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DOES THE WATER TO CEMENT RATIO OF CONCRETE IMPACT THE VALUE OF ITS CRITICAL DEGREE OF SATURATION?

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Abstract: This study examines the influence of the water to cement ratio (w/c) on the critical degree of saturation (DOS_{CR}) of cement paste samples using length change measurements. Length change was measured using thermomechanical analysis (TMA) for cement paste samples with different degrees of saturation (DOS), ranging from 100% DOS to 0% DOS. The damage induced by a freezing and thawing cycle (FT cycle) was deduced from length change measurements. The results obtained from length change measurements were correlated with the amount of freezable water obtained from low-temperature differential scanning calorimeter (LT-DSC) tests. It was observed that samples with a DOS greater than DOS_{CR} exhibited damage while those with a DOS less than DOS_{CR} did not show damage. It was concluded that the DOS_{CR} slightly increases when the w/c increases from 0.35 to 0.45. However, there was not a significant increase in DOS_{CR} when the w/c increases from 0.45 to 0.55. However, it should be noted that freeze-thaw performance is dependent on w/c. Indeed, permeability of cementitious materials and the amount of freezable water are directly dependent on the w/c and directly affect the freeze-thaw performance of concrete.

1 INTRODUCTION

The durability of concrete is impacted by the environmental conditions [1, 2]. Jones et al. [3] stated that the damage induced by FT is the second most important durability problem behind the corrosion of steel in reinforced concrete structures. The resistance of cementitious materials to FT damage is dependent on their w/c, DOS, air volume, and air void spacing [4-11].

The damage that develops in concrete as a result of freezing is related to the fact that when the fluid in the pores of concrete changes into ice, pressure develops in the cementitious matrix [12]. A theory has been proposed which says that concrete is resistant to FT damage as long as the DOS remains below a critical value [8, 9, 13, 14].

The DOS in the concrete is defined as the ratio of the volume of pores that are fluid-filled to the total volume of pores. The DOS_{CR} can be defined as the DOS below which damage does not occur during the FT cycle.

Several studies have shown that the porosity of concrete is an essential factor in specifying for durability [15-25]. Kim et al. [26] discussed the impact of porosity on the durability performance of concrete. An increase in the w/c leads to an increase in the porosity, chloride diffusion coefficient, air permeability, and moisture diffusion coefficient; and a decrease in the compressive strength. A cementitious matrix with a lower w/c provides improved FT resistance due to a higher strength, lower porosity and lower permeability, which limits the penetration of fluid. Further, the percentage of smaller pores increases with the decrease in w/c. Consequently, the percentage of freezable water decreases with the decrease in w/c [27].

Beaudoin and MacInnis [28, 29] measured the length change of cement paste samples subjected to FT cycles. They deduced that the dilation and the residual volume change can be expressed as non-linear functions of the free water per unit volume of paste and w/c. However, the influence of w/c on the DOS_{CR} is not yet defined. The objective of this paper is to examine a relationship between the w/c and DOS_{CR}. Ghantous et al. [30] developed a procedure that enables determining DOS_{CR} based on length change measurements on cement paste samples using TMA. This procedure will be used in this study to fulfill the objective of this paper.

2 EXPERIMENTAL PROGRAM

Two different experiments were conducted in this study in order to determine:

- DOS_{CR} from length change measurements on cement paste mixtures with three different w/c exposed to FT cycles
- Amount of ice that develops in a cement paste exposed to FT cycles at different DOS using a LT-DSC.

2.1 Materials and Mixtures

This paper uses neat cement paste samples to assess the impact of w/c on DOS_{CR}. A type I ordinary portland cement was used. The chemical composition of the cement is given in Table 1. The mixture proportions of the cement pastes are provided in Table 2.

The cement and water were mixed in a vacuum mixer at 400 revolutions per minute for 2.5 minutes. The mixer was stopped for 15 seconds in order to scrape down the side of the bowl. An additional 2.5 minutes of mixing at 400 revolutions per minute was performed.

Table 1: Chemical composition of Type I portland cement

Item	Percentage by mass
Silicon dioxide	20.4
Aluminum oxide	4.7
Ferric oxide	3.3
Calcium oxide	63.2
Magnesium oxide	2.5
Sulfur trioxide	2.8
Equivalent alkali	0.54
Tricalcium silicate	55
Dicalcium silicate	17
Tricalcium aluminate	7
Tetracalium aluminoferrite	10
Loss on ignition	1.3

Table 2: Mixture proportions of the cement paste samples

w/c	Cement (kg/m^3)	Water (kg/m^3)
0.35	1498	524
0.45	1303	586
0.55	1153	634

2.2 Samples geometry

Cylinders (50.8 mm in diameter, 101.6 mm in height) were cast in two layers. Each layer of the cement paste was vibrated. To minimize bleeding, the cement paste cylinders were spun on a roller for 24 hours. The samples were then cured for 28 days in a sealed state at 23 ± 1°C.

