HYDROTHERMAL LOW-CYCLE FATIGUE OF CONCRETE
- DURABILITY OF ENERGY STORAGE WATER TANKS -

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Abstract
In this paper, experimental investigations were carried out on the behaviour of high
performance concrete intended for hot water concrete tanks to store water at a temperature
above 100°C. The tested concrete has been subjected to heating-cooling cycles from ambient
conditions to a temperature of 200°C and a pressure of 15 bars. The autoclave technique was
used to load the concrete specimens with repeated cycles of high pressure and temperature
with heating/cooling rates of about 1/0.5 K/min respectively. In mix design, the packing
density concept of the aggregates and fines according to the modified Fuller curve have been
applied. Normal and fine fly ash and silica fume have been used. The water/cement ratio was
regulated in order not to produce capillary pores. CEM III/B was used and the total mass of the
cementitious material was 312 kg/m³. Experimental studies involving the measurements of
strength, porosity, and permeability will be presented. The results indicated that the
incorporation of mineral admixtures can effectively improve the packing density which results
in reducing the total porosity of HPC to less than 6%. The air permeability is noticeably reduced
and the compressive strength increased from 70 to about 100 MPa during the autoclave cycles.

Key words: Concrete, durability, impermeability, hydrothermal attack

1. INTRODUCTION

Storage of solar thermal energy or of waste heat from heat and power cogeneration plants
can significantly contribute to substitute fossil fuels in future energy systems. Some solar
energy storage tanks have been built in the last few years [1], but these tanks were limited
with maximum temperature of 95°C and the stored energy is used for heating only. Normal
cement concrete alone cannot be used as a construction material for these tanks because its high
porosity which increases with increasing the temperature [2, 3]. The construction costs are
very high because these tanks need stainless steel liner to prevent water leakage [1]. In recent
years, some tanks without liner have been built with high performance concrete to store hot
water at 95°C [4]. However, to make a practical use of the stored energy such as industrial
processes and steam generation, the storing temperature must be increased above 100°C.
The present paper is a part of an extensive investigation on "Hot water concrete tank to store solar generated energy". The purpose of this article is the presentation of research, that aims to optimize a low porosity/high durability concrete mixture to be used in the construction of the closed energy storage tank to store water and steam at a temperature of 200°C and a pressure of about 15 bars.

2. CONCRETE MIXTURE OPTIMIZATION

The aggregate, the matrix, and the bond between them affect concrete strength and durability. The matrix depends not only on w/c ratio but also on the granulometry and reactivity of the cementitious material. Therefore, concrete mixture optimization is primarily based on three fundamental aspects:

1- Enhancing packing density of aggregate
2- Designing of dense cement matrix
3- Optimization of water/cement ratio in the relevant context

2.1 Enhancing packing density of aggregate

The production of extremely dense concrete to resist hydrothermal conditions is based on the designing of a system with highly compatible well graded components. Uniform grading with proper amount of each size results in mixture with high packing density [5] and in concrete with minimum binder content and low water demand. As a result, the concrete will have less durability problems such as permeability, shrinkage, and thermal degradation. An additional object is to block and lengthen the access path of contaminants to the concrete.

Fuller [6] stated that if the aggregate is graded according to Equation 1, the resulting mix requires less cement and gives higher compressive strength. The Fuller curve despite its historical value is still the base for proportioning of the aggregate in many national concrete standards [7]. The problems of applying this curve are the low workability and probability of segregation in fresh state. To overcome these problems, some modifications have been done to achieve better workability and mix stability and have better particle packing as shown in figure 1 [8].

\[ P = \left( \frac{d}{D_{\text{max}}} \right)^n \]  

(1)

Where P: cumulative percent finer than d, d: particle size, D_{max}: maximum particle size, n \approx 0.5.

![Figure (1): The grading curve for aggregate and binder according to modified Fuller curve](image-url)
In this research, the mixture components proportioning has been calculated according to the modified curve (figure 1). For the maximum aggregate size of 16 mm, the aggregate volume ($d > 125 \ \mu m$) is 85.1%, while the cement content ($d<63 \ \mu m$) is 12.9% by volume. Quartz powder (QP) ($63 < d < 125 \ \mu m$) and quartz sand were used to fill the gap between cement and aggregate.

2.2 Designing of dense cement matrix

All transport processes depend primarily on the structure of the hydrated cement paste [9]. During the hydration process, the size and the interconnectivity of the pores would control the permeability of the hardening concrete. If the hydration process of cement is too fast, large amounts of hydration products with capillary pores are generated on the surface of cement particles at early age and the microstructure is not dense as desired. In contrast, if the hydration rate is slow, a denser microstructure is formed [10]. In addition, Portland cement hydration produces about one-third of its mass of calcium hydroxide (CH), which is associated with greater permeability and lower durability. The use of pozzolans improves the durability through the pore refinement and the reduction in the CH [11]. However, several researchers observed the formation of a network of coarse pores in mortars and concrete containing pozzolanic materials. They suggested that the presence of these pores is due to the dissolution of CH crystals during the pozzolanic reaction on the pozzolans surfaces [12]. Therefore, from durability aspects it is important to reduce the generated quantity of CH during the cement hydration.

