Water to Cement Ratio Effect on Cement Paste Microstructural Development by Electrical Resistivity Measurements and Computer Illustration

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Abstract  The effect of the water-to-cement ratio on cement paste microstructural development was investigated using electrical resistivity measurements and computer modelling. Three cement pastes with 0.3, 0.35, and 0.4 w/c ratios were used in this study. The electrical resistivity measurements curve as a function of time for the three pastes shows that the lower the w/c ratio the higher the electrical resistivity through the whole time. The effect of overall porosity and initial distances between particles significantly influence the measurements. Although low w/c ratio paste has low liquid electrical resistivity comparing to other samples, still has high bulk electrical at all ages. The influence of particles proximity due to lower water amount was interpreted through monitoring the electrical resistivity development and computer illustration. The demonstration provides more explanation about the importance of water-to-cement ratio. Through the conducted experiments, empirical correlations were developed regard predicting compressive strength and autogenous shrinkage of cement pastes when all parameters are related to porosity. Setting time was also predicted by monitoring the critical points on the electrical resistivity curve. Scanning electron microscopy (SEM) was employed to elucidate the effect of the w/c ratio on the morphology of hydration products, and it was observed that high w/c ratio paste has more fibers per unite area comparing to lower w/c ratio pastes due to the long distances between hydrates for expanding.

Keywords: water-to-cement ratio, electrical resistivity, computer illustration, cement hydration, cement strength, cement setting

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1. Introduction

The most important parameters regarding cement microstructural development have always been the water-to-cement ratio (w/c) [1,2]. Water-to-cement ratio has a major influence on both fresh and hardened states of cement paste, affecting its rheology, mechanical properties, permeability, and durability [3,4]. The w/c ratio is directly related to the average spaces between particles within cement paste [5]. The initial distances between cement particles right after mixing with water and before hydrating are fundamentally determined by w/c ratio [6]. These initial distances whether are large or small dramatically affect the rate of cement hydration, setting time, strength and shrinkage [1-6]. Hydration of cement is chemical-physical process and cement particles segmentation [7]. Through cement-water reaction, hydrates expand from the original boundaries of cement particles, occupying the neighboring empty spaces until hydrates impingement [8]. The consumed time for hydrates impingement is not only related to rate of reaction, particles size distribution or curing temperature but significantly to the distances between cement particles [9,10]. Cement setting was widely understood as percolation theory when the process is related to solids connectivity [11]. The connectivity of hydration products [12] is related to rate of reaction and porosity. The connectivity of capillary porosity is related to w/c ratio, when w/c is high there will be a higher percentage of connected pores. Pores are depercolated through cement hydration and hydrates expansion. The time for pores to depercolate or hydrates to percolate is w/c dependent as well as rate of reaction. Compressive strength is porosity dependent and w/c related [5]. Cement paste as porous material [13] has higher strength with low pores, and capillary porosity is determined by w/c ratio [14]. Thereby, w/c significantly affects the strength properties, when strength is always higher with lower w/c ratio.

The importance of w/c ratio was studied through many methods for example and not limited to; ultrasonic pulse velocity (UPV) [15], electrical resistivity [16], and computer modelling [17]. Dale P. Bentz [18] demonstrated the hidden meaning of water-to-cement ratio though computer modelling and emphasized the importance of the distance
between particles, the study employed the computer modelling as a tool to determine the water-to-cement ratio distance. UPV was used as tool to measure the volume fraction of solids and connected solids. UPV usually employed to measure the setting time of cement and evaluate the early age strength [19].

Electrical resistivity is porosity dependent [20,21,22], and the electrical resistivity development follows the porosity development of the cement paste. Electrical resistivity of cement paste increased with decreasing the volume fraction of pores. Studies emphasized that overall electrical resistivity is determined by pores solution electrical resistivity which related to ionic concentration, capillary porosity, and pores connectivity [23]. Many studies were conducted using electrical resistivity measurements to investigate the effect of w/c ratio, and they suggested that electrical resistivity can be used as method to estimate porosity, and monitor the cement hydration process [24,25]. Literature is so rich with many studies suggesting that electrical resistivity follows the microstructural development of material through cement-water reaction [26,27,28,29,30]. Resistivity mainly starts increasing with hydrates expansion due to capillary porosity dis-connectivity. Pores act as conductive channels for electrical current to pass through. The number of conductive mobile ions in the pore solution, cross section of pores (pore size), and connectivity of pores (length of the conductive channel) (tortuosity) significantly influence the conductivity/resistivity development. The proximity of cement particles and constrained spaces will increase the rate of resistivity development and the method can be used to investigate the effect of water-to-cement ratio on cement microstructural development.

One of the most promising methods to understand the microstructural development of Portland cement is computer modelling. Simulation was and still a powerful tool to interpret the cement-water reaction. A three-dimensional cement hydration model (CEMHYD3D) [31] was developed at the national institute of standards and technology (NIST) by Bentz [32]. Jennings and Johnson, Van Breugel [33] have developed a similar microstructure simulation model called HYMOSTRUC [34]. A new platform for modelling the hydration of cements has been developed by Shashank Bishnoi and Karen L. Scrivener called μic [35]. For more comprehensive understanding of cement microstructural development, Power’s model [36,37] experimentally depicted the microstructural development of cement through series of simple mathematical equations. All these models have provided adequate mathematical and visual interpreting of cement microstructural development. The factors which influence the process were identified and included in the formulas. This paved the way to interpret the mechanism action of admixtures and for further comprehend evaluation of cement paste properties.

In this study, an investigation was done to demonstrate the effect of w/c ratio on cement paste properties using non-contact electrical resistivity measurement and computer modelling.

The significant of study comes as the study provides comprehensive research about the influence of water-to-cement ratio on the early properties of cement paste, most importantly setting time and compressive strength. Non-contact electrical resistivity measurements [24] and computer illustration were used to demonstrate the importance of w/c ratio on the microstructural development of cement paste.

2. Experimental

2.1. Materials

32.5 ordinary Portland cement type I was used in this study, the chemical composition is listed in Table. 1. Three cement pastes were prepared with different water-to-cement ratios (0.3, 0.35, and 0.4). Each paste was mixed for 2 min at 45 rpm and for further 2 min at 90 rpm, using a planetary-type mixer at room temperature (20±2°C).

| Table 1. Cement chemical composition (Wt%) |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| CaO             | SiO₂   | Al₂O₃  | Fe₂O₃  | MnO    | SO₃    | K₂O    |
| 59.53           | 24.27  | 7.55   | 2.76   | 0.28   | 4.66   | 0.95   |

2.2. Methods

2.2.1. Non-contact Electrical Resistivity Measurements

A non-contact electrical resistivity measurement apparatus was used to measure the bulk electrical resistivity of three cement pastes. Details of the operational principle of the device can be found in [24,25].

The test were conducted for the three cement pastes at room temperature (20 ± 2°C). The first measurement was recored after 15 min of mixing up to 72h at intervals of 1 minute.

2.2.2. Liquid Electrical Resistivity

Cement pastes solution was extracted and filtered using the vacuums pump at different time after mixing. Electrical conductivity of the extracted solution was measured using a digital portable conductivity meter.

The test were conducted for the three cement pastes at room temperature (20±2°C). The measurements were recorded at 10min, 30min, 60min, 90min, 120min, 150min, and 180min.

2.2.3. Setting Time

Both initial and finial setting time of cement pastes were determined using the Vicat apparatus as described in [26]. The testing temperature was 20±2°C, and the relative humidity was 95±5%.

2.2.4. Compressive Strength

A compressive strength test was performed using paste cubes 40 × 40 × 40 mm. All the cubes were cured in water until the desired ages (1, 3, 7, and 28 d). The compressive strength test was conducted using a compression testing machine at a loading rate of 2.4 kN/s.

2.2.5. SEM Observation

Scanning electron microscopy (SEM) was conducted for the three cement paste after being immersed in absolute ethyl alcohol to stop hydration at the desired ages and then dried in a vacuum drying chamber for 24 h. A
fractured and small piece of each sample was selected for scanning after being coated by a thin layer of gold. The images of each sample were captured at a magnification of 30µm. More details regarding the procedure is available in reference [39].

2.2.6. Autogenous Shrinkage

The autogenous shrinkage of the cement pastes was measured using the vertical method. The instrument used consists of six displacement sensors, one temperature sensor, and a humidity sensor. All the sensors are connected to the data recorder. The measuring range of the displacement sensors is 0–2 mm with a non-linear error of 0.05%. Two paste prisms with dimensions of 40 × 40 × 160 mm were prepared for each sample. A mixture of 1000 g of cement at different w/c ratios was cast in moulds and cured in a curing chamber with a relative humidity of 95 ± 5% and temperature of 20 ± 2 °C. The specimens were demoulded after curing for one day. Each specimen was sealed with two layers of plastic film to avoid moisture loss and was then placed vertically under the displacement sensors. The first measurement was recorded 24 h after the mixing, and the measurements continued up to 192 h. The room temperature was 20 ± 2°C.

2.2.7. Computer Modelling

It was considered that cement particles are spherical and randomly distributed in the system. Cement hydrates expand inward and outward the original boundaries of cement core, occupying the empty spaces between particles as it shown in Figure 1.

![Figure 1. Schematic of a partially hydrated cement particle](image1)

A code was written using Matlab software, to draw several cement particles in limited space as in Figure 2. The figure represents a 2D (500×500) µm² binary image of randomly distributed particles with varied diameters. Based on w/c ratio, the volume of clinker and water-filled spaces were estimated by considering that total volume of the paste equals to 250,000 µm³. Figure 2 (a) illustrates a cement paste with 0.3 w/c ratio, having 128,206 µm³ cement clinker and 121,794 µm³ empty spaces. The initial total porosity in the system is estimated to be 0.48. Comparing to Figure 2 (b) which is 0.6 w/c cement paste with 0.65 initial total porosity, the 0.3 w/c system is denser, less porous, and has more cement particles with shorter distance between each other. The simulation assumed as it demonstrated in Figure 1, that hydration products grow internally inside the original particle (inner hydrates) and externally outside the cement core, occupying the empty spaces (outer products). Theoretically speaking, three circles can represent the hydrated cement particle, while the thickness of inner and outer shell of unreacted core can be estimated by calculating the area of these circles.

![Figure 2. 2D pictures of randomly distributed unreacted cement particles with varied diameters: (a) Cement particles at 0.3 w/c, (b) Cement particles at 0.6 w/c](image2)

Figure 3 illustrates the three circles of partially hydrated cement particle with three certain areas to be calculated as in equations below.

![Figure 3. Schematic of areas of three circles of partially hydrated cement particle](image3)
$$A_{total} = A_1 + A_2 + A_3 = (R + b)^2 \pi$$  
(1)

$$A_1 = (R - \gamma R)^2 \pi$$  
(2)

$$A_2 = R^2 \pi$$  
(3)

Assume $A_2 = A_3$

$$(R - \gamma R)^2 \pi + 2R^2 \pi = (R + b)^2 \pi$$  
(4)

$$b = R \left[ \sqrt{1 + 2\gamma - \gamma^2} - 1 \right]$$  
(5)

Where $R$: radius of partially reacted clinker,  
$\gamma$: degree of hydration.

By estimating the thickness of outer shell which is determined by degree of hydration, the program automatically estimates the total volume of solid and total porosity through hydration time.

### 3. Results and Discussion

#### 3.1. Bulk Electrical Resistivity Measurements

The electrical resistivity of three cement pastes with different water-to-cement ratios was measured as it shown in Figure 4.

![Figure 4. Bulk electrical resistivity measurements as function of time: (a) Electrical resistivity development with time, (b) Rate of electrical resistivity development with time](image-url)
The results show that the electrical resistivity of low w/c ratio paste has always higher resistivity, whether at initial hours right after mixing or after 72h. As it mentioned previously, porosity is a function of w/c, and can be traced by monitoring the resistivity development. Theoretically speaking, the lower the w/c ratio the lower the capillary porosity, the pores connectivity, and pores size. The lower capillary porosity the longer conductive pathway for ions to pass and subsequently the higher electrical resistivity. The prominence of w/c ratio on the microstructural development is presented by determining the initial distances between particles. The higher the w/c ratio the larger the distances between particles.

Figure 4.b shows the rate of electrical resistivity development with time. Three critical points were observed on electrical resistivity rate curve. The first point (point m) which refers to calcium hydroxide precipitation and solution supersaturation with respect to CH [40], appears earlier with 0.3 cement paste rather than other pastes. The gradual decreasing of electrical resistivity right after first measurements till point m is ascribed to cement particles rapid dissolution, releasing more conductive ions and increasing the electrical conductivity of the system. The earlier point m for 32.5p0.3 cement paste indicates a faster CH precipitation and solution supersaturation for the lower w/c ratio pastes. Second critical point (P1) occurred after approximately 6h of hydration. After 6h of cement-water reaction, the paste gained adequate strength to reach rigidity and hardiness. Thus, P1 can refer to hydrates percolation and connectivity. The percolation of solid through water-fill spaces will disconnect the capillary porosity and consume the free water through reaction. When pores lose their connectivity and moisture content, electrical resistivity will be highly dependent on the tortuosity of capillary pores. The effect of pore structure (size and connectivity) is more dominant after P1 point. When saturation degree of pores [41] is dramatically decreased due to reaction, adsorption, and evaporation, or in other word the drop in internal relative humidity will cause the electrical current to be more reliable on the length of the conductive pathway (tortuosity) than ionic content of pore solution. Thus P1 point can be employed as indicator of paste setting time as it proven in section 3.4. The most prominent critical point on electrical resistivity rate curve is the third critical point (P2). P2 point for 32.5p0.3 is higher, faster and sharper. The point can be regarded as beginning of pores depercolation due to excessive growth of hydrates, and the time for cement hydration rate to change from phase-boundary mechanism to diffusion control [42]. The spaces between cement particles are intensively constrained due to hydrates impingement. The depercolation of pores due to hydrates expansion is continuous as long as there are empty spaces available for hydrate to expand and ample amount of water as reaction source. With time, pores are small and water is remarkably consumed, slowing the rate of electrical resistivity development. These three critical points are microstructural indicators and can help assess the cement hydration process.

3.2. Computer Illustration of Cement Pastes with Different w/c Ratios

Figure 5. Modelling cement particles hydrating of 0.3 w/c cement particles: (a) At 0 degree of hydration, (b) At 25% degree of hydration, (c) At 50% degree of hydration, (d) At 75% degree of hydration
Figure 6. Modelling cement particles hydrating of 0.35 w/c cement particles: (a) At 0 degree of hydration, (b) At 25% degree of hydration, (c) At 50% degree of hydration, (d) At 75% degree of hydration

Figure 7. Modelling cement particles hydrating of 0.4 w/c cement particles: (a) At 0 degree of hydration, (b) At 25% degree of hydration, (c) At 50% degree of hydration, (d) At 75% degree of hydration
Figure 5, Figure 6, and Figure 7 are the modelling of the three cement pastes with different water-to-cement ratios. The computer illustration justifies the higher electrical resistivity of lower w/c ratio pastes at the initial hours after mixing. The shorter initial distances between particles will hamper the electrical current from passing easily, restraining the ions movement and rapidly increasing the rate of paste electrical resistivity development. Electrical resistivity is porosity dependent, and computer simulation for the three cement pastes with 0.3, 0.35, and 0.4 w/c ratios shows that cement paste is two-component model with solid part and liquid part. By increasing the solid part, the total porosity will decrease and resistivity is increased. The simulation for the 0.3 w/c ratio cement paste was done using the same written code in certain degrees of hydration as it demonstrated in Figure 5.

The percentages of solids which presented by unreacted cement particles surrounded by inner and external hydrates as well as total porosity were automatically estimated. Figure 6 shows the modelling of hydrates expansion of 0.35 w/c cement paste.

Figure 7 shows the modelling of hydrates expansion of 0.4 w/c cement paste. The porosity of the three cement pastes was estimated by the program and plotted as function of degree of hydration as in Figure 8. The Figure shows that porosity is always lower with lower water to cement ratio, and that cement paste microstructural develops faster and denser than higher w/c ratio. Comparing with 0.4 w/c cement paste, 0.3 w/c paste has higher percentage of connected hydrates and shorter distances between particles for hydrates to converge. High percentage of connected solids significantly affects the early age properties of cement and accelerates the early strength gain rate. Simulating the hydrates expansion through the empty spaces with different w/c ratio pastes, demonstrates the effect of water to cement ratio on porosity and subsequently the electrical resistivity measurements. The electrical resistivity is porosity dependent and can be used as a tool to determine the pore/solid percentage in cement-water system.

### 3.3. Compressive Strength

Table 2 listed the results of cement pastes compressive strength at 24h, 3d, 7d, and 28d. From the table it shows that the lower the w/c ratio the higher the compressive strength at all ages. Increasing the amount of water into the paste will increase the pores volume, pores size and pores connectivity, resulting in slower microstructure development, week strength growth and subsequently lower 28d compressive strength [43].

| Code | 1 day (MPa) | 3 day (MPa) | 7 day (MPa) | 28 day (MPa) |
|------|-------------|-------------|-------------|--------------|
| 32.5p0.3 | 24.00 | 44.20 | 55.00 | 66.80 |
| 32.5p0.35 | 11.00 | 29.00 | 39.00 | 52.00 |
| 32.5p0.4 | 9.50 | 22.00 | 30.00 | 46.20 |

The previous simple computer illustration emphasizes the importance of w/c on porosity, in which strength depends on. Hydrates-to-pores ratio or gel-to-space ratio is a function of w/c ratio, while cement compressive strength is a function of porosity [44].

In cement paste the porosity is changed through cement hydration. Thus, it is plausible to develop a relationship between compressive strength and electrical resistivity since both parameters are related to capillary porosity. Simple linear regression was used to build the empirical correlation as in Figure 9 and Eq.6.

\[
f_{c(28)} = 7.16 \rho_{72h} - 7.14, \quad R^2 = 0.98
\]

Where \( f_{c(28)} \) = cement paste compressive strength at 28d, \( \rho_{72h} \) = electrical resistivity measurements of cement paste at 72h.
Thereby, electrical resistivity measurements is worthwhile method to investigate the strength properties of cement.

3.4. Setting Time

Table 3 lists the results of cement pastes setting time that were determined using the Vicat needle. The results show that both initial and final setting times are shorter with lower w/c ratio pastes. As mentioned in computer modelling section, the spaces between particles are shorter and hydrates can collide faster. It was mentioned also through computer illustrations that the percentage of connected solids is higher with lower w/c ratio, due to denser microstructure per square unit comparing with higher w/c ratio paste. Setting time can be explained as a percolation theory [11], when solid percolates into the empty spaces and connected the isolated clusters into a connected network. It is believed that setting initially occurred when hydrates start overlapping each other [12]. Figure 10 is an illustration which demonstrates the theory in more obvious manner. The illustration shows that there are two systems, each system includes two cement particles with same size and same degree of hydration but have different initial distances. The shorter the distance takes place with the lower w/c ratio paste. Each cycle represents 10 percent of cement particle hydration, and it can be seen that cement particles with low w/c ratio takes only few cycles to overlap each other by outer hydrates expansion. On other hand, the particles with higher w/c ratio, have longer distance and they need about 10 cycles to reach the overlapping.

![Figure 10. Cement particles overlapping by computer modelling](image)
Table 3. Cement pastes setting time by Vicat needle

| Code     | Initial setting time (hour) | Final setting time (hour) |
|----------|----------------------------|--------------------------|
| 32.5p0.3 | 3.97                       | 5.31                     |
| 32.5p0.35| 4.48                       | 5.60                     |
| 32.5p0.4 | 5.10                       | 6.40                     |

By increasing the percentage of connected solids, the paste will gain strength rapidly and transform from viscous fluid to rigid material. The solidification process of cement can be observed and determined by monitoring the rate of cement paste electrical resistivity development. As it mentioned in electrical resistivity development, mainly three critical points were detected on the rate curve. The second critical point (P₁) coincides with paste setting time as it shows in Table 4.

The second and third critical points on the rate curve are indicators for hydrates percolation into the water-filled spaces during the reaction, the faster the rate of reaction the shorter time for critical points to occur. With different w/c ratio pastes, the capillary porosity dominates the strength gain rate and early ages properties.

Table 4. Cement pastes setting time by Vicat needle

| Code     | Initial setting time (hour) | Final setting time (hour) | P₁ time on electrical resistivity rate curve (hour) |
|----------|----------------------------|--------------------------|-----------------------------------------------|
| 32.5p0.3 | 3.97                       | 5.31                     | 6.00                                           |
| 32.5p0.35| 4.48                       | 5.60                     | 6.80                                           |
| 32.5p0.4 | 5.10                       | 6.40                     | 7.00                                           |

3.5. Liquid Electrical Resistivity

Figure 11 shows the results of liquid electrical resistivity measurements for the three cement pastes up to 180 min. The higher w/c ratio paste has higher electrical resistivity measurements, contradicting the trend of bulk electrical resistivity measurements. As it mentioned previously in this study, cement paste is two components material which consists of liquid part and solid part. By extracting the liquid from the paste and measuring its electrical resistivity, the measurements can be determined by number, mobility, and concentration of ions in the solution. Thereby, it can be easily concluded that lower w/c ratio paste solution has more number of conductive ions, favoring higher electrical conductivity comparing to high w/c ratio paste. On the other hand, ion concentration is related to the chemical composition of cement, and since same kind of cement is being used in this study, then w/c ratio has further effect on liquid electrical resistivity as well as ionic concentration. Higher number of cement particles per square unit area, and the constrained spaces between particles in low w/c ratio paste will increase the solution ionic concentration and lowering the liquid electrical resistivity.

Through observing the early trend of bulk electrical resistivity measurement in Figure 4 (a), it can be noticed that lower w/c ratio paste has always higher electrical resistivity. Thus, it can be concluded that capillary porosity of cement paste has the dominated effect on the development process of cement electrical resistivity at all ages.

3.6. Autogenous Shrinkage

Figure 12 shows the results of cement pastes autogenous shrinkage after 24h of mixing and up to 8 days. The figure shows that low w/c ratio paste has higher autogenous shrinkage at 192h. The lower the w/c ratio the higher the shrinkage. The mechanism of autogenous shrinkage is numerous [45,46,47,48], on the other hand the capillary tension theory is among the most suitable theory which explicates the phenomena using pore structure, relative humidity, self-stress, degree of hydration and interface structure [47].

This study is focusing on the effect of water to cement ratio, and theoretically speaking, w/c ratio has direct effect on capillary porosity of cement paste. Thus, porosity effect on autogenous shrinkage is dominant in this study.

Figure 11. Liquid electrical resistivity vs. time
By reducing the connectivity of the capillary pores, increasing the percentage of fine pore (5-50 nm) the autogenous shrinkage will increase [48]. The pore structure represented by pores size and connectivity, affects the autogenous shrinkage measurements of cement pastes. The relative humidity which is one of main factor influences the autogenous shrinkage was observed to drop rapidly with lower water to cement ratio paste [49]. The rapid dis-connectivity of capillary pores with low w/c ratio paste due to denser microstructure, will block the migration of free water from saturated to unsaturated pores, consuming the paste moisture and dropping the internal relative humidity, accelerating the self-desiccation. The refinement of pore structure through low w/c ratio will promote the capillary stress by increasing the surface tension of liquid water. By increasing the capillary stress which equals to degree of saturation and capillary pressure that occurred due to consumption of water through hydration, creating voids that can’t be replaced by hydrates, will activate the autogenous shrinkage. Mainly, lower w/c ratio increases the percentage of finer pores and this will increase the self-desiccation and subsequently the autogenous shrinkage. The lower the w/c ratio the higher the rate of self-desiccation. Since electrical resistivity is capillary porosity dependent as it emphasised in this study, electrical resistivity measurements can be used as a tool to predict the autogenous shrinkage of cement paste. Empirical correlation can be developed between the two parameters to determine the autogenous shrinkage by measuring the electrical resistivity of cement paste as in Eq.7, Figure 13

\[ \varepsilon_{92h} = 99.3 \rho_{92h} - 324.7, R^2 = 0.98 \]  

Through hydration and the continuous consumption of water by reaction, adsorption, and evaporation, the paste moisture will drop, creating more empty pores that are disconnected by hydration products. The disconnected finer pores increase both electrical resistivity and autogenous shrinkage. Lower w/c ratio increases the self-desiccation and electrical resistivity development of cement paste.

![Figure 12. Autogenous shrinkage of cement pastes vs. time](image)

![Figure 13. Autogenous shrinkage and electrical resistivity correlation](image)
Figure 14(a-b). SEM pictures for cement pastes with different w/c ratio at 1, 3, 7, 28 days at 30µm magnification.
3.7. SEM Observation

The effect of water to cement ratio on the morphology of hydrates was considered in this study. The microstructure of the three cement pastes with different w/c ratio was investigated using scanning electron microscopy at (30µm) magnification as in Figure 14. Water to cement ratio is one of the factors that affects the morphology of C-S-H beside others like curing temperature, degree of hydration, admixtures and cement chemical composition [50]. The morphology of C-S-H mainly changes with hydration time and the spaces for C-S-H growth. Through hydration time the morphology of C-S-H changes from flak-like structure to fiber/needle like. With adequate spaces available for C-S-H to grow, the morphology is more likely to be fibrous, while with constrained spaces, the C-S-H becomes honeycomb or foil-like structure [50]. These observations emphasise the importance of water to cement ratio on the morphology of C-S-H.

It was reported that high w/c ratio specimen has more fibrous C-S-H morphologies per unit area comparing to low w/c ratio, when high amount of water on the surface provides more spaces for fibers to grow [50]. The large spaces between cement particles with higher amount of water will influence the growth of C-S-H, when less impingement is occurred due to longer distance between adjacent particles. More dark points can be observed with 32.5p0.4 paste which refers to the pores in which that was less observed with other pastes.

Specimens with lower w/c ratio have more unreacted cement particles, due to the lack of water, resulting in coarser medium and denser microstructural. Figure 15 is SEM pictures for the three cement pastes at 28d with 5µm magnification. More fibers can be observed with 0.35 and 0.4 comparing to 0.3, due to higher amount of water, allowing longer spaces for fibers to expand. The distances between cement particles which determine by w/c ratio control the densification rate of the matrix. The lower the w/c ratio the faster the densification of hydrates. The higher the w/c ratio the faster for hydrates to expand due to more available spaces, but the slower the densification rate. It was reported that C-S-H with higher w/c ratio grows in in a lengthened manner, and the greater is the w/c ratio, the more elongated is the C-S-H gel [51].
4. Conclusion

The effect of water-to-cement on the microstructural development of cement paste was demonstrated in this study through measuring the electrical resistivity of cement. The w/c ratio fundamentally determines the initial distances between cement particles, affecting the early age properties of cement paste like setting time and compressive strength. The lower the w/c ratio paste has always higher electrical resistivity measurements over hydration time, despite having lower liquid electrical resistivity. A computer program was used as a tool to illustrate the influence of the constrained spaces of low w/c ratio pastes and large spaces of high w/c ratio pastes. Empirical correlation was built between electrical resistivity and compressive strength when both are capillary porosity dependent, the higher the electrical resistivity of cement paste the higher the compressive strength. Setting time was assessed based on the critical points of the resistivity rate curve, the critical points shift to shorted time with lower w/c pastes due to faster rate of hydrates impingement with shorter distance between the particles. Empirical correlation was built between electrical resistivity and autogenous shrinkage when both parameters are related to pore structure and internal relative humidity. SEM was used to investigate the effect of w/c ratio on the morphology of hydration products. With 5µm magnification, it was observed that higher w/c ratio paste has higher percentage of fibers per unite area than lower w/c ratio due to larger spaces between particles, making the hydrates grow in lengthened manner. Thus, the thickening rate is faster with higher w/c ratio but the densification rate is lower comparing with low w/c ratio pastes.

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