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INFLUENCE OF POROSITY, DEGREE OF HYDRATION, AND EFFECT OF TEMPERATURE ON COMPRESSIVE STRENGTH OF OPC PASTE

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ABSTRACT

Ordinary Portland cement (OPC) is used worldwide as basic construction material. Studying its physical, chemical and microstructural properties is important. In this study, the influence of porosity, degree of hydration and the effect of temperature on the strength of Japan OPC were evaluated using the water/cement ratio (w/c) of 0.40 and intensive procedures in sample preparation and testing. High early compressive strength development, fast degree of hydration and decreased porosity were observed in 3-day cement cured at 40oC. However, the strength and degree of hydration begun to decline after 28 days of curing period which was nearly comparable to cement cured at room temperature.

Keywords: porosity, degree of hydration, temperature, compressive strength

I. INTRODUCTION

Ordinary Portland cement (OPC) hydration is affected by many variables that include chemical composition, water cement ratio (w/c) and fineness [1]. The gradual increase in strength as a result of chemical reaction (hydration) between cement and water for specific mixture at any age is related to degree of hydration [2]. The fact that reduction of porosity as a result of hydration in cement-based materials increases its strength was recognized long ago.

It has been discovered that porosity has an important role in the frost resistance of concrete. Furthermore, it affects the mechanical behavior and properties of cement paste and concrete such as compressive strength-modulus of elasticity relationship. There are many excellent reviews of the effect of porosity on the strength of cement paste and concrete. One of this is done by Balshin (1949). He presented some of the more important empirical and theoretical equation relating strength to porosity [3].

The degree of hydration and porosity of cement is also affected by temperature. The increase in temperature promotes accelerated hydration and early strength development [8].

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There are many experimental techniques used to measure the degree of hydration of OPC, such as measuring the non-evaporable water content by Loss of Ignition (LOI) and measuring the amount of calcium hydroxide produced in the hydration reactions. These methods are based on comparisons of the measured parameters for a fully hydrated paste [4].

In recent years, scanning electron microscope (SEM) has been used in cement systems to directly estimate the degree of hydration. Researchers collect backscattered electron images (BEI) and then quantitatively analyze these based on the different brightness of the hydrated cement paste. Each phase have different density, therefore brightness of each phase were different. However, this technique can only examine a very small field of view and it requires several minutes of processing.

Ordinary Portland cement is used worldwide as a basic construction material. Therefore, studying its physical, chemical and microstructural properties is important. In this study, the influence of porosity, degree of hydration and the effect of temperature on the strength of Japan OPC were evaluated.

II. MATERIALS AND METHODS

2.1. Materials and sample preparation

Ordinary Portland Cement (OPC) from Japan was used in forming cement paste. The chemical analysis, mineral composition, Rietveld analysis, its density and surface area is given in Table 1. The cement was mixed with deionized water using rotary mixer at constant speed for at least 3 minutes in water/cement ratio (w/c) of 0.40, cast in 50mm diameter x 100mm height cylindrical stainless steel mold and covered with parafilm to avoid water evaporation for 24hrs at room temperature. After the cement paste hardened, this was removed from the mold and cured at 20 and 40^{o}C in a water bath for 3 and 28 days curing period.

Table 1. Composition of Japan OPC used.

Chemical Analysis (%)		**Normative Phase Composition**	**Bogue Eqn. (%)**	**Rietveld Method (%)**	**Density (g/cm^3)**	**Surface Area (cm^2/g)**
SiO_2	21.56	C_3S	70.76	65.60	3.16	3310
Al_2O_3	4.68	C_2S	8.83	12.40		
Fe_2O_3	2.98	C_3A	7.37	7.20		
CaO	65.63	C_4AF	9.06	12.50		
MgO	1.30	$CaSO_4.2H_2O$		0.00		
SO_3	1.90	$CaSO_4.1/2H_2O$		2.20		
Na_2O	0.33	MgO		0.00		
K_2O	0.39	$CaSO_4$		0.10		
TiO_2	0.23	CaO		0.00		
P_2O_3	0.27					
MnO	0.14					
Cl	0.005					

a. Determination of compressive strength

The hardened cement pastes cured at different temperatures and time were tested for compressive strength using digital compression machine model ME-732-1-020, Hi-Actis-2000 of Marui & Co., Ltd., Japan with a compression speed ranging from 0.20 to 1.0 N/mm^2.sec. Three specimens were prepared for every measurement.

b. Determination Porosity and of Loss of ignition (LOI)

After the compressive strength test, the fragments obtained from the 3-and 28-day samples were cut into cubes of dimensions 5x5x5mm using a diamond saw. Weigh then oven dried at 40^{o}C and 105^{o}C for 24hrs, fired and soaked for 1 hr at 950^{o}C using muffle furnace. The porosity and loss of ignition (LOI) were determined using the following equation;

$$Porosity = \frac{Initial\ weight\ of\ specimen - Weight\ of\ dried\ specimen\ at\ 105C}{Weight\ of\ dried\ specimen\ at\ 105C - Weight\ of\ the\ crucible}$$

$$LOI = \frac{Weight\ of\ dried\ specimen\ at\ 105C - Weight\ of\ fired\ specimen\ at\ 950C}{Weight\ of\ fired\ specimen\ at\ 950C - Weight\ of\ the\ crucible}$$

Determination of degree of hydration by Loss of Ignition (LOI)

The degree of hydration was determined as a ratio of the measured LOI of cement paste to the amount at fully hydrated OPC.

$$Degree\ of\ hydration\ by\ LOI = \frac{Loss\ of\ ignition\ (LOI)}{0.23}$$

(Note: 0.23 is constant value for LOI of fully hydrated OPC)

c. Observation of microstructure of cement paste

To check the accuracy of the LOI results, porosity was obtained through Backscattering Electron Images (BEI).

The remaining samples used in porosity and LOI determination were immersed in acetone to interrupt hydration reaction then subsequently placed in a vacuum desiccator for 24hrs. These were molded into epoxy resin and hardened for at least 48hrs. Their surfaces were polished using course to fine abrasive paper. Finally, a 0.25µm diamond paste was used for final polishing. These were then freeze dried using Eyela Freeze Dryer model FD-1000 for 24hrs.

Prior to Scanning Electron Microscope (SEM) analysis, the samples were coated with Platinum (Pt) ions using Jeol Auto fine coater model JFC-1600. Backscattering Electron Images (BEI) were obtained using Shimadzu model SSX-550 Superscan Scanning Electron Microscope to separate each phase such as unreacted cement particle (UH), calcium hydroxide (CH), calcium silicate hydrate (C-S-H) and pores. Each phase have different density, therefore the brightness of each

phase were different. White appearance is identified as UH, bright gray is CH, dark gray is C-S-H and the black spots are pores.

The BEI images used in counting the pores and unreacted cement are shown in Figure 1. The equation below was used to measure the following properties;

$$Porosity\ by\ BEI\ = \frac{Number\ of\ pore\ count}{Total\ points}$$

$$Volume\ of\ unreacted\ cement = \frac{Number\ of\ unreacted\ cement\ count}{Total\ points}$$

$$Initial\ volume\ of\ cement = \frac{Volume\ of\ unhydrated\ cement}{Volume\ of\ unhydrated\ cement + Volume\ of\ water}$$

$$Degree\ of\ hydration\ by\ BEI = 1 - \left[\frac{Volume\ of\ unreacted\ cement}{Initial\ volume\ of\ cement}\right]$$

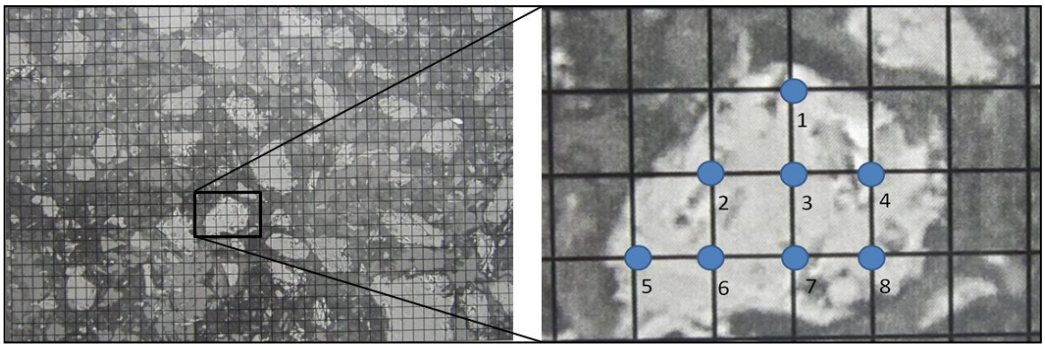

Figure 1. A representative typical field view of BEI image (150x200μm) used for point counting on pores and unreacted cement particle. *Note:* actual grid size (30points x 48points=1,440total points); unreacted cement particle (white color), calcium hydroxide (light gray), calcium silicate hydrate (dark gray), and pores (black spot).

The point counting procedure involved a grid superimposed on top of the BEI image of a cut and polished hardened cement paste. The pores and the unreacted cement phase were determined and counted at each grid point by an expert human operator. The SEM magnification was set at 500X and a 30x48point grid was selected to obtain reasonable estimates. Each point that fell into a pore or on the unreacted cement phase were counted and recorded as shown in Figure 1.

III. RESULTS AND DISCUSSION

3.1 Morphology of hardened cement paste

The type, shape, amount, size and distribution of phases present in hardened cement paste constitute its microstructure. The unhydrated OPC is composed of angular particles typically in size range from 1-50μm [7]. When mixed with water in a water/cement ratio (w/c) of 0.40, several interactions happened and formed into a rigid hydrated cement paste. Under SEM examination, the presence of unreacted cement and pores were observed.

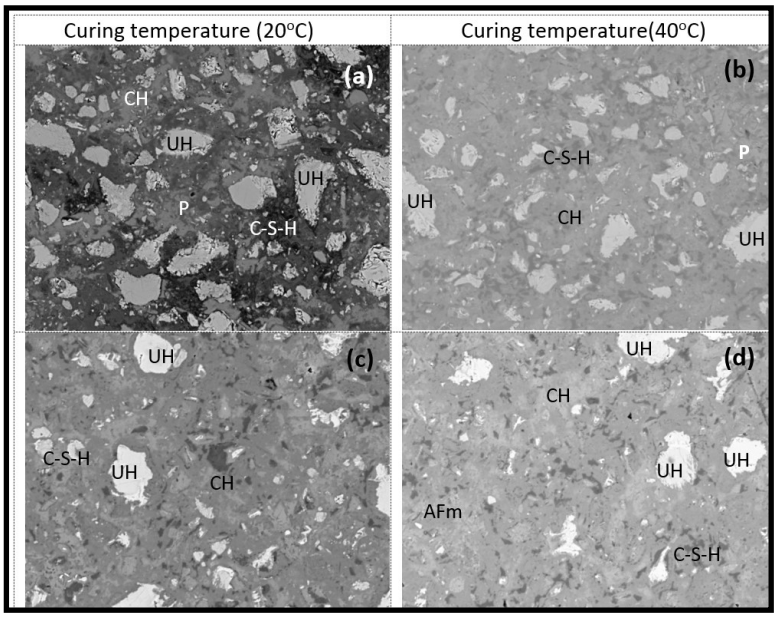

Figure 2. The comparative BEI images (150x200μm) of cement paste in a water/cement ratio (w/c) of 0.40 cured at different time and temperature: 3 days at (a)20°C, (b)40°C and 28 days at (c)20°C, (d) 40°C. *Note:* UH: unreacted cement particle (white color), CH: calcium hydroxide (light gray), C-S-H: calcium silicate hydrate (dark gray), p: pores (black spot), AFm: monosulfoaluminate.

The degree of hydration of cement paste as a function of time was determined by loss of ignition (LOI) and BEI point counting. The microstructure of the hydrated products shown in Figure 2 reveals the presence of unreacted cement particle (white color), calcium hydroxide (light gray), calcium silicate hydrate(dark gray), and pores (black spot). The main characteristic features are the presence of monosulfoaluminate (AFm) phase, reduction of pores and unreacted cement particles at 40°C curing temperature and 28 days of curing period.

Many studies have been made to establish relationship between strength and microstructural properties of cement paste such as pore structure and size distribution. It is considered to have a significant impact on compressive strength. Generally, compressive strength increases linearly with density [2].

Porosity plays an important role in the development of mechanical properties and can provide

further information about the performance of cement paste. The low initial rates of hydration may be said to favor the controlled precipitation of reaction products in interstitial space, raising the gel/ space ratio and with its compressive strength throughout the curing period [1].

In other words, the compressive strength is closely related to how and where cement hydration products precipitate as well as pore size distribution.

3.2 Influence of porosity, degree of hydration and effect of temperature on compressive strength of cement paste

3.2.1 Compressive strength against porosity

Porosity is dependent on the water cement ratio (w/c), curing temperature and time. The compressive strength for instance, has an inverse relation between its porosity. The lower the porosity the stronger the hardened cement pastes as shown in Figure 3.

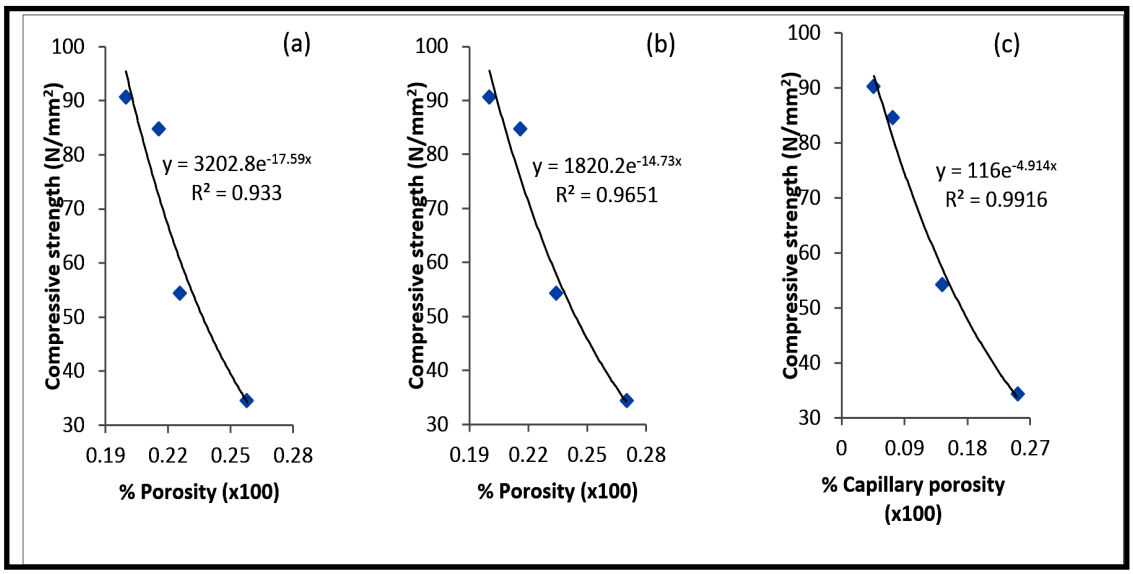

Figure 3. The relationship between compressive strength and porosity over the range of curing time and temperature, in this case 3 and 28 days period oven dried at (a) 40°C (b) 105°C and (c) calculated using Powers model at 40°C .

Figure 3 (a), (b) and (c) shows the exponential correlation coefficient between porosity and capillary porosity using Powers model over compressive strength at various curing temperature and hydration period. The correlation of the two methods came up with nearly the same results which are above 0.90. The capillary porosity determination by Powers model method purely corresponds to the relationship between the water cement ratio and the density of cement. Thus, this showed higher correlation of 0.99 as compared to the porosity determination which corresponds to weight changes of the sample was had correlation of 0.93.

Therefore, it is clear that the compressive strength of hardened cement paste is affected by porosity. It affects the entire physical characteristic, properties and performance of cement and concrete. Scientists and engineers until now have still to find the optimum time and temperature to

reduce porosity and thereby increase compressive strength. This is added information to the pool of knowledge in this area. This information is useful to the cement industry and construction companies. This will ultimately improve the quality of infrastructure.

The results of porosity and of capillary porosity by Powers model as a function of water and cement ratio (w/c) ratio of 0.40, shows an adverse effect on the strength of hardened cement paste. For instance, the lower the permeability and high degree of hydration, the higher the strength of cement.

The remnants of the voids that were occupied by the mixed water which have not been filled by the hydration products exist as capillary porosity and other pores of smaller diameter trap between aggregates of the hydration product primarily the (C-S-H) known as gel pores[5]. The main adverse factor influencing the strength of hardened cement paste was the formation of pores with a radius greater than 10 nm, while pores with a radius less than 10 nm were advantageous since gel pore formation is related to certain amount of hydrates [6].

3.2.2 Compressive strength against degree of hydration

The compressive strength of cement is directly related to the degree of hydration. The higher the hydration products, the stronger the strength of cement paste as shown in figure 4. The hardened cement paste consists of hydrates with various morphologies and densities. The intrinsic strength of the dense, crystalline particles and the bonding properties of well-crystallized material generate bulk strength.

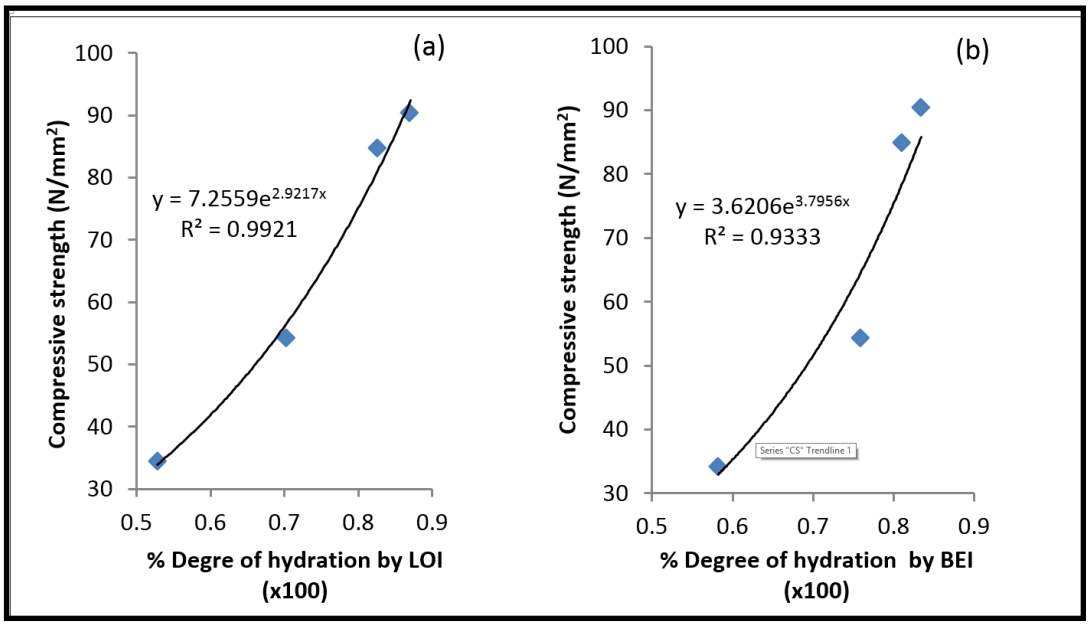

Figure 4. The relationship between compressive strength and degree of hydration over the range of curing temperature and time, in this case 20 and 40°C for 3and 28 days period. (a) degree of hydration by LOI and (b) degree of hydration by BEI using point counting method.

There is a better correlation between compressive strength and hydration. Exponential correlation coefficient between the compressive strength and the degree of hydration are 0.99 and 0.93 in LOI and BEI point counting method respectively. See Figure 4. This means that although both methods are reliable since their correlation coefficients are above 0.90, the LOI method is more accurate than the BEI point counting method. This is because the LOI method is able to measure the whole sample while the BEI point counting method is limited to the part of sample which was viewed under the SEM.

Therefore, it can be inferred that the compressive strength depends primarily on the amount of hydrates. Hence, the amount of hydrates plays a very important role in the strength development of hardened cement paste. The relative amount of hydrates is expressed as the degree of hydration [6].

The curing temperature and time are the basic fundamentals that contribute to the hardening and strength development of cement paste and concrete. The 40°C curing temperature for instance provides for a faster and higher degree of hydration compared to sample cured at room temperature as revealed in Figure 5.

3.2.3 Effect of temperature on compressive strength of hardened cement paste

Three hardened cement paste specimens cured at different temperatures and time were tested for compressive strength test. Figure 5 shows that the higher the curing temperature and time, the stronger the cement paste.

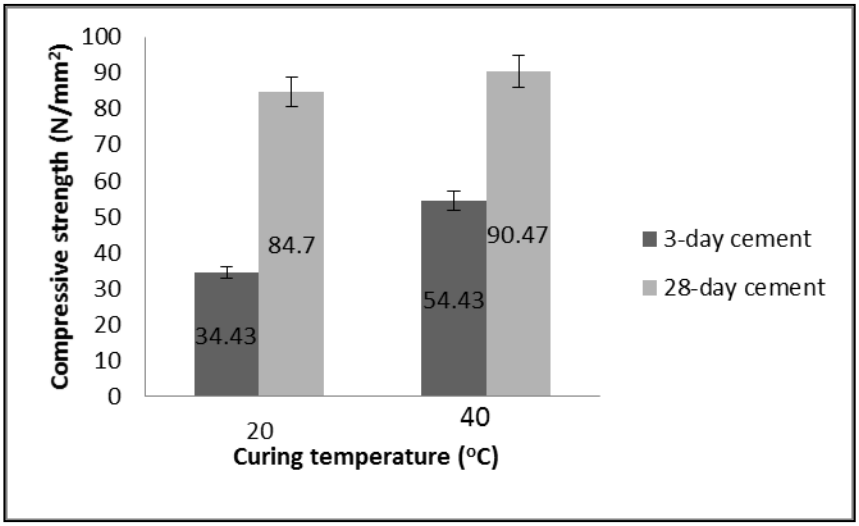

Figure 5. The compressive strength against curing temperature of cement paste at different curing time.

These finding concur with other studies [1], wherein the strength of early age of cement paste increases progressively with high temperature. The hydration of cement paste is sensitive to temperature. Increasing the temperature promotes the hydration leading to high early strength [8]. This phenomenon is due to accelerated hydration of cement phase which results in an increased amount of hydrates that modified the pore structures.

When heat evolution is faster and higher, the hardening of cement paste is rapid. For the cement paste cured at 40°C, the compressive strength begun to decline in nearly the same strength with cement paste cured at 20°C after 28 days as revealed in Figure 5. This occurs generally when the hydration of C_3S slows down. During this time there is already sufficient buildup of hydration products. This finding is consistent with Lothenbach et al. (2007) which posit that high temperatures advance hydration and strength of cement early on [8].

The strength development of cement paste is almost entirely due to the hydration of calcium silicates (C_3S and C_2S) in the early days of hydration. The major component responsible for the strength generation is calcium silicate hydrate (C-S-H) [5]. When referring to the early hydration reaction, attention should be given to the relatively high rates of heat evolution that occur. This rise is particularly affected by the C_3S and C_3A which are characterized by highly exothermic reactions. The increase in temperature can be favorable because it can accelerate reaction and thereby the rates of strength gain [5].

The fast hydration in the initial stage leads to a more heterogeneous distribution of the hydration products as the hydrate precipitate around the clinker particles and build up a dense inner shell around the clinker. At low temperature for instance, hydration starts very slowly which allows the dissolved ions more time for diffusion before the hydrates precipitate [8].

IV. CONCLUSION

The compressive strength of hardened cement paste is influenced by porosity, degree of hydration and effect of temperature. It has an inverse relation between porosity and directly related to the degree of hydration. For instance, the lower porosity and the higher degree of hydration lead to stronger hardened cement pastes in a water/cement ratio (w/c) of 0.40. The 40°C curing temperature provides for a faster and higher degree of hydration compared to cement paste cured at room temperature.

This study provides vital information about the influence of porosity, degree of hydration, and effect of temperature on the compressive strength of ordinary Portland cement paste.

V. ACKNOWLEDGEMENT

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