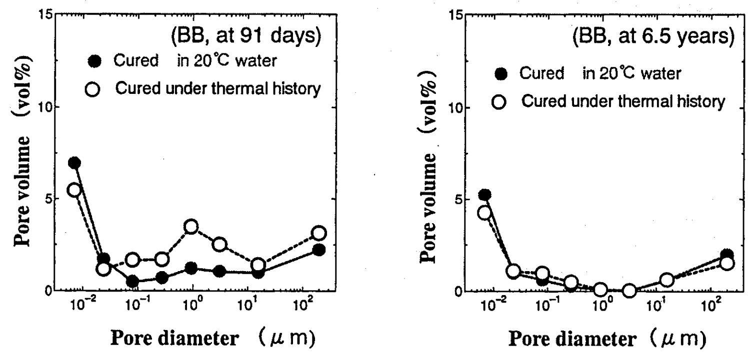


Fig. 20 Pore size distribution of BB mortar

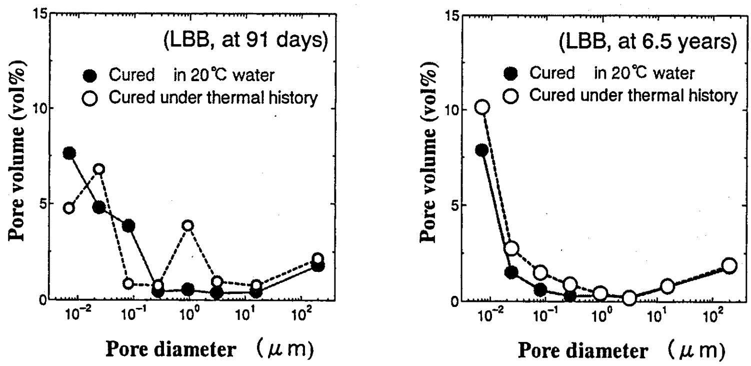


Fig. 21 Pore size distribution of LBB mortar

standard curing. At the age of 6.5 years, the overall pore count had decreased, but even then there were more pores measuring 0.3-10 μm in specimens subjected to the thermal history. This range is made up of capillary pores said to be from 0.03 to 30 μm in size [19], and it is considered that the effects of thermal history on capillary pores were great.

On the other hand, gel pores in the range corresponding to 1-3 nm, and entrained and entrapped air corresponding to pores 30 μm and larger, the effects of the thermal history were not very prominent, and, apparently, changes with advancing age were less than in the case of capillary pores.

Table 9 Changes in total pore volume of mortar in Series 1

	Type of cement and the pore volume at 91 days and 6.5 years								
	OPC			BB			LBB		
	91 days	6.5 years	Ratio	91 days	6.5 years	Ratio	91 days	6.5 years	Ratio
In water	18.38	12.37	0.67	16.92	0.059	0.66	19.98	15.12	0.76
Thermal history	20.04	12.53	0.63	23.62	0.056	0.47	26.24	19.91	0.76

Unit : vol. % Ratio = 6.5 years / 91 days

The total pore volume, as indicated in **Table 9**, tended to increase when specimens were subjected to the thermal history, irrespective of the type of cement. However, the total pore volume decreased with age, and the ratio of total pore volume at 6.5 years to that at 91 days ranged from 0.67 to 0.76 for standard-cured specimens, while it was 0.47 for BB and 0.63-0.76 for the other cements. Aside from the case of BB, there was no significant difference between the standard-cured and thermal history. These results confirm that even when an extreme thermal history is experienced, if the mortar is sealed and cured, the hydration reaction will progress over the long term similarly to that in standard-cured mortar, particularly in the case of BB.

b) Block specimens in Series 3

Pore size distributions of cores taken from block specimens and of standard-cured specimens are shown in **Fig. 22.**

Differences in pore size distribution between the cores and standard-cured specimens are not as distinct as with the mortar specimens. However, at the age of 4.5 years, pore volumes tended to be lower than at 28 days, and it can be seen that the decrease in capillary pore count was especially prominent. On the other hand, with thermal history specimens at 4.5 years, the quantity of pores in the range 0.1-2 μm was greater than in standard-cured specimens, a trend similar to that with mortar specimens.

