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Microstructure of Concrete

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Abstract

Concrete is a composite material that consists of a binding medium and aggregate particles and can be formed in several types. It may be considered to consist of three phases: a cement paste, the aggregate, and the interfacial transition zone (ITZ) between them. In addition to ordinary Portland cement, the essential components of the base of concrete are aggregates and water. For practical requirements, additives and admixtures can be added to these raw materials to improve some desirable characteristics. The following requirements should be considered in producing high performance concrete (HPC): (i) low water/cement (w/c) ratio; (ii) fine aggregate; (iii) large quantity of mineral additives, silica fume, and fly ash; (iv) high dosage of superplasticizer; and (v) high-pressure steam curing. The microstructure of high performance concrete (HPC) is more homogenous than that of normal concrete (NC) due to the physical and chemical contribution of the additives (silica fume and fly ash) as well as it is less porous due to reduced w/c ratio with the addition of a superplasticizer. Inclusion of additives (individually or in combination) helped in improving the strength and durability of concrete mixes due to the additional reduction in porosity of cement paste and an improved interface between it and the aggregate.

Keywords: concrete, mineral additives, microstructure, strength, durability

1. Introduction

Concrete is a construction material that is extensively used because of its excellent properties such as durability, workability, satisfactory strength, and the easy availability of raw materials (cement, aggregates, and water), which are used to produce it [1].

By definition, concrete is a composite material that consists of a binding medium and aggregate particles and can be formed in several types [2]. It may be considered to consist of three phases:

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© 2016 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. a cement paste, the aggregate, and the interfacial transition zone (ITZ) between them [3]. Concrete is a heterogeneous substance. On a macroscopic scale, it is a mixture of cement paste and aggregates, whereas on a microscopic scale, the cement paste itself consists of unreacted cement grains, amorphous hydration products (crystals of calcium hydroxide, needles of ettringite, and fibrous crystals of calcium silicate hydrate), and pores [4] (see **Figure 1**).



Figure 1. Left: polished section of concrete specimen. Right: microstructure of a hydrated cement paste [1].

Concrete with superior properties such as high compressive strength and excellent durability can be produced by taking into account the following: (i) optimizing particle size distribution to obtain high density; (ii) using water reducer agents to reduce water/cement (w/c) ratio; (iii) adding pozzolanic admixtures to improve rheological properties, fill voids, and form additional calcium silicate hydrate; and (iv) preventing brittle failure to include steel fibers [5].

	Regular (plain)	High strength	Very high strength	
Compressive strength (MPa)	<50	50-100	100–150	
Water/cement ratio	>0.45	0.30-0.45	0.25–0.30	
Chemical admixtures	Not required	Superplasticizer	Superplasticizer	
Mineral admixtures	Not required	Fly ash	Silica fume	
Permeability (m/s)	>10 ⁻¹²	10-13	<10 ⁻¹⁴	

Table 1. Characteristics of concrete mixes in terms of strength and permeability [6].

To produce a concrete with specific requirements such as high performance concrete (HPC), additives and admixtures should be added to raw materials of normal concrete to improve some properties by pozzolanic and physical actions. The pozzolanic reactions resulted in changes in pore structure caused by the reduction in the grain size, while the obstruction of pores and voids by the finer grains is called the physical or filer effect. This means that the enhancement of paste microstructure caused by not only the pozzolanic reactions but also the filler effect of the finer particles. These two effects improve the concrete microstructure by making it denser, more homogeneous, and uniform, leading to enhance its properties such as strength and durability compared to the plain mix (see **Table 1**). Porosity of cement paste has a significant effect on the strength of concrete, while its permeability has affected by the pore structure and pore connectivity. Usually, a high permeability indicates a low durability and vice versa.

To achieve high strength and good durability requirements (prevent a concrete deterioration, see **Figure 2**) [7], reducing the capillary porosity and also a substantial reduction in the total porosity should be achieved by reducing the gel porosity as well. This leads to change the C-S-H structure from porous to more crystalline phase, i.e., change in concrete microstructure. It is well known that the microstructure of concrete (cementitious paste, pore structure, and interfacial transition zone between the cement paste and the aggregate) has a significant role in effecting its properties such as strength and durability due to controlling the porosity, permeability, and pore size distribution. Therefore, understanding how performance of concrete links to its microstructure is important.



Figure 2. Deterioration of normal concrete [7].

2. Microstructure investigation methods

Mercury intrusion porosimetry, light optical microscopy with an associated digital image analysis, scanning electron microscopy, and X-ray computed tomography with image processing were, in addition to others, methods suited to examining concrete samples.