After curing, cores with flat and parallel surfaces (10 ± 0.2 mm diameter and 20.2 ± 0.4 mm height) were taken from the cast cement paste cylinders (Figure 1) for length change measurements. The preparation of these cores is described in greater details in [30].

Figure 1: Geometry of the samples used for length change measurements

Samples were prepared to determine the amount of ice in the cement paste mixtures. To perform these tests, slices of hardened cement paste of 2.7 ± 0.2 mm thick were cut from the cast cement paste cylinders using a water lubricated diamond saw.

2.3 Preconditioning samples

After cutting, the cores and slices were oven-dried at 60 ± 2 °C until reaching a constant mass recorded as an oven dried mass “m_{OD}”. It should be noted that the mass of the cores is considered constant when their mass evolution over 24 hours is less than 0.1%.

After drying, the cement paste cores were saturated with a saturated lime-water solution using a vacuum saturator at 6 Torr pressure as recommended by [31]. After being removed from the vacuum saturator, they were kept in the solution for 72 ± 4 hours.

For the ice quantification experiment, slab-shaped samples of 22 ± 1 mg were obtained from the dry slices and their oven dried mass (m_{OD}) was recorded (Figure 2). Replicates of these slab shaped cement paste samples were used to quantify the amount of ice formation in cement pastes having different DOS. These samples were saturated in 0.25 ml of lime-saturated water in a microcentrifuge tube for 48 hours.

Samples that needed to be tested at DOS other than 100% and 0% were dried at 23 ± 1°C until the desired saturation level was reached. Cores were then placed in a sealed bag for 1 week at 23 ± 1°C which allowed the internal moisture content to equilibrate. Slab shaped cement paste samples were sealed after reaching the desired DOS in a high volume (100µL) stainless steel pan.

Samples having 100% DOS were tested immediately after the end of the saturation time; while samples having 0% DOS were tested immediately after the drying phase.

The DOS evaluated in this study for every mixture is listed in Table 3 and Table 4.

Figure 2 : Final geometry of samples used for ice quantification

Table 3: Number of cores and DOS tested for every mixture for length change measurements

w/c	DOS (%)	Number of cores
0.35	75, 77, 83, 90, 95, 100	18
0.45	0, 50, 65, 75, 80, 85, 90, 95 and 100	27
0.55	80, 85, 90, 95, 97	15

Table 4: Number of slab-shaped samples and DOS tested for every mixture for ice quantification measurements

w/c	DOS (%)	Number of cores
0.35	24, 35, 40, 45, 50, 60, 65, 75, 77, 85, 95, 100	17
0.45	0, 20, 28, 35, 45, 50, 55, 65, 75, 80, 85, 90, 95 and 100	26
0.55	25, 35, 40, 50, 55, 60, 65, 70, 75, 80, 90, 95	15

2.4 Length change measurements

A thermomechanical analyzer (Q400 TMA), equipped with a macroexpansion probe, was used to measure the length change of the cement paste cores during FT cycle. A mechanical cooling unit was connected to the TMA in order to reach temperatures below freezing. The test was run under 50ml/min nitrogen flow. Details about the TMA can be found in [30].

In order to minimize moisture loss during the duration of the test, the vertical surface of the cement paste core was sealed with aluminum tape (Figure 3).

Figure 3: Photo of the cement paste sample inside the furnace of the TMA

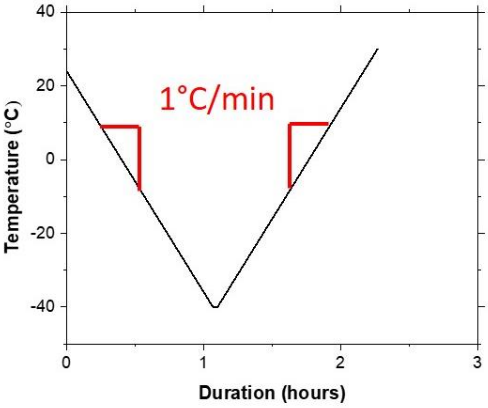

Figure 4: FT cycle in TMA

Figure 4 shows the FT cycle applied to the cement paste samples. Fagerlund [32] showed experimentally that the freezing rate does not impact DOS_{CR}. Minimizing moisture loss from the sample during length change measurements by the TMA is crucial. Therefore, a suitable heating/cooling rate (1°C/min) was implemented to reduce the duration of the testing and subsequently the mass loss from the sample, based on preliminary experiments [30].

