Development of Strength and Microstructure in High Strength Massive Concrete

K.B. Park¹, I. Maruyama², T. Noguchi², K. van Breugel¹

ABSTRACT

High strength concrete undergoes a quicker early age temperature development and correspondingly a higher early-age strength. However, the high early temperatures can adversely affect the long-term strength and the durability of the concrete. This paper investigates the influence of temperature on microstructure, hydration, and compressive strength of high strength concrete in massive concrete structures. The aim is to identify mechanisms, which affect or even jeopardize the long-term performance of high strength concrete structure, which contain substantial hydration-related strength gradients. Experimental work has been done on concrete walls. Research parameters were the depth of the wall, the size of the wall and type of cement. Temperature histories at different locations in the walls are recorded and the degree of hydration, amount of hydration products and microstructure of concrete at those locations were measured using DSC and MIP. The effects of cement type and curing temperature on the hydration processes, hydration products, microstructure development and compressive strength were presented.

1 Introduction

High strength concrete (HSC) is being used increasingly in construction of high-rise buildings, bridges and marine structures. HSC can be made using a high cement content and a low water-cement ratio. If HSC used for columns or other large section members of massive concrete structures, the center temperature of the members will rise rapidly at early ages due to hydration heat and the high temperatures will remain in the member for a relatively long period of time due to the relatively low thermal conductivity of concrete.

It is well known that the high temperatures reduce the long-term strength of concrete and it will result in physical and chemical transformations in concrete [1-6]. Various researchers have studied the microstructure and hydration on this subject. It has been reported that the loss of long-term strength is induced by both physical effects and chemical effects. The physical effects are the increase of porosity and the microcracking in cement paste which is caused by the large differences in the thermal expansion coefficients of concrete constituents [7-14]. The chemical effects are the changes of the structure of hydration products and the loss of water in concrete [15-18].

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However there is not enough information available for the high early temperature occurring in real scale concrete structures. Therefore, it is needed to investigate these two effects in a real scale concrete member in order to identify the mechanisms.

In this study, experimental work has been done on concrete walls of different depth made of ordinary Portland cement (OPC) and belite-rich Portland cement (BPC). Temperature histories at different locations in the walls are recorded and the degree of hydration, amount of hydration products and microstructure of concrete at those locations were measured using DSC and MIP. The effects of cement type and curing temperature on the hydration processes, hydration products, microstructure development and compressive strength were presented.

2 Experimental

2.1 Materials and mixing

Two types of concrete were used in this study; concrete made with ordinary Portland cement (OPC) and belite-rich Portland cement (BPC), which has been increasingly used for high strength concrete members and massive concrete structures. The properties of the cements are shown in Table 1. The aggregate consisted of crushed sandstone (maximum size: 20mm, specific gravity: 2.65 g/cm\(^3\), absorption: 0.72 %, fineness modulus, 6.0) and land sand (specific gravity: 2.58 g/cm\(^3\), absorption: 2.07 %, fineness modulus: 2.69). An air entraining and high-range water reducing agent were used as admixture. The concretes were mixed in a twin shaft type mixer (200L). After first mixing the mortar (50 sec.), coarse aggregate was added and concrete was mixed (90 sec.). In table 2, the composition and the properties in the fresh state of the concrete are presented.

<table>
<thead>
<tr>
<th>Cement</th>
<th>Blaine (g/cm(^2))</th>
<th>Density (g/cm(^3))</th>
<th>Mineralogical properties (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>3280</td>
<td>3.16</td>
<td>C(_3)S 24  C(_2)S 9  C(_3)A 9</td>
</tr>
<tr>
<td>LH</td>
<td>4080</td>
<td>3.20</td>
<td>C(_4)AF 3  C(_2)A 54</td>
</tr>
</tbody>
</table>

NO: normal Portland cement, LH: belite-rich Portland cement

<table>
<thead>
<tr>
<th>Concrete</th>
<th>W/C (%)</th>
<th>S/A (%)</th>
<th>Unit content (kg/m(^3))</th>
<th>Slump (cm)</th>
<th>Flow (cm)</th>
<th>Air (%)</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>33</td>
<td>49</td>
<td>170 516 840 22  38.5 4.9 31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPC</td>
<td>33</td>
<td>53</td>
<td>170 516 854 776 - 63.5 4.8 30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Development of Strength and Microstructure in High Strength Massive Concrete

