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Portland Cement Paste Microstructure Characterization using Autogenous Shrinkage and Heat of Hydration

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ABSTRACT

The core objective of this study was to characterize the microstructure of Ordinary Portland Cement paste using autogenous shrinkage and heat of hydration parameters. The relevance of the research was the need to advance the knowledge on understanding the underlying mechanism of autogenous shrinkage and heat of hydration parameters and their influence on the evolution of cement paste microstructure. The advanced awareness will to enable Engineers to develop performance-based specifications of water to cement ratio in concrete and cement paste in future to achieve durable and high quality mixes.

The research was limited to cement paste and concrete mixes of water/cement (w/c) ratios of 0.35 and 0.45. The study used type K temperature probes, Extech differential temperature data logger, strain gauges, Madge Tech bridge/strain data logger and stereo microscopes.

The research findings were that samples with lower w/c ratios recorded higher autogenous shrinkage, bigger pores and increased risk of developing cracks than the rest of the samples. Curing in saturated conditions ensures replacement and availability of more water for hydration of Ordinary Portland Cement paste leading to reduced autogenous shrinkage. Availability of water for curing reduces the temperature due to cooling aided by the presence of water. Further research is required to relate the development of pore structure with autogenous shrinkage.

Key Words: Portland, Cement, microstructure, autogenous, shrinkage, heat, hydration

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INTRODUCTION

Background and Study Justification

The cement paste of a modern, high-performance concrete typically shows low porosity and a discontinuous capillary pore structure. High-performance concrete can contain low water to cement ratio (w/c) and have silica fume added to it.

While modern concretes can possess some advantageous properties compared with traditional concrete regarding good workability, high strength from early ages, low permeability, and improved durability, they may also exhibit unwanted behavior such as autogenous strain (Pietro *et al*., 2008).

The motivation of this research was the need to advance knowledge on understanding the underlying mechanism of autogenous shrinkage and production of heat during cement hydration and their influence in the evolution of Ordinary Portland Cement paste microstructure. This study will provide a solution to prevailing concrete production quality problems in Kenya and allow engineers to develop performance-based specifications to reduce shrinkage cracking.

Objectives of Research

The overall objective of this research was to characterize the microstructure of Ordinary Portland Cement paste as a function of autogenous shrinkage and heat of hydration. The experimental investigation was limited to the following variables:

- CEM I (Ordinary Portland cement).
- Water/cement ratios of 0.35 and 0.45.
- Saturated and unsaturated curing conditions as a function of age.
- Each specimen was tested from ages zero to 10 days.

LITERATURE REVIEW

Cement Hydration Process

Table 1: Composition of Portland cement (Http://matse1.matse.illinois.edu/concrete/prin.html)

Cement Compound	**Weight Percentage**	**Chemical Formula**
Tricalcium Silicate	50 %	Ca3SiO5 (or 3CaO.SiO2)
Dicalcium Silicate	25 %	Ca2SiO4 (or 2CaO.SiO2)
Tricalcium Aluminate	10 %	Ca3Al2O6 (or 3CaO .Al2O3)
Tetracalcium Aluminoferrite	10 %	Ca4Al2Fe2O10 (or 4CaO.Al2O3.Fe2O3)
Gypsum	5 %	CaSO4.2H2O

Table 1 shows the composition of a typical Portland cement

Hydration Reactions

Addition of water to cement results into each of the compounds listed in Table 1 undergoing hydration and contributes to the final concrete product. Only the calcium silicates contribute to strength. Tricalcium silicate is responsible for most of the early strength (first seven days). Dicalcium silicate, which reacts more slowly, contributes only to the strength at later stages. The following equations present an approximation of hydration of the constitutive clinker phases considering the addition of gypsum into account (Http://matse1.matse.illinois.edu/concrete/prin.html);

$2C_3S+10.6H\rightarrow C_{3.4}S_2H_8+2.6CH$ Equation (2.1)

$2C_2S+8.6H\rightarrow C_{3.4}S_2H_8+0.6CH$ Equation (2.2)

$C_3A+3C\bar{S}H_2+26H\rightarrow C_6A\bar{S}_3H_{32}$ Equation (2.3)

$2C_3A+C_6A\bar{S}_3H_{32}+4H\rightarrow 3C_4A\bar{S}H_{12}$ Equation (2.4)