2.5 Ice quantification

A Q20 LT-DSC was used to measure the amount of ice that develops during a freezing and cooling cycle. Figure 5 shows the characteristics of the FT cycle that was applied using LT-DSC. A slow rate of 0.1°C/min was used to better quantify freezable water.

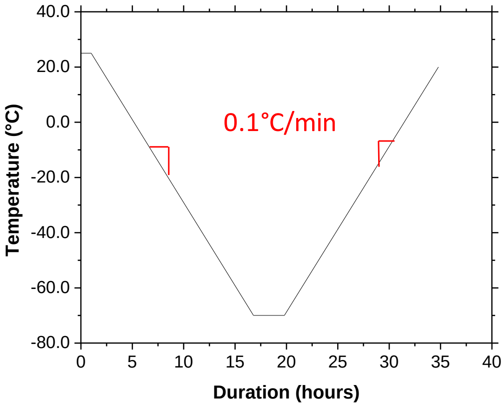

Figure 5: FT cycle in LT-DSC

3 DATA ANALYSIS

3.1 Strain-Temperature plot from TMA experiment

Figure 6 shows a strain-temperature plot of a saturated cement paste sample exposed to a FT cycle in TMA.

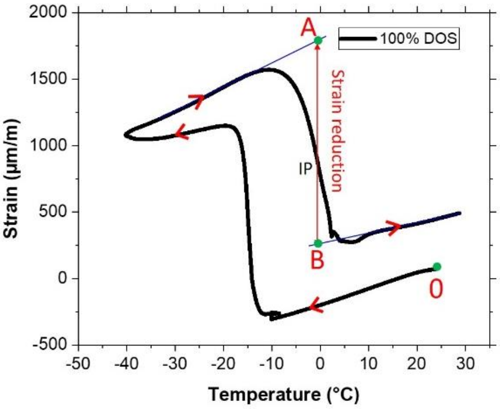

Figure 6: Strain evolution with respect to temperature

Strain reduction (μm/m) is determined using the strain at point A and B from Figure 6. A systematic methodology has been defined in the previous study [30]. In [30], data collected based on length change measurements in TMA were compared with those collected using a traditional method for FT damage quantification, such as UPV. Based on this comparison, it has been proved that the DOS$_{CR}$ can be determined by identifying the DOS associated with a strain reduction less than 100 μm/m [30]. Due to the experimental variation in the study [30], 100 μm/m was proven to be a threshold for the strain reduction. Cement paste samples that show a strain reduction above this value are considered damaged. However, those developing a strain reduction below 100 μm/m are assumed to not exhibit FT damage.

3.2 Heat flow from LT-DSC experiment.

The data collected during the cooling phase in LT-DSC were not used to quantify the amount of ice that developed, because the temperature at which the phase change occurred during the cooling stage was altered by nucleation. The energy associated with ice melting between - 10°C and -1°C was measured using the LT-DSC (Figure 7). The measured energy was then divided by the latent heat of ice melting (334 J/g) in order to quantify the amount of ice that developed in the measured cement paste.

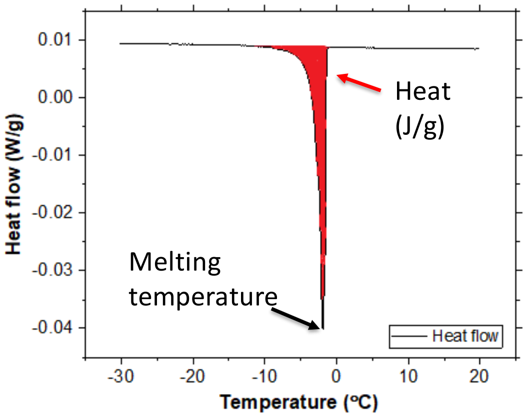

Figure 7: Heat flow signal due to ice melting

4 RESULTS

Figure 8 shows the strain reduction for paste samples with three different w/c: 0.35 w/c (Figure 8(a)), 0.45 w/c (Figure 8(b)) and 0.55 w/c (Figure 8(c)). Samples with a high DOS (higher than DOS$_{CR}$) show a strain reduction higher than 100 μm/m. On the other hand, samples with a DOS lower than DOS$_{CR}$ show a nearly linear response in length change throughout the FT cycle. The DOS$_{CR}$ can be obtained by fitting a line, as shown in Figure 8, and identifying the DOS associated with strain reduction that is equal to 100 μm/m [30]. The data shows that the DOS$_{CR}$ of the 0.35 w/c cement paste mixture is slightly higher (by approximately 2-3 %) than the DOS$_{CR}$ of the 0.45w/c cement paste mixture. The DOS$_{CR}$ of the 0.55 w/c mixture is slightly lower (1%) than the DOS$_{CR}$ of the 0.45 w/c mixture. This difference is considered to be linked to the variability of the measurements. In a previous study [33], the impact of the air void volume and air void quality on DOS$_{CR}$ was examined. It was proven that for all mixtures, the DOS$_{CR}$ value fell within 80-91% DOS, which was consistent with other studies [6, 14, 34].

Consequently, considering that the maximum change that can be measured for the DOSCR value has been shown to be equal to 11%, the 2-3% difference in DOSCR measured in this study between 0.35 w/c and other mixtures is non-negligible.

The values of strain reduction (i.e., FT damage) measured on 0.35 w/c samples with a DOS higher than DOSCR is smaller than those measured on the 0.45 and 0.55 w/c cement paste samples (Figure 8). Both the 0.45 and 0.55 w/c mixtures show similar values for strain reduction measured at high DOS (Figure 8). The difference observed between the 0.35 w/c mixture and the other mixtures can be attributed to the greater amount of freezable water in the samples with higher w/c (Figure 9 and Figure 10). Figure 9 shows the amount of ice that develops in 1 gram of cement paste for three different w/c at different DOS measured by LT-DSC. Based on Figure 9, the percentage of freezable water increases with an increase of w/c due to the greater amount of capillary pores in the high w/c mixtures [19] . Water in these capillaries is the most susceptible to freezing [12, 27]**.** It should be noted that the difference in the freezable water is more significant between 0.35 and 0.45 w/c than between 0.45 and 0.55 w/c (Figure 9, Figure 10). This could explain the similarity observed in the strain reduction values measured on 0.45 and 0.55 w/c cement paste samples.

In summary, DOSCR for 0.35 w/c cement paste samples is slightly higher than the ones measured on 0.45 and 0.55 w/c, which show similar values for DOSCR. This implies that a 0.35 w/c cement paste mixture may resist FT damage at higher levels of saturation than 0.45 and 0.55 w/c mixtures. In addition, one should keep in mind that a lower w/c mixture provides better resistance to FT damage. This is because concrete with low w/c has a lower sorptivity, which implies that a longer time is needed in order to reach DOSCR above which FT damage occurs [24, 26, 35].

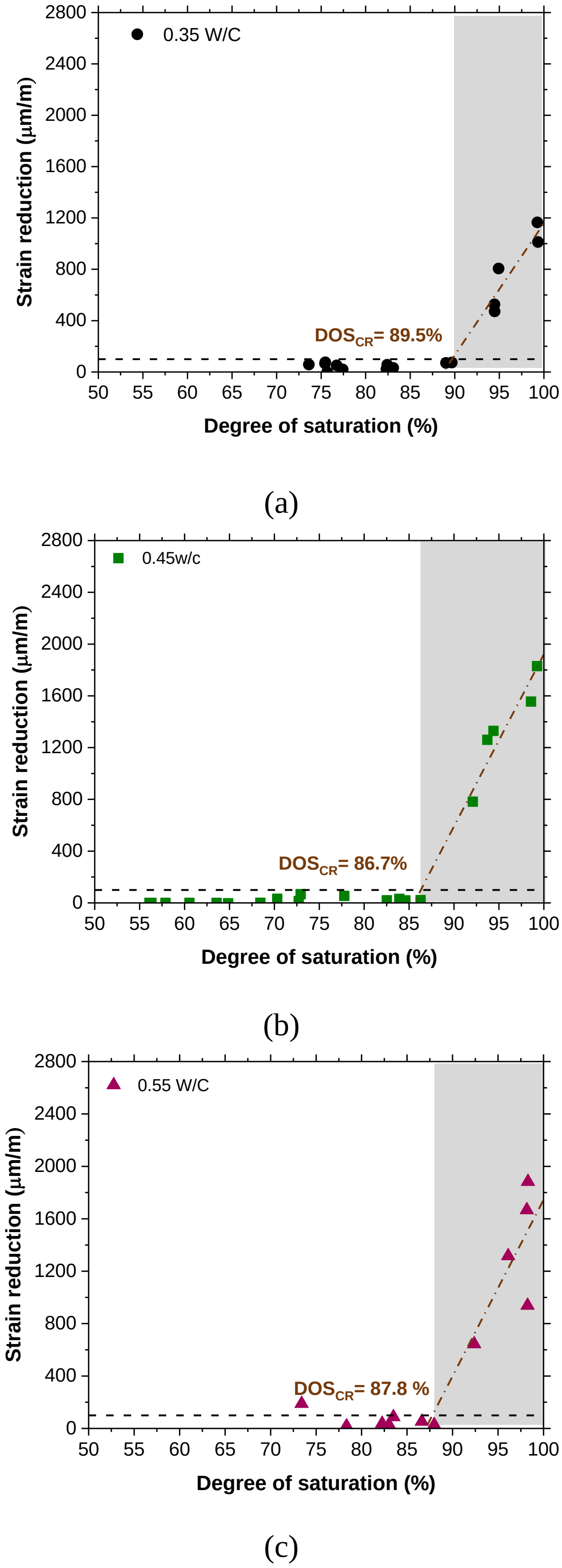

Figure 8: Strain reduction in cement paste with different DOS during FT cycle (a) 0.35 w/c (b) 0.45 w/c (c) 0.55 w/c

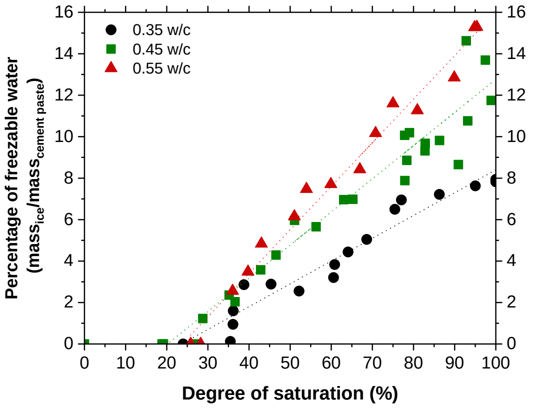

Figure 9: Percentage of ice that develops in 1 gram of cement paste exposed to FT cycle with respect to 3 different water to cement ratios and different DOS.

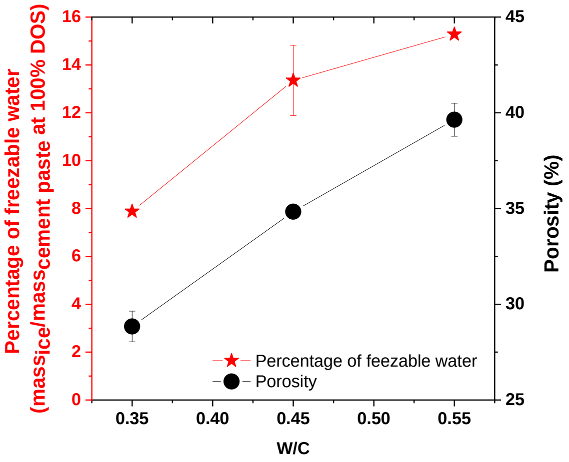

Figure 10: Percentage of freezable water and porosity of the cement paste samples with different w/c

5 CONCLUSIONS

This paper measured the length change of cement paste samples which were heated and cooled using a TMA. Sample preparation and testing procedures were explained. The interpretation of the strain-temperature response obtained from length change measurements was described. This length change behavior was used to investigate the influence of w/c on DOS$_{CR}$.

Experimental results indicate that samples with a high DOS (i.e., a DOS greater than DOS$_{CR}$) show strain reduction during ice melting. Alternatively, cement paste with lower DOS show a linear length change during melting which corresponds to absence of FT damage.

Results indicate that the measured strain reduction during ice melting is smaller in 0.35 w/c compared to 0.45 and 0.55 w/c mixtures when DOS>DOS$_{CR}$. The increase in w/c corresponds to an increase in capillary porosity and consequently in the amount of ice that develops. Therefore, the higher amount of ice in the 0.45 and 0.55 w/c samples could explain the increase in FT damage compared to the 0.35 w/c mixture.

Results show that DOS$_{CR}$ for 0.35 w/c cement paste samples is slightly higher than the one measured for 0.45 and 0.55 w/c, which portray similar values for the DOS$_{CR}$. Consequently, a 0.35 w/c cement paste mixture will need a longer time to reach critical saturation level and will be more resistant to FT cycles. In addition, it should be kept in mind that w/c influences the DOS, mass of ice, mass of water, water absorption and permeability of concrete. Therefore, a lower w/c mixture provides better resistance to FT damage.

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