![Diagram of model walls](image)

**Figure 1. Model walls**

### 2.2 Design of model walls and curing

To investigate the variation of long-term strength in actual concrete walls subjected to different curing temperatures, three model walls were designed. The model walls are shown in Figure 1. The depths of the walls were similar to those in an actual nuclear power plant, viz.: 1.5 m, 0.8 m and 0.3 m. In order to simulate the actual long wall, the circumference of the wall depths direction was insulated by 200 mm polystyrene and the square surfaces of the wall were exposed to the open air. The walls were cast in 20 mm plywood formwork. The formwork was removed at 72 hours after casting. Core cylinders (φ 100×200 mm) were taken from the walls at 3, 7, 28 and 91 days and used for compressive strength, pore structure and hydration products measurements. For comparison, concrete cylinders were also cast in steel moulds. All cylinders were removed from the steel moulds at 24 hours after casting. Sealed cured cylinders were sealed in polyethylene sheeting and stored at 20°C, standard cured cylinders were stored in water at 20°C.

### 2.3 Test procedure

**Compressive Strength.** Cores, standard cured and sealed cured cylinders (φ 100×200 mm) were tested for compressive strength at 3, 7, 28 and 91 days. The test was conducted in accordance with JIS A 1108. The compressive strength was determined using the average of the compression strength of the three cylinder specimens.

**Sample Preparation for MIP, DSC and Ig.Loss Test.** In order to prepare the samples for the analysis of the microstructure and evolution of hydration in concrete, the concrete cylinders were cut into approximately 5 mm cubes using a diamond saw. Specimen fragments were immediately immersed in acetone to prevent further hydration. Thereafter, all the fragments were dried in a chamber of 40°C for 1 hour.
Analysis of Hydration Products. For determination of ettringite (AFt), monosulfate (AFm) and calcium hydroxide (CH) contents, the fragments were carefully ground by hand and the sample powder gained to pass a mesh of 45 μm. The hydration products were examined by differential scanning calorimeter (DSC) where 20 mg sample was heated at 20°C/min in a N₂ atmosphere. Ettringite measurement was carried out immediately after drying at 40°C for 1 hour in order to prevent the overlap between the peaks of AFt and belite [19]. Samples for AFm, CH and Ig.loss measurements were D-dried for about 2 weeks prior to testing.

Bound Water Content. The bound water content was determined as the ignition loss of samples. Ignition loss of hydrated samples was measured by burning at 1050°C for 1 hour.

Pore Structure. The porosity and pore size distribution were determined using mercury intrusion porosimetry (MIP). The pressure applied was from zero to 240 MPa. The 5 mm cubes for MIP measurements were also D-dried for about 2 weeks before testing.

3 Test results

3.1 Compressive strength

The temperature histories of the walls are shown in Figure 2. The maximum temperature at the center of the 1.5 m depth walls made with the OPC and BPC were 94°C and 78°C respectively. The maximum temperature in the OPC wall was achieved at 22 hours after casting, while that in the BPC wall 31 hours after casting. The high early age temperature in the wall is sustained for a relatively long period of time, after which gradual cooling of the concrete commences.

![Figure 2. Temperature history in model walls](image-url)
Table 3. Compressive strength of concretes

<table>
<thead>
<tr>
<th>Concrete</th>
<th>Curing states</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 days</td>
<td>7 days</td>
</tr>
<tr>
<td>OPC</td>
<td>Standard</td>
<td>47.9</td>
</tr>
<tr>
<td>Sealed curing</td>
<td>43.8</td>
<td>54.6</td>
</tr>
<tr>
<td>1.5m_center</td>
<td>51.7</td>
<td>55.8</td>
</tr>
<tr>
<td>1.5m_surface</td>
<td>47.9</td>
<td>49.2</td>
</tr>
<tr>
<td>0.8m_center</td>
<td>54.9</td>
<td>58.7</td>
</tr>
<tr>
<td>0.8m_surface</td>
<td>57.8</td>
<td>62.6</td>
</tr>
<tr>
<td>BPC</td>
<td>Standard</td>
<td>33.9</td>
</tr>
<tr>
<td>Sealed curing</td>
<td>33.8</td>
<td>41.0</td>
</tr>
<tr>
<td>1.5m_center</td>
<td>60.7</td>
<td>63.8</td>
</tr>
<tr>
<td>1.5m_surface</td>
<td>48.5</td>
<td>58.0</td>
</tr>
<tr>
<td>0.8m_center</td>
<td>67.5</td>
<td>70.1</td>
</tr>
<tr>
<td>0.8m_surface</td>
<td>67.7</td>
<td>70.4</td>
</tr>
</tbody>
</table>

Compressive strengths of core specimens and standard specimens (cured in water at 20°C), measured on φ100×200mm cylinders, are listed in Table 3. For the standard and the sealed curing specimens, the compressive strengths of the OPC at early ages are higher than that of the BPC. The 28-day compressive strengths of the OPC and BPC were 70 and 75 MPa respectively in the water cured conditions.

The influence of temperature on strength can be clearly described in terms of the relative strength ratio to the strengths of standard water cured specimens at 20°C. Figure 3 shows the effect of temperature on all of the compressive strength data. We can see that the center of 1.5 m depth wall made with BPC has a 3-day compressive strength which is 180% of that at 20°C, while the center of 1.5 m wall made with OPC has a 3-day compressive strength which is 108% of that at 20°C. At 91 days, however, the strength ratios were 79% and 77% respectively.

![Figure 3. Effect of temperature on strength of concrete in real scale members](image_url)

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Figure 4. Effect of temperature on total porosity

3.2 Pore structure

Figure 4 shows the total porosity values of OPC and BPC as determined by mercury intrusion porosimetry. Comparing the total porosity values for the OPC with high early temperatures, it can be seen that the total porosity at center in 1.5 m depth wall at 3 days reduced only 2.3% than that of standard specimen, while that in the BPC reduced by 5%. After 7 days, the total porosity of the OPC increases with the increase of the temperature in concrete. In the case of BPC, the total porosity exhibits a slight increase at 28 days and 91 days.

Figure 5 shows the pore size distribution curves of the OPC and BPC at 91 days. It can be seen that the pore size distribution was also changed with the increase of the temperature in concrete. With the increase of temperature the number of pores with a larger pore radius decreases and smaller radius increases. This suggests that as the hydration process proceeds, pore sizes are reduced and the peak of the distribution curve is shifted toward the direction of smaller pores.

Figure 5. Pore size distribution curve of concretes at 91 days
3.3 Hydration products

Figure 6 shows the ettringite contents at different hydration times. In both OPC and BPC cases, the amount of ettringite decreases with the progress of hydration under standard curing conditions. But at 28 days under standard curing, more ettringite is found in BPC than in OPC. This might be explained by the lower percentage of C₃A (3%) in BPC than in OPC (C₃A: 9%), which is not enough for the conversion of AFt to AFm because most of the C₃A has been consumed in the reaction forming ettringite in BPC specimen.

But for samples that experienced higher early age temperatures, there are no ettringite found at age up to 28 days. However, ettringite was found at age older than 28 days which might be explained by the secondary ettringite formation from the reaction of hydrogarnet with gypsum [20].

It can also be found in Figure 6 that for OPC specimen, the amount of monosulfate increased until the age of 28 days for standard curing and thereafter, a decrease was found. But for BPC specimen, the increase of the amount of monosulfate lasted only 3 days and it began to decreased slowly with the progress of hydration.

![Graphs showing the effect of temperature on AFt and AFm](image_url)

*Figure 6. Effect of temperature on AFt and AFm*
Nevertheless, for OPC samples that experienced higher early age temperatures, there was no monosulfate found at age up to 28 days. However, the amount of monosulfate increased drastically after 28 days. However, for BPC specimens under higher early age temperature it exhibited a slow increase of the amount of monosulfate until 28 days and then decrease slightly afterwards.