Concrete durability can be improved significantly by using cements containing blast furnace slag. These cements, in contrast to ordinary Portland cement (OPC), show lower permeability, lower hydration heat, lower effective alkali content, and lower steel corrosion. The beneficial effects of blast furnace slag arise from the low CH content and making the pore space being filled with CSH. The slag retains the alkali and CH in its hydration products (i.e. CSH). This results in a hardened cement paste with denser microstructure and smaller pore sizes than equivalent OPC paste, thus permeability and ionic diffusivity are reduced [13]. Due to their pozzolanic reactivity, using pozzolanic materials with slag cement enhances the concrete impermeability by the formation of additional CSH phases. In this research, the amount of cementitious materials is about 312 kg/m$^3$ (12.9% by volume). CEM III/B 32.5, fly ash, fine fly ash (M10 and M20) and silica fume were used as cementitious materials.

2.3 Optimization of water/cement ratio

The durability of concrete cannot be characterized with a uniform value, but the impermeability of concrete against water and gases is always of the most crucial aspects. The transport of liquids and gases, which can be harmful to concrete, occur exclusively through the capillary pore system of the cement matrix. Accordingly, the minimization of the fraction of capillary pores is of vital importance for concrete impermeability and durability. It is theoretically known that, capillary pores begin to form at a water/cement ratio higher than 0.42. However, there is a physical limit to how low the w/c ratio can be. This is because the water added must be at least sufficient to fill up the voids between solid particles [14]. Because of the low cement content, small increase in the water content may lead to high increase in w/c ratio [15].

In this research, the water/cement ratio was 0.42 (mixing water) for all mixes with k factor of 0.4 and 1 for fly ash and silica fume respectively. To calculate the water required to fill the voids between solid particles (required water), Rene LCPC software has been used [16].
3. RENE LCPC SOFTWARE

Rene LCPC software which is based on the compressible packing model developed by Larrard [16] was used to calculate the porosity of the dry mixture. This model is based on the concept of virtual packing density and compaction index. Two interaction effects should be considered in this calculation: the wall effect exerted by coarser grains, and the loosening effect, exerted by the finer particles. This model aims to predict the packing density and porosity of polydisperse mix, from the knowledge of three types of parameters: packing density of monosized classes, size distribution of the mix and compaction index (K). The calculated porosity was used to determine the Required water assuming the air content of concrete is 1%.

\[
\text{required water} = \text{calculated porosity} - \text{air content.} \quad (2)
\]

4. MATERIALS AND METHODS

4.1 Materials and concrete mixes

In this experiment, CEM III/B 32,5 N-LH/HS/NA with slag content of 68,8% according to DIN EN 197-4, fly ash according to DIN EN 450-1, and silica fume (SF) according to DIN EN 13263-1 have been employed as cementitious materials. Three types of fly ash have been used; normal (FA) and fine fly ash (M20 and M10). Figure 2 shows the particle size distribution of fine materials. Superplasticizer (Muraplast FK63.30) was used to achieve a desirable consistency (class F4) according to DIN EN 206-1. Table 1 shows the physical properties of the used materials. Ten mixes have been prepared and tested (table 2). The autoclave technique was used to load the concrete specimens with repeated cycles of high pressure (15 bars) and temperature (200 °C) with heating and cooling rates of 1 K/min and 0,5 K/min respectively.

![Figure 2: Particle size distribution of fine materials](image)

**Table 1: Physical properties of the used materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>CEMIII/B</th>
<th>FA</th>
<th>M 10</th>
<th>M20</th>
<th>SF</th>
<th>QP</th>
<th>QS</th>
<th>Aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Density</td>
<td>2,96</td>
<td>2,29</td>
<td>2,49</td>
<td>2,45</td>
<td>2,2</td>
<td>2,69</td>
<td>2,67</td>
<td>2,61</td>
</tr>
<tr>
<td>Surface area cm²/gm</td>
<td>4156</td>
<td>2877</td>
<td>6400</td>
<td>6000</td>
<td>20000</td>
<td>2683</td>
<td>760</td>
<td>-</td>
</tr>
<tr>
<td>Water demand (15)</td>
<td>22,6</td>
<td>18,5</td>
<td>23</td>
<td>21,6</td>
<td>49,9</td>
<td>24,4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2: Mixes composition and fresh properties of concrete

<table>
<thead>
<tr>
<th>Mix</th>
<th>Composition % of cementitious materials (M%)</th>
<th>SP Kg/m^3</th>
<th>Flow diameter (cm)</th>
<th>Air Content (V %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement FA M20 M10 SF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>100 - - 0,7 1984 53 1,5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>70 30 - 1 1984 52 1,3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>70 - 30 1 1984 48 1,6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>70 - - 30 1 1984 51 1,4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>70 - 15 15 1 1984 51 1,3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>70 20 5 5 0,9 1984 54 1,3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>90 10 0,7 1984 48 2,3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>65 25 10 1,1 1984 50 2,0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>65 12,5 12,5 10 1 1984 50 2,2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>65 15 5 5 10 1 1984 50 2,0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2 Test procedures