The ratios of total pore volumes between the standard-cured and thermal history at 28 days and 4.5 years are given in Table 10. Goto et al.[20] reported that, for a maximum temperature of 70°C, no large differences in pore size distribution at 7 days and 128 days were seen. However, within the scope of the present experiments, the total pore volume at 4.5 years had decreased to 0.62 compared with 28

Table 10 Changes in total pore volume of concrete in Series 3

	Pore volume at 28 days and 4.5 years and ratio		
	28days	4.5years	Ratio
Cured in water	29.322	18.09	0.62
Cores	26.354	20.766	0.79

Unit : vol. % Ratio = 6.5 years / 28 days

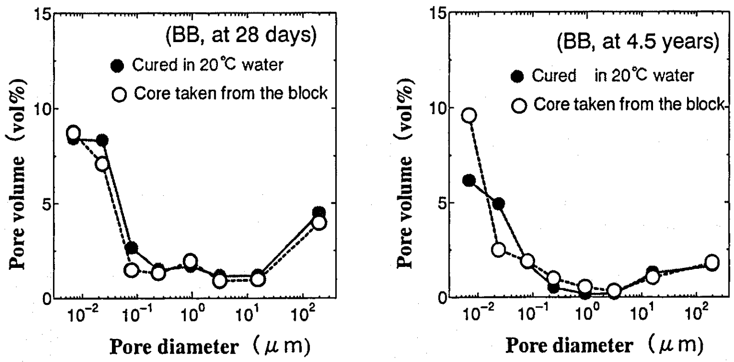


Fig. 22 Pore size distribution of specimens taken from block

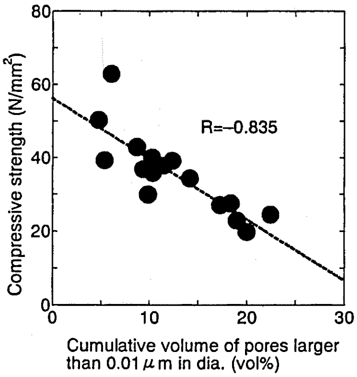


Fig. 23 Relationship between cumulative volume of pores larger than 0.01 μm in dia. and compressive strength

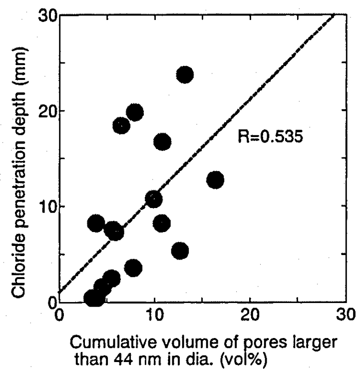


Fig. 24 Relationship between cumulative volume of pores larger than 0.044 μm in dia. and chloride penetration depth

days for standard-cured specimens. The ratio was 0.79 for thermal-history specimens. Thus, progress of the hydration reaction in thermal-history specimens over the long term was confirmed to be similar to that in mortar specimens.

According to the above, the influence of thermal history on pore size distribution, and especially on capillary pore volumes, is significant. It also confirms that it remains significant over the long term. We surmise that the effects of thermal history on pore size distribution are strongly related to the influence that thermal history has on physical values such as compressive strength, chloride ion penetration, and carbonation depth.

c) Relationship between pore volume and compressive strength

The relationship between compressive strength and the volume of pores 10 nm or more in diameter is shown in **Fig. 23**. There is no observable influence of thermal history, and compressive strength decreased with rising pore volume. The correlation factor (-0.835) obtained here is larger than the correlation factor (-0.754) between total pore volume and compressive strength, and is similar to what has been reported previously [21]. This confirms that a strong correlation exists between the volume of pores above a specific diameter and compressive strength.

d) Pore volume, chloride ion penetration depth, and carbonation depth

The correlation between the volume of pores over 44 nm in diameter and chloride ion penetration depth is shown in **Fig. 24**. The penetration depth tends to increase with rising pore volume, but the correlation factor is not large. This is thought to be because the penetration properties of chloride ions do not depend simply on pore volume, but also on other factors: differences in the fixation of aluminate phase chloride ions according to type of cement [20], and the influence of continuity and surface area of pores 4 nm and less in diameter [22].