$C_3A+6H \rightarrow C_3AH_6$ Equation (2.5)

$C_4AF+3C\bar{S}H_2+30H \rightarrow C_6A\bar{S}_3H_{32}+CH+FH_3$ Equation (2.6)

$2C_4AF+C_6A\bar{S}_3H_{32}+12H \rightarrow 3C_4A\bar{S}H_{12}+2CH+2FH_3$ Equation (2.7)

$C_4AF+10H \rightarrow C_3AH_6+CH+FH_3$ Equation (2.8)

The principal hydration product is the calcium silicate hydrate (C-S-H), which is usually in gel form and of a composition that varies over a wide range. The formula $C_{3.4}S_2H_8$ (designated as C-S-H) is only approximate. Other major hydration products include calcium hydroxide (CH) and calcium sulfoaluminate hydrate that mainly consists of ettringite ($C_6A\bar{S}_3H_{32}$) and monosulfoaluminate ($C_4A\bar{S}H_{12}$), all of which are in crystal forms (Feng, 2006).

Stages in Cement Hydration

The data from heat of hydration studies can be used for characterizing the setting and hardening behavior of cements, and for predicting the temperature rise (Mehta, 2006 and http://matse1.matse.illinois.edu/concrete/prin.html).

- In Stage I (the dissolution stage), the reaction occurs right after contact with water because ions dissolved in water react with C_3A and gypsum. The formation of ettringite produced after initial hydration reactions sharply reduces the rate of the reaction in the latter part of Stage I. This stage has little effect on concrete strength. The system then enters a dormant period (Stage II).
- In Stage II (the induction [dormant] period), the concentration of ions in the solution gradually increases along with the solution of solid phase. Cement paste remains in the plastic state. This stage does not develop concrete strength.
- In Stage III (the acceleration stage), the Tricalcium Silicate (C_3S) and Dicalcium Silicate (C_2S) in the cement start to hydrate and release heat. In this stage, concrete setting begins and heat generation increases. The silicate reaches a high rate of hydration at the end of the Stage III. Concrete strength develops in stage III with final setting ending and early hardening has begun.
- In stage IV (the deceleration stage), the rate of heat generation again decreases and shifts to a diffusion-controlled process. In this phase, the thickness of hydrated particles increases. The layer of cement hydrates acts as a diffusion area to govern the permeability of the water and dissolved ions. Ettringite converts to mono-sulfate phase (sometimes noted as the heat contribution of C_3A hydration).
- In stage V (the steady stage), the thicker layer of hydrates around the cement particles reduces the rate of hydration remarkably. In this stage, hydrates do not precipitate easily because the space formerly filled by water contains hydrated cement. The diffusion process controls hydration.

Complete hydration of cement is assumed to require a water/cement ratio of about 0.4 and a minimum w/c ratio of 0.42 (Mindess et al. 2003). The heat evolution rate starts to decrease as the w/c ratio decreases after a certain time (Byfors 1980).

Development of Pore Structure

With cement hydration, the solid phase (hydration products) and pore structure develop. The formation of pore: structure mainly depends on the degree of hydration and w/c ratios. There are three main types of pores: gel pores, capillary pores, and air voids (Mindess and Young, 1981).

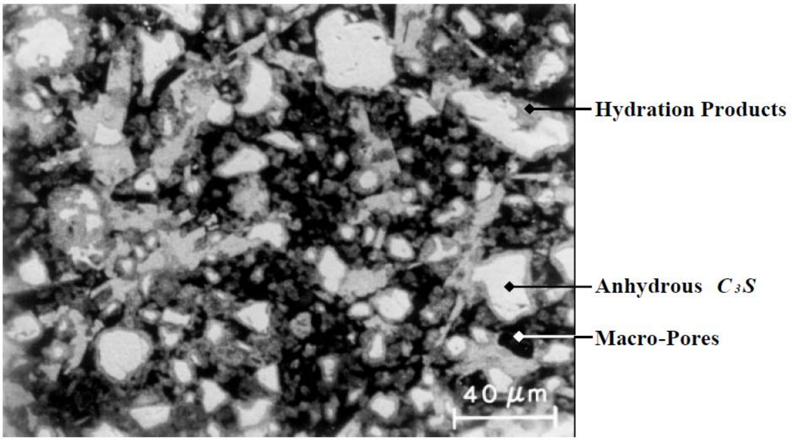

Figure 1: Scanning Electron Micrograph of a C-S-H Paste (Tennis et al., 1997)

Heat of Hydration

Cement hydration results into generation of heat due to the breaking and making of chemical bonds during hydration. The heat generated as a function of time is as shown in Figure 2. In stage I, hydrolysis of the cement compounds occurs rapidly with a temperature increase of several degrees. Stage II is the dormancy period. The evolution of heat slows dramatically in this stage. During this period, the concrete is in a plastic state. It is at the end of this stage that initial setting begins. In stages III and IV, the concrete starts to harden, and the heat evolution increases due primarily to the hydration of tricalcium silicate. Stage V occurs after 36 hours. The slow formation of hydrate products occurs and continues as long as water and non-hydrated silicates are present (Http://matse1.matse.illinois.edu/concrete/prin.html).

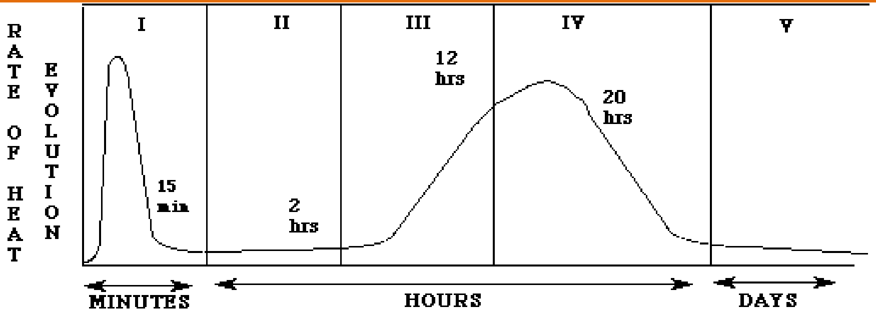

Figure 2: Rate of heat evolution during the hydration of Portland cement (Http://matse1.matse.illinois.edu/concrete/prin.html)

MATERIALS AND METHODS

The objective of this study was to obtain data by experimental methods for characterizing hydrating Ordinary Portland Cement paste microstructure using autogenous shrinkage and heat of hydration parameters. This section presents the measuring techniques and materials used in this study. The tests included:

- Measurement of the heat of hydration of Ordinary Portland Cement paste using type K temperature probes and Extech Differential Temperature Data logger.

- Measurement of the autogenous shrinkage strain of hydrating Ordinary Portland Cement paste using a strain gauge and MadgeTech Bridge/Strain Data logger.
- Use of a stereo microscope to evaluate the microstructure evolution of a hydrating Ordinary Portland Cement paste (as a function of pores formation and cracking).

Materials, Curing Conditions, and Mix Proportioning

This study used Ordinary Portland Cement (OPC). In concrete mixtures, the coarse aggregate was crushed limestone with a maximum aggregate size of 10mm. The fine aggregate was natural river sand. To investigate the effect of aggregate content and size on autogenous shrinkage, concrete samples with different aggregate contents (less than the normal range of aggregate content) and with small sized aggregates (maximum aggregate size of 10mm) formed the specimens in this research.

Table 2: Mix proportioning for paste (φ_A=0%) and concrete

Sample no.	1 (Sealed-unsaturated curing)	2 (Sealed-unsaturated curing)	3 (Sealed-unsaturated curing)	4 (Sealed-unsaturated curing)	5 (Sealed-unsaturated curing)	6 (Sealed-unsaturated curing)	7 (Sealed-unsaturated curing)	8 (Sealed-unsaturated curing)
Material	w/c=0.35 (φ_A =0%)	w/c=0.45 (φ_A =0%)	w/c=0.35 (φ_A =40%)	w/c=0.45 (φA =40%)	w/c=0.45 (φA=40%)	w/c=0.35 (φ_A =40%)	w/c=0.45 (φ_A =0%)	w/c=0.35 (φ_A =0%)
Cement (kg)	1.5	1.305	0.763	0.660	0.660	0.763	1.305	1.5
Water (kg)	0.525	0.587	0.267	0.297	0.297	0.267	0.587	0.525
Limestone (kg)	n. a.	n. a.	0.268	0.268	0.268	0.268	n. a.	n. a.
Sand (kg/m^3)	n. a.	n. a.	0.763	0.763	0.763	0.763	n. a.	n. a.

n. a. = not available.

Table 2 shows mix proportions for w/c=0.35 and 0.45 and the aggregate contents of 0% and 40% of total mix by volume. In all the concrete mixtures, the ratio of sand to coarse aggregate by volume was constant. However, the total aggregate content varied. Curing conditions to investigate the effectiveness of internal curing on mitigating autogenous shrinkage and cracking included:

- Sealed/saturated curing using distilled water
- Sealed/unsaturated curing

Measurement of Heat of Hydration and Autogenous Shrinkage

The schematic of the specimen and test method for the hydration temperature and deformation of Ordinary Portland Cement paste and concrete were as shown in Figure 3.

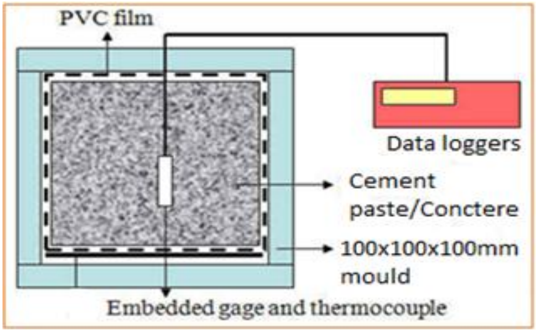

Figure 3: Schematic of the Test Method for the Hydration Temperature and Deformation of Concrete

The 100×100×100mm specimen was cast in a mold made with impervious pvc film. The inner temperature and deformation of the specimen were measured using a thermocouple and an embedded strain gauge every ten minutes after casting for 10 days per specimen. Eight specimens were tested corresponding to their w/c ratios, aggregate content and curing conditions described in the previous section 3.2. The strain gauges used had a resistance of 60±0.5 ohms (Ω) and a gauge factor of 1.68±3%.

RESULTS AND DISCUSSION

Heat of Hydration

Ordinary Portland Cement is composed largely of four types of minerals amongst others: Tricalcium Silicates (C_3S), Dicalcium Silicates (C_2S), Tricalcium Aluminate (C_3A), and Tetracalcium Alumino-ferrite (C_4AF). When these minerals mix with water, hydration products form. Heat is evolved with cement hydration due to breaking and development of chemical bonds during hydration raising the temperature of concrete.

The heat generated described as a function of time is shown in Figures 4 and 5 of this section representing results of samples one (1) to six (6) as described previously in Table 2. This study recorded the heat of hydration data after every 10 minutes for 9 to 10 days.

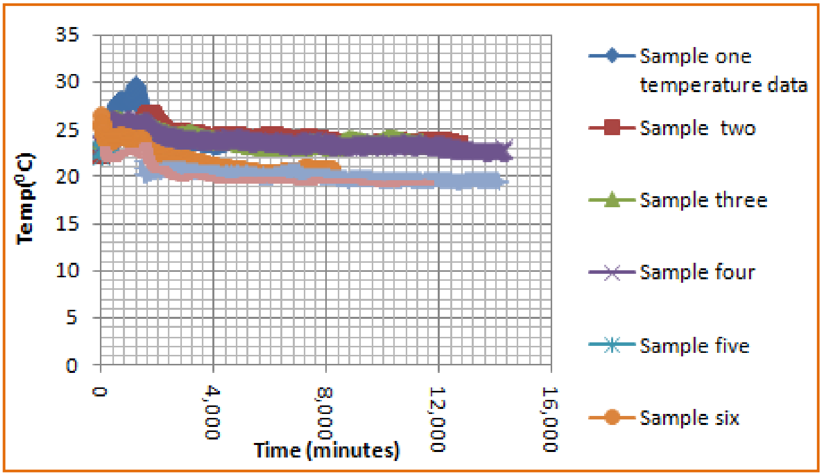

Figure 4: Samples one to six temperature against date

The results of this research as shown in Figure 4 are comparable to the literature. For example, http://matse1.matse.illinois.edu/concrete/prin.html expressed heat of hydration as a function of time as illustrated in Figure 5.

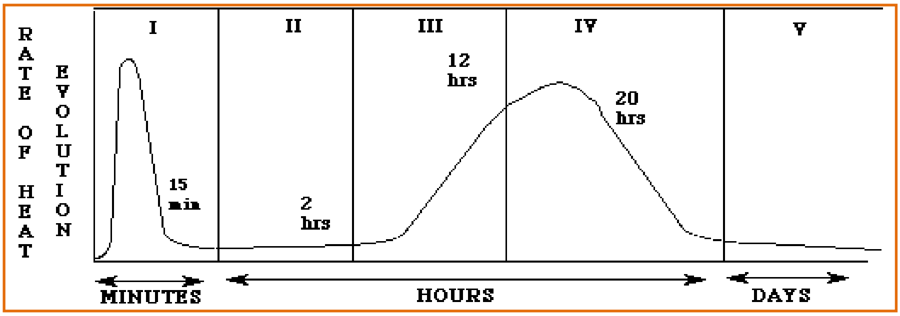

Figure 5: Rate of heat evolution during the hydration of Portland cement (Http://matse1.matse.illinois.edu/concrete/prin.html)

As shown in Figure 4, temperature increased rapidly (Stage I) then dropped (Dormancy Stage II). The recorded temperature increased again signifying Stages III and IV and thereafter dropped, marking Stage V.

In Stage I hydrolysis of the cement compounds occurs rapidly with a temperature increase of several degrees. Stage II is the dormancy period. The evolution of heat slows dramatically in this stage. During this period, the concrete is in a plastic state. Initial setting begins at the end of this stage. At Stages III and IV, the concrete starts to harden, and the heat evolution increases due primarily to the hydration of tricalcium silicate. Stage V occurs after 36 hours. The slow formation of hydrate products occurs and continues as long as water and non-hydrated silicates are present. (http://matse1.matse.illinois.edu/concrete/prin.html).

Autogenous Shrinkage Results

This study made use of a 30mV (millivolt) Bridge/Strain101A Data logger manufactured by MadgeTech (see www.madgetech.com for more details). This logger is made to interface with and measure strain gauges and load cells. The device provides an excitation voltage of 2.5V and has a ±30mV (millivolt) input.

The strain gauges used had a resistance of 60±0.5 ohms (Ω) and a gauge factor of 1.68±3%. A fundamental parameter of the strain gauge is its sensitivity to strain, expressed quantitatively as the gauge factor (GF). This is the ratio of fractional change in electrical resistance (R) to the fractional change in length (strain) (Http://www.ni.com):

$$GF = \frac{\Delta R/R}{\Delta L/L} = \frac{\Delta R}{\varepsilon} \qquad \text{Equation 4.1}$$

The strain-induced change in resistance, ΔR is:

$\Delta R = R \cdot GF \cdot \varepsilon$ where ε is the strain and R is the nominal resistance of the strain gauge.

The results obtained from the strain gauge data logger in voltage converted to strain-induced resistance expressed in ohms(Ω) are demonstrated in Table 3 for sample one. These were then converted to strain.

Table 3: Sample One Strain Data

Date	Time	Voltage (V)	Conversion of recorded voltage to resistance (Ω)	Strain
2/4/2015	3:17:05 PM	0.000001	0.0000048	4.7619E-08
2/4/2015	3:27:05 PM	0.000002	0.0000096	9.52381E-08
2/4/2015	3:37:05 PM	0.000001	0.0000048	4.7619E-08

Autogenous shrinkage strain is the self-created bulk strain of cement paste, mortar or concrete during hydration with no moisture lost to the surrounding environment. Figures 6 and 7 show graphs of strain against time for samples one and two; seven and eight respectively. The mix and curing conditions details are as presented in Table 2.

Positive strain values signify an increase in volume while negative strain values signify shrinkage. Positive strain values in a hydrating cement paste indicate the formation of hydration products and absorption of more water by the hydrating cement paste while negative strain values indicate shrinkage. For samples cured under sealed conditions with no moisture loss to the surrounding environment, this strain is autogenous shrinkage.

From Table 2, samples one and two were similar except that sample one had a w/c ratio of 0.35 while sample two had a w/c ratio of 0.45. Both cured under sealed but unsaturated conditions.

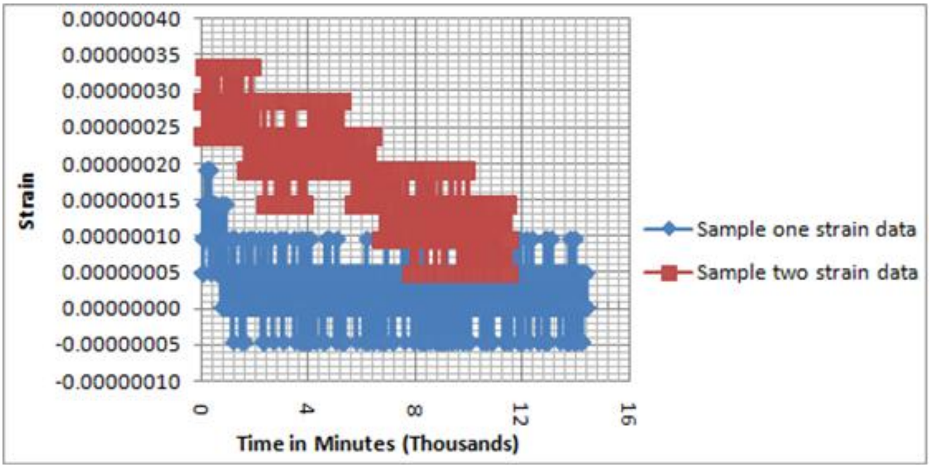

Figure 6: Samples one and two strain against date

Figure 6 show that sample two-recorded higher positive strain compared to sample one. Sample one recorded more negative strain values. This meant that there was higher autogenous shrinkage in sample one. No negative strain was observed in sample two indicating no autogenous shrinkage within the testing period. This means that higher w/c ratio reduces autogenous shrinkage.

Even though samples seven and eight cured under saturated conditions, autogenous shrinkage strain occurred. Contrary to drying shrinkage, autogenous shrinkage occurs without any loss of moisture from the concrete. In low water-to-cement (w/c) high-performance concretes (HPC), the traditional external curing may not work since due to a very fine structure of porosity, water provided on the surfaces is not able to penetrate the interior of the element. This explains why even in curing under sealed and saturated conditions, autogenous shrinkage was still observed in samples seven and eight.

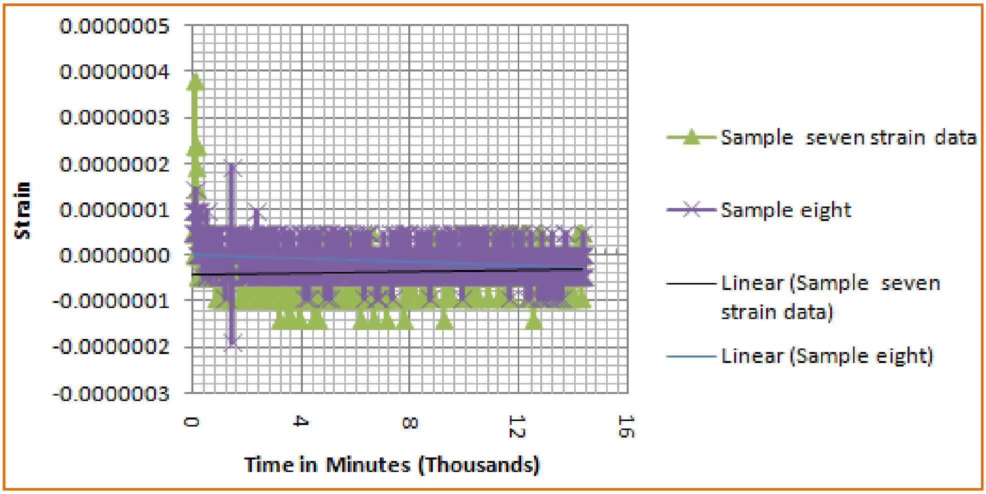

Figure 7: Samples seven and eight strain against date

Sample seven showed higher autogenous shrinkage strain than sample eight, which had a lower w/c ratio than sample seven. Curing under saturated conditions can actually make up for the lower w/c ratio and lead to reduced autogenous shrinkage. Concretes that contain much less water than would be required for complete hydration undergo autogenous shrinkage. The relative surplus of cement leads to an internal drying, irrespective of whether the concrete dries out to the ambient air or not.

Stereo Microscopy Images

Cracking in Hydrating Ordinary Portland Cement Paste

Figure 8 shows microscopy image of sample one after hydrating under sealed and unsaturated conditions for ten days. The darkest areas indicate the macro-pores. Of all the samples tested, cracks were observed in sample one only. This sample cured under sealed but unsaturated conditions, drawing to the observation that conventional curing by sealing the surface to prevent evaporation is not enough and water curing is essential.

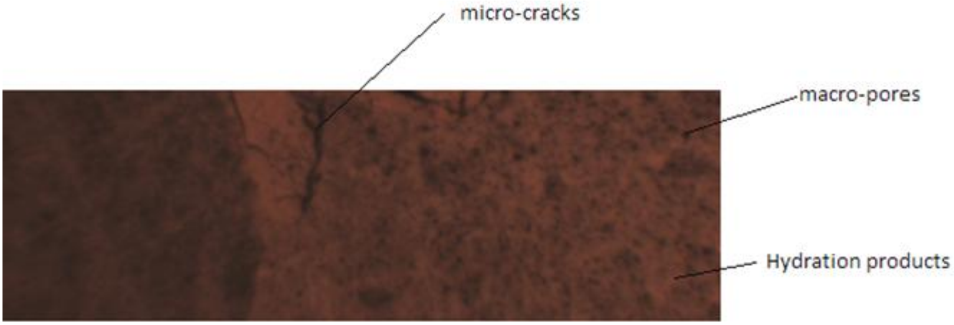

Figure 8: x80 magnification location 1 - sample one

At low water/cement ratios, demand for more water for cement hydration creates very fine capillaries. The surface tension within the capillaries causes autogenous shrinkage which can lead to cracking. This can be reduced by curing under saturated conditions where water is drawn into the capillaries and the shrinkage is reduced. The results indicated that curing under saturated conditions leads to a decrease in cracking due to the presence of enough water required for hydration and cooling hence reduced risk of cracking.

The Pore Structure of Hydrating Ordinary Portland Cement Paste

Scans of the various samples as presented in this section show that the formation of pore structure depends on w/c ratios. Higher w/c ratios lead to reduced pore sizes as shown for samples three, four and seven as compared to the rest of the samples with lower w/c ratios. Stereo Microscopy was done for various locations within each sample and a similar pattern as that one shown in Figure 9 observed.

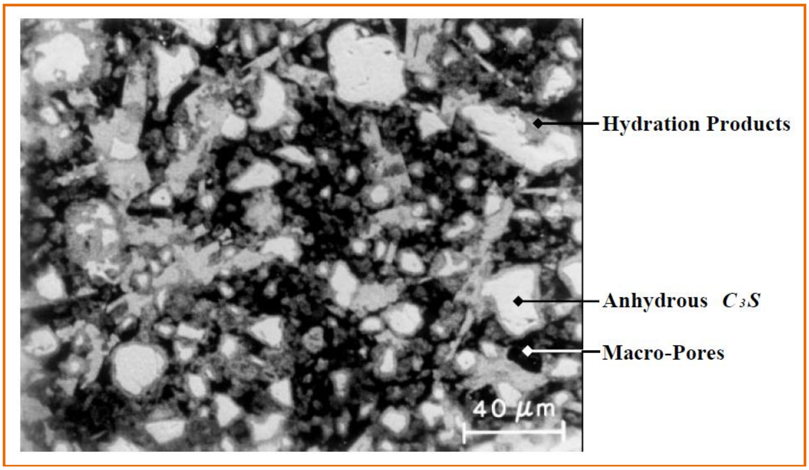

Figure 9: Scanning Electron Micrograph of a *C-S-H* Paste (Tennis *et al.*,1997)

Higher w/c ratios provide more water for hydration hence increasing the formation of hydration products. Therefore, the pores sizes reduce with increasing w/c ratios as hydration products occupy the pore spaces previously occupied by water. Lower w/c ratios results in the taking of water for cement hydration leading to larger pores that had previously been occupied by water.

Figures 10 and 11 shows microscopy images of samples one and two taken at a magnification of x1000. At equal magnification, sample one showed bigger pores than sample two. Sample two showed a higher degree of hydration than sample one which could be due to the availability of more water for hydration in sample two than in sample one. As presented in Table 2, sample one had a w/c ratio of 0.35 while sample two had a w/c ratio of 0.45.