In this experimental work, the porosity of dry mixture have been measured using Rene LCPC software. The porosity of hardened concrete was measured using Helium Pycnometer. The air permeability of concrete according to TGL 21094-12 (Equation 3) was measured. The compressive strength of concrete specimens according to DIN EN 206-1 for 100 mm cubes was tested. All tests of hardened concrete were made after 56 days in two cases; normal and after autoclaving. Flow diameter and air content were measured according to DIN 1048-Part1.

\[
K = \frac{V \cdot h \cdot \eta}{A \cdot t \cdot p}
\]

Where: \(K\) = gas permeability coefficient (cm²), \(V\): flow volume (cm³), \(t\): passing time (seconds), \(h\): height (cm), \(A\): cross section area (cm²), \(p\): pressure N/cm², \(\eta\): dynamic viscosity of the air N/cm².

5. RESULTS

5.1 Water requirement

The mixing water and required water contents of all mixes are given in table 3. For mixes 8, 9, and 10, the required water is higher than the mixing water which means that the voids between solid particles are not fully filled with water. In contrast, mixes 1, 2, 6, and 7, the mixing water is more than the required water; the volume of the added water is larger than the available volume between solid particles. While mixes (3, 4, and 5), the mixing and required water are approximately the same; little escape as free water, and no voids is still empty.

Table 3: Mixing and required water content of mixes.

<table>
<thead>
<tr>
<th>Mix</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>mixing water</td>
<td>131,3</td>
<td>107,7</td>
<td>107,7</td>
<td>107,7</td>
<td>107,7</td>
<td>107,7</td>
<td>131,3</td>
<td>111,6</td>
<td>111,6</td>
<td>111,6</td>
</tr>
<tr>
<td>required water</td>
<td>110,7</td>
<td>105,8</td>
<td>107,3</td>
<td>107,3</td>
<td>107,2</td>
<td>106,1</td>
<td>119,8</td>
<td>116,3</td>
<td>118</td>
<td>116,9</td>
</tr>
</tbody>
</table>
5.2 Porosity

The test results showed that optimizing concrete mixture results in reducing the porosity of all mixes as seen in figure 3. In dry mixture, fly ash with its spherical shape enhances the packing density and reduces the water demand. In hardened concrete, fine fly ash (M10 and M20) enhance the packing density and reduce the porosity to less than 6% (mix 5). The porosity of mixes with silica fume is higher than other mixes because the ultra fine nature and lower density of silica fume particles which makes the particle dispersion inhomogeneous and reduces the packing density [17]. After autoclaving for 15 cycles a slight increase in porosity for all mixes can be observed. Due to the hydrothermal conditions, contrary to heating alone, the volume of fine pores tend to increase and the volume of big pores decreases. This phenomena is due to the autoclaving effect, which is associated with a decrease in the phases (C3S +\(\beta\)-C2S) and in an increase in CH content [3].

![Figure 3: Porosity of normal and autoclaved concrete at age 56 days.](image)

5.3 Air permeability

It can be seen from figure 4 that the air permeability of all mixes is low. This can be due to the higher packing density of the mixture which reduces the porosity and the required cement paste. In the same time, the high content of aggregate lengthens the flow paths and makes them unconnected. Mixes containing fine fly ash exhibited lower air permeability. It reacts with CH to form CSH, which fills large capillary voids and disrupts their continuity. By autoclaving for 15 cycles, the air permeability of concrete reduced to 1.8*10\(^{-17}\) m\(^2\) (mix 5). The hydrothermal process increases the reaction of fine fly ash with calcium hydroxide and this reaction leads to two important effects. First, the volume of calcium hydroxide is reduced because it is substituted by CSH product which makes the microstructure denser and as a result the permeability is reduced. Secondly, the hydration products of this reaction fill the voids and reduce its size and connectivity and consequently the permeability is also reduced.
5.4 Compressive strength

Results of compressive strength at 56 days are given in figure 5. For mixes with pozzolanic materials, hydrothermal process improves concrete strength because this process accelerates the reaction of cement components with water as well as the pozzolanic reactions between fly ash and silica fume with CH. As seen from figure 5, the increase of strength in the first stage of autoclaving (5 cycles) is more noticeable, while in the later stages of autoclaving (10 and 15 cycles) the compressive strength is approximately constant. In the next part of this project, the concrete specimens will be exposed to more autoclaving cycles in order to study the effect of intensive autoclaving cycles on concrete properties.

6. CONCLUSIONS

The results of the research work show that the initial target to design a concrete mix with high durability and high stability to resist high pressure and high temperature in solar energy...
storage concrete tank without a liner could be proved. The following conclusions can be drawn from the present investigation:

1- With optimization of concrete mixture, it is possible to produce low porosity, highly durable concrete with desirable workability and strength by using a low cement content.
2- Incorporation of fine fly ash enhances the packing density and reduces the water requirement as well as it reduces the concrete porosity and permeability.
3- After hydrothermal treatment, the optimized concrete showed very stable properties with regarding to durability. The changes in the matrix morphology, microstructure, mineral and chemical composition were limited and can be neglected in the applied hydrothermal conditions.

REFERENCES