Figure 7 shows the changes of the amount of portlandite with the progress of hydration. For OPC specimens that experienced a higher early temperature, the amount of portlandite is also higher in comparison with specimens under standard curing at age up to 28 days. At age older than 28 days, the effect of the early age curing diminished and all the specimens had similar amount of portlandite. However, no significant difference was found in BPC specimens under different curing situations.

Changes in the amount of bound water in the hydration products up to 28 days are shown in Figure 7. Higher amount of bound water was found in the center of 1.5 m depth walls of both OPC and BPC in the early age within 3 days. However, at age older than 7 days the amount of bound water for OPC wall was lower than that of standard curing. But BPC wall shows the decrease of the amount of bound water at age older than 28 days.

Figure 7. Effect of temperature on CH and Bound water
4 Discussion

In comparison with the standard cylinders, core cylinders experienced elevated temperature show the highest early age strength gain. This can be explained by the acceleration of the elevated internal temperatures in the wall. However, long-term strength gain of core cylinders is lower than that of standard cylinders, which means that elevated temperature results in a coarser pore structure therefore a decrease in the strength. It has also been suggested that curing at elevated temperatures may lead to the reduced surface area of the hydrates and the changes of hydration products [21].

It might be important to notice that the trend of variations in porosity in Figure 4 agree quite well with the trend of variations of the compressive strength ratios in Figure 3. The changes in the measured pore size distribution in OPC at elevated curing temperature shows an increase of pores within the range of 50 and 1000 Å. For BPC specimens, pores within the range of 50 and 2000 Å are increased with the increase of curing temperature (Fig. 5). This is in good agreement with the findings of Kjellsen et al. [22] that increases in curing temperature result in increased porosity, particularly for pores of radius 200-1000 Å as measured by mercury intrusion porosimetry. However, Ödder et al. [23] reported that variations of temperature had little effect on the pore size distribution of fully hydrated pastes.

Higher temperature will also change the microstructure of hydrates change and the degree of hydration. Verbeck and Helmuth [24] suggested that hydration at normal temperatures provides sufficient time for the hydration product to diffuse and precipitate relatively uniformly throughout the interstitial space between the cement grains. But accelerated hydration by an increased curing temperature does not allow time for the diffusion of the hydrates. Consequently it will produce a highly non-uniform distribution of the hydrated products in the paste. In addition, heating C-S-H may result in increased polymerisation and structural disorder [25]. The polymerisation can be expressed as:

\[
2\text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}↑
\]

It has also been suggested the dissolution of the calcium leaching originates mostly from the portlandite and the decomposition of ettringite at high temperature will contribute to the increase in porosity [26]. And the re-formed ettringite shown in Figure 6 will cause expansion of the gel and generate microcracks, which is also reported by [27, 28]. Nevertheless, the content of CH in later stage exhibits no correlation with curing temperature (Fig. 7).

Shideler and Chamberlin [29] have reported that strength loss associated with microcracks of concrete cured at temperatures higher than 85°C with steam curing temperature condition. However, the microcracks of high strength massive structure at early age are not only a consequence of the hydration heat but also autogenous shrinkage due to self-desiccation and chemical reactions of the sulphate phase can also be important.
5 Conclusions

The experimental results discussed above lead to the following conclusions:

1. In comparison with the standard cylinders, core cylinders experienced elevated temperature show the highest early age strength gain. However, long-term strength gain of core cylinders is lower than that of standard cylinders.
2. The total porosity of the OPC and BPC at later ages increases with the increase of the temperature in concrete.
3. With the increase of temperature the pore sizes are reduced and the peak of the distribution curve is shifted toward the direction of smaller pores.
4. Due to the temperature rise, the AFt-phase becomes unstable and the AFm-phase is formed instead. However, there is no significant correlation found in the content of CH with temperature variation.

This paper discusses the effect of high early age temperature on the microstructure and strength development in massive concrete members. The effect of the elevated internal temperatures on the strength development has been discussed in terms of the microstructures and hydration products.

Acknowledgements

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References