2.1. Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry characterizes a material porosity by applying a pressure to a sample immersed in mercury. The size of the accessible pores that will be filled by mercury is inversely proportional to the pressure applied. For each externally applied pressure, the pore diameter (mercury-pore space interface) is determined by the Washburn equation:



where P_c is the capillary pressure, ρ is the surface tension, θ is the contact angle, and *d* is the diameter of the pore space [8]. See **Figure 3** as presented in Ref. [9].



Figure 3. Left: different angles of contact for wetting and non-wetting liquids. Right: mercury (not-wetting liquid) does not penetrate pores by capillary, but it must be forced into them by the application of external pressure [9].

In a review of mercury porosimetry (MIP), Diamond [10] concluded that this technique is an inappropriate method for the measurement of pore size distributions in cement-based materials. However, he added that MIP measurements are useful to provide threshold diameters and intrudable pore volume, which may be helpful as comparative indices of the cement paste or concrete pores. This is because the Washburn equation is applicable to a pore system characterized by percolative chains with ever finer pores at each step from the surface to the middle of sample (**Figure 4a**). From this figure, the larger pore (open to the exterior) fills with mercury at pressure P_1 , whereas the smaller pore (open to the large pore) will not fill until a higher pressure P_2 , corresponding to its smaller diameter, is reached.

In a hydrated cement system, a pore structure illustrated in **Figure 4b** is likely to occur leading to mistakenly allocating a large pore and the diameter of a small pore at high pressure step P_2 . Therefore, the MIP technique was used in this project to determine the total porosity, the



Figure 4. (a) A small cylindrical pore connected to the exterior of a specimen through a large cylindrical pore (MIP model is applicable). **(b)** A large cylindrical pore connected to the exterior of a specimen through a small cylindrical pore (the large diameter pore will not be detected) [10].

characteristic length (l_c), and the conductivity factor of the selected mixes not to investigate the pore size distribution of them.

2.2. Optical microscopy (OM)

Optical and electron microscopies are the two principle microscopy techniques widely used for studying cementitious materials. An optical microscope uses normal (visible) light and a system of lenses to magnify images of small samples. It has been extensively used for studying cementitious materials due to its easy use and rapid operation. However, the main limitation of this technique is the resolution [11].

2.3. Scanning electron microscopy (SEM)

In general, the SEM consists of an electron gun, condenser lenses (to de-magnify the electron beam), objective lenses (to focus the probe onto the specimen surface), a control system for the beam movement, platform for specimen, electron detector, signal amplifier, and display unit [11]. The SEM principle can be described briefly as follows: when the electron beam (primary electrons) hits the specimen surface, it may elastically change its direction with no loss of energy (elastic scattering process), or a detectable amount of the primary electron energy may be absorbed resulting in most of the primary electrons being stopped while a few of them are

backscattered (inelastic scattering process). In general, these processes produce other types of electrons, which are useful for the materials analysis, as shown in **Figure 5** [11].



Figure 5. Left: the results of interaction of electron beam with specimen. Right: the interaction volume and the regions of the various signals that may be detected after [11].

In the elastic scattering process, most of the primary electrons will stop in the specimen forming a volume of a tear drop shape below the specimen surface known as the interaction volume, which affects the lateral resolution of the image produced from each signal. The depth and shape of the interaction volume depend on both the average atomic number of the sample and the accelerating voltage. The secondary electrons (SE) are used to describe those having energy less than about 50 eV (electron volts). Being close to the specimen surface, they will be able to leave the specimen giving information about the first very thin layer below the surface. Thus, they are very useful for investigating the topography of the material surface. For this reason, the secondary electron (SE) mode uses to qualify, analyze, and investigate the microstructure of concrete mixes.

Backscattered electrons (BSEs) are primary electrons leaving the specimen surface with energy greater than 50 eV (from 50 eV to that of the primary electrons). Compared to secondary electrons, they have very high energy. The BSE mode, in combination with the ImageJ software, uses to perform quantitative image analysis of the void structure and the ITZ of concrete mixes.