There have in the past been attempts to tie the ease of mass transport within concrete to representative pore diameters [21][23][24][25], but within the scope of these experiments no distinct correlation of this type was noted.

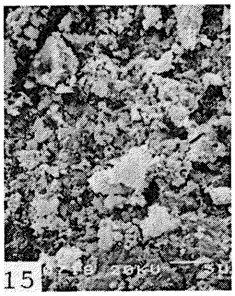
The carbonation depth, as with chloride ion penetration depth, increased with rising pore volume, but the correlation was not as strong as in the case of compressive strength.

(5) Microstructure of Hardened Mortar and Concrete

The results of observations of the microstructure of hardened mortar specimens at the ages of 91 days and 6.5 years, both standard-cured and subject to the artificial thermal history, are shown in **Photos 1** to **6**.

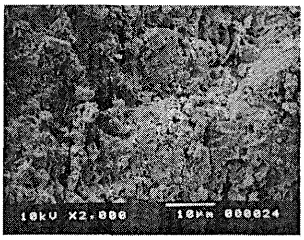
With standard-cured specimens of OPC, dense Type III or Type IV C-S-H structures were confirmed at 91 days. On the other hand, specimens subjected to the thermal history indicated granular hydration products at 91 days. These were thought to have been unable to grow sufficiently due to the influence of the thermal history. At the age of 6.5 years, it could be seen that the granular hydration products visible at the age of 91 days had been covered

Standard cured specimen

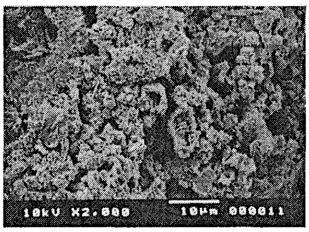


Specimen subjected to thermal history

Photo 1 SEM observations of OPC mortar at the age of 91 days



Standard cured specimen



Specimen subjected to thermal history

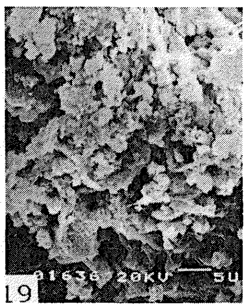
Photo 2 SEM observations of mortar Specimens at the age of 6.5 years

by C-S-H, but even then it appeared that comparatively large voids measuring 1-3 μm remained in the interior. It has previously been pointed out that the composition or configuration of C-S-H differs with curing temperature in blended cement [26]. These results indicate that even with OPC the C-S-H structure is influenced by thermal history.

In the case of standard-cured specimens using cement BB, dense structures of Type III or Type IV C-S-H had already been formed at 91 days. On the other hand, specimens subjected to the thermal history included many granular hydration products at the microstructure surface at 91, as was the case with OPC. Here also, the surface of this initial granular structure was covered with C-S-H at 6.5 years. Further, as can be surmised from the ratio of pore volume reduction as given in **Table 9**, it appears that the hydration product had become denser in comparison with other cements. However, unlike standard-cured specimens, there remained voids of approximately 1-3 μm in the interior.

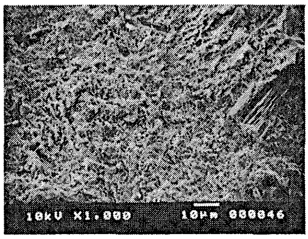
The hydration products in standard-cured specimens of LBB resembled those in BB, except that, in 6.5-year-old specimens, calcium aluminate hydration products were seen in some places. Specimens subjected to the thermal history were confirmed to have granular hydration products at 91 days, and it was concluded that the influence of thermal history on the hydration reaction was the same as with the other cements. At the age of 6.5 years, the initial granular hydration products were covered with C-S-H and there were voids of approximately 1-3 μm in the interior as above.

Standard cured specimen

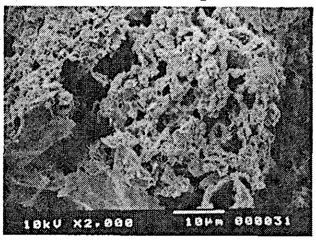


Specimen subjected to thermal history

Photo 3 SEM observations of BB mortar at the age of 91 days



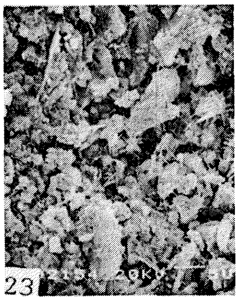
Standard cured specimen



Specimen subjected to thermal history

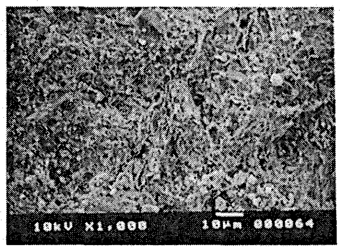
Photo 4 SEM observations of BB mortar at the age of 6.5 years

Standard cured specimen

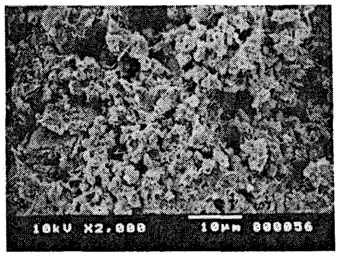


Specimen subjected to thermal history

Photo 5 SEM observations of LBB mortar at the age of 91 days



Standard cured specimen



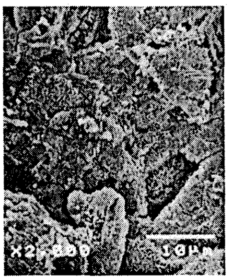
Specimen subjected to thermal history

Photo 6 SEM observations of LBB mortar at the age of 6.5 years

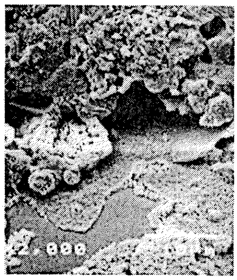
The block specimens, also, exhibited a hydration product growth process similar to that of the mortar specimens, as shown in **Photos 7** and **8**. However, in cores taken from block specimens at 4.5 years, although there were numerous voids of approximately 1-3 μm, they were not as prominent as in the mortar specimens.

From these results, it may be said that when mortar and block specimens are subjected to an extreme thermal history, the early granular C-S-H is unable to grow completely, but becomes covered by the growth of C-S-H over the long term. This leaves comparatively large voids of around 1-3 μm in the interior. It is concluded that such differences in pore structure affect the mechanical characteristics and permeability of massive concrete.

When a rapid temperature rise is experienced at an early age, a dense C-S-H phase is formed on the surface of unhydrated cement particles, making diffusion and moisture penetration difficult. At the same time, the progress of hydration is delayed since it is difficult for ions such as Ca^{2+} and SiO_4^{4-} to diffuse to the exterior. As a consequence, more free water remains than is the case with standard curing, and water-filled voids form. Specimens subjected to such a thermal history were sealed to simulate conditions in the interior of mass concrete, so it is possible that local air voids resulted due to the volumetric difference between the water consumed in hydration and the hydration products

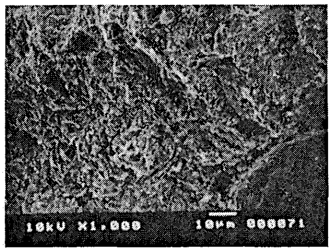


Standard cured specimen

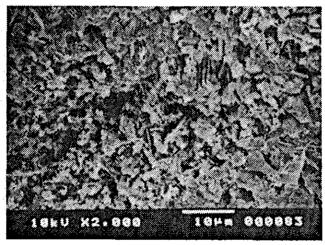


Core specimen from block

Photo 7 SEM observations of the concrete specimens in Series 3 at the age of 28 days



Standard cured specimen



Core specimen from block

Photo 8 SEM observations of the concrete specimens in Series 3 at the age of 4.45 years

formed. It is thought that, in SEM observations made at the age of 91 days, the coarse structure resulting from the above water voids and local air voids was observed. With advancing age, C-S-H gradually formed in the remaining free water, thus decreasing the volume of water-filled voids. However, since the hydrated phase will not develop in air voids formed as hydration progresses, even with C-S-H in the vicinity, the air voids remained. It is surmised that it is these remaining air voids that were captured in SEM observations made at the ages of 4.5-6.5 years. The localized air void formation process described above is quite plausible if the similarity to the mechanism of autogenous shrinkage strain development is taken into consideration [27].

Cores taken from block specimens were cured in water for approximately 3 years before carrying out the advanced-age tests. Accordingly, some of the above-mentioned local air voids were refilled with free water and hydration products were formed, and it is thought that this explains the reduction in voids of around 1-3 μm as compared with the mortar specimens. That the compressive strengths of standard-cured specimens and cores differed little, as in the case of mortar specimens, is thought to have been due to this reasoning.

5. CONCLUSIONS

This long-term study looked into the influences of the thermal history induced by heat of hydration on the mechanical characteristics and durability of massive concrete. The following findings were revealed by the study:

(1) Mechanical Characteristics

(1-1) It was ascertained that specimens subjected to an extreme thermal history induced by heat of hydration are higher in compressive and tensile strength at the age of 7 days than standard-cured specimens. However, subsequent strength gain is slow, and by around 28 days the two converge, while over the long term, the compressive strength of specimens that experienced the thermal history is lower. Moreover, this influence was seen to continue up to 6.5 years, which was the maximum scope of these experiments.

(1-2) LBB, when standard-cured, shows a strength gain over the long term, but in cases where concrete strength is specified at 91 days, it should be noted that structures subjected an extreme thermal history may fail to reach the specified strength.

(2) Chloride Ion Penetration Depth

(2-1) It was ascertained that chloride ion penetration depth is greater for all cements, OPC, BB, and LBB, when subjected to the severe thermal history. The penetration depth decreases with age, but it is confirmed to be greater for thermal history specimens even at the age of 6.5 years.

(2-2) Chloride penetration depths for BB and LBB, which contained finely ground blast-furnace slag, are confirmed to be less than for OPC even when the severe thermal history is experienced. In the case of LBB, this is particularly notable.

(2-3) With mortar specimens, chloride ion penetration depth decreases with rising compressive strength. However, where compressive strength varies with depth, as in block specimens, no equivalent correlation between chloride ion penetration depth and compressive strength is seen.

(3) Carbonation

(3-1) With all cements, it is ascertained that the carbonation depth is greater where the thermal history has been experienced in comparison with standard curing. This trend continues up to 6.5 years in the case of mortar specimens.

(3-2) A positive correlation is confirmed to exist between chloride ion penetration depth and carbonation depth in mortar specimens.

(4) Pore Size Distribution and Microstructure of Mortar and Concrete

(4-1) There is a tendency for capillary pore volume to be higher when the severe thermal history is experienced. Although the number of such voids decreases as hydration progresses, the trend continues even up to the age of 6.5 years.

(4-2) A strong correlation was recognized between the volume of pores 10 nm and larger and compressive strength. However, no distinct correlation is seen for chloride ion penetration depth or carbonation depth.

(4-3) Through observations of the microstructure of hardened mortar and concrete, it is confirmed that granular C-S-H is present, and it is thought that this is unable to grow sufficiently at early age as a result of the thermal history. Over the long term, the surface of these initial granular hydration products becomes covered with C-S-H formed by subsequent hydration reactions. However, it is confirmed that air voids of approximately 1-3 μm remain within the concrete and mortar.

(4-4) No influence of the thermal history on chloride ion permeability in the transition zone around the aggregates is recognized.

From the standpoint of preventing thermal cracking and securing durability, it may be said to be important that the post-placement temperature rise be held to the minimum when working with massive concrete.

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