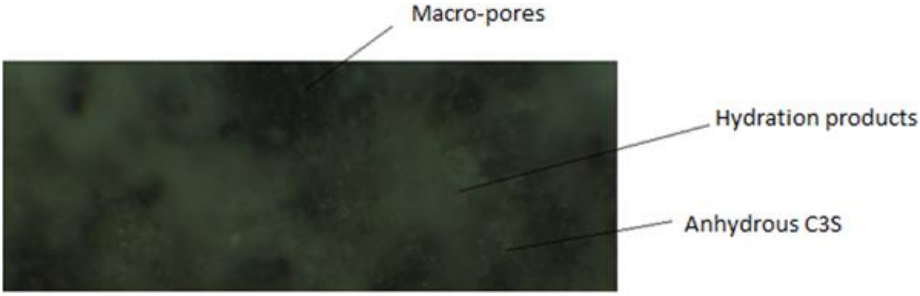

Figure 10: x1000 magnification - sample one

Figure 11: x1000 magnification - sample two

Figures 12 and 13 shows microscopy images of samples three and four taken at a magnification of x200. Sample three showed bigger pores than sample four. The lower the w/c ratio, the larger the pores and the lesser the hydration products.

Figure 12: x200 magnification - sample three

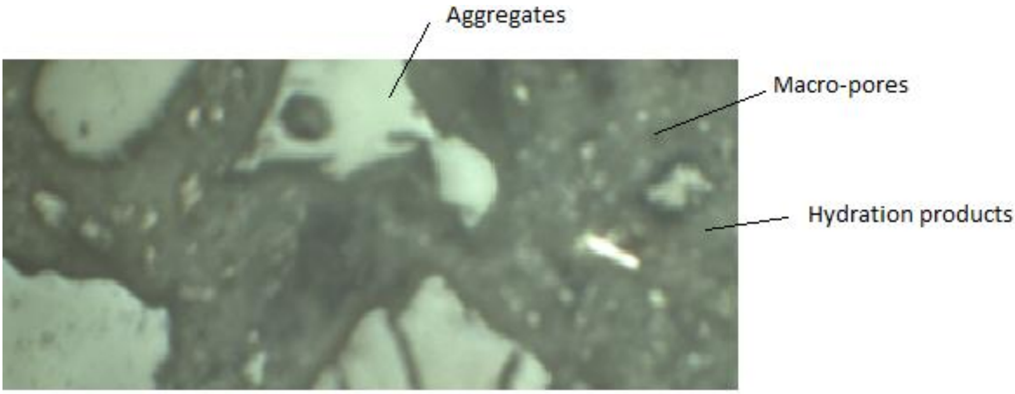

Figure 13: x200 magnification - sample four

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This study observed that the pores sizes of a hydrating Ordinary Portland Cement that contain much less water than is required for complete hydration reduce with increasing w/c ratios.. Higher w/c ratios provide more water for hydration hence increasing the formation of hydration products. Lower w/c ratios results in reduced water available for complete cement hydration leading to drawing of water from pores for further hydration and consequently leading to larger empty spaces (pores). The risk of cracking increases with increasing autogenous shrinkage. Autogenous shrinkage was observed to be minimized by curing in a saturated condition and increasing the water to cement ratio.

Lower water to cement (w/c) ratio led to increased autogenous shrinkage as seen in the comparison of autogenous shrinkage-induced strain results of sample one and two. Sample one recorded autogenous strain within the tested period unlike sample two. Sample one had a lower w/c ratio than sample two.

Mixes with higher water-cement ratios have more water and microstructural space available for hydration of the cement (more cement hydrates at a faster rate), resulting in an increased rate of heat development. Samples two and four recorded higher heat of hydration than samples one and three which had a lower w/c ratio.

Curing under saturated conditions was seen to reduce autogenous shrinkage irrespective of the initial water to cement ratio.Curing in saturated conditions ensures replacement and availability of more water for hydration of Ordinary Portland Cement paste. This reduces self-dessication and thereby autogenous shrinkage. Presence of curing water thus results in less recorded pores and cracking. Availability of water for curing reduces internal temperature due to cooling aided by the presence of water.

Recommendations for Further Research

- Autogenous shrinkage affects the pore structure of hydrating cement. Further research is recommended to relate the development of pore structure with autogenous shrinkage.
- It was initially intended for this research to also evaluate the effect of aggregates on autogenous shrinkage which was not successful. Further research is required to investigate the effect of aggregates on autogenous shrinkage.

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