2.4. Micro-computed tomography (µCT)

A μ CT scanner consists of a source for the X-ray beam with a collimator. The beam is transmitted through the sample and then detected by a detector, as shown in **Figure 6**. This technique utilizes the ability of X-rays, which are produced by accelerated electrons striking the X-ray tube target (e.g. tungsten), to penetrate objects and measures the intensity before and after passing through the objects. Its principle is as follows: when an X-ray beam passes through a sample, some of the X-ray radiation is absorbed and scattered (with intensity I_o),



Figure 6. The key components of μ CT scanner [13].

while the rest penetrates through the sample (with intensity *I*) (see **Figure 7**). The amount of penetration depends on the X-rays' energy, molecule atomic number, and the density and thickness of the object. Depending on the material density, the amount of absorption is a function of the linear attenuation coefficient (L_{att}) at each point. The denser the material, the more the absorbed radiation. The L_{att} can be expressed as L_{att} (x, y), where x and y are the Cartesian coordinates of the locations within the scanned section. The raw data of a series of intensity measurements, at different orientations around the sample, are converted to form a 2-D slice image by a mathematical process within the software indicating the different internal features and their distribution within the scanned section. Depending on the differences in density within the scanned object, the image consists of a range in the gray spectrum [0 (black) to 255 (white) for an eight-bit image]. Within the composite material, the higher the difference in component densities, the better the identification and distinguishing between them. Finally, the 2-D images may be converted to a three-dimensional (3-D) image to observe the location of voids, defects, or inclusions without sectioning the sample, i.e., allowing the three-dimensional internal structure of a specimen to be determined non-destructively [12].

2.5. Vacuum saturation method

Total porosity of concrete samples can be determined using a vacuum saturation approach, in which porosity measurements are conducted on dry samples (dried at $100 \pm 5^{\circ}$ C until a constant weight) that placed in a desiccator under vacuum for at least 3 hours. After that, the desiccator is filled with de-ionized water to 30 mm above the samples and left under a vacuum pump for another 3 hours. Then, the samples are remained under water overnight. Finally, the samples are weighed in air and water to calculate their total (vacuum determined) porosity from Eq. (2), assuming them to now be fully saturated.



Figure 7. Intensity distribution in X-ray tomography after [14].

$$\phi_T = \frac{W_{s,a} - W_{dry}}{W_{s,a} - W_{s,w}} \times 100$$
(2)

where ϕ_T is the total porosity (%), $W_{s,a}$ is the weight of a saturated sample in air, $W_{s,w}$ is the weight of the saturated sample in water, and W_{dry} is the weight of the oven-dried sample.

Table 2 illustrates the limitations of the above methods used in investigating the concrete microstructure in terms of pore size distribution, pore volume (porosity), and pore connectivity.

Method	Pore range	Image processing	2-Dimention	3-Dimention	Gel pores (<10 nm)	Capillary pores (10nm-10µm)	Entrapped pores (>10 µm)	Pore size distribution	Pore volume (porosity)	Pore connectivity
MIP	4nm-400µm			٧	V	V		٧	V	٧
ом	>10 µm	1	1				٧	V	٧	
SEM	>1 nm	1	1		V	V		٧	1	
μСТ	>10 µm	1	1	٧			٧	1	1	٧
Vac. Satu.	accessible pores			٧	1	V	۷		V	

Table 2. The limitations of microstructure investigation methods.

3. Microstructure of concrete

Concrete has a heterogeneous microstructure, which consists of three components, namely, cement paste, pore structure, and interfacial transition zone between the cement paste and aggregates. Improving these three components leads to enhance mechanical strength and durability of concrete.

3.1. Cementitious binder

Cement mainly consists of silica (SiO_2) or (S), alumina (Al_2O_3) or (A), lime (CaO) or (C), and iron oxide (Fe_2O_3) or (F). The main compounds of ordinary Portland cement are tri-calcium silicate (C_3S) , di-calcium silicate (C_2S) , tri-calcium aluminate (C_3A) , and tetra-calcium aluminoferrite (C_4AF) .

The main phases present in hydrated cement paste microstructure can be listed as follows: (i) calcium silicate hydrate (C-S-H); (ii) calcium hydroxide (CH); (iii) ettringite; (iv) monosulfate; (v) unhydrated (UH) cement particles; and (vi) air voids [1].

In addition to ordinary Portland cement, the essential components of the base of concrete are aggregate and water. For practical requirements, additives with various particle sizes and specific surface areas can be added to the raw materials to improve some desirable characteristics of the final product. **Figure 8** represents the raw materials of concrete and some supplementary additives in terms of their particle size and specific surface area [15].



Figure 8. Raw materials of concrete and some supplementary additives [15].

Cement is the most commonly used binder; however, other supplementary materials can also be used. The most available supplementary cementing materials are silica fume, a by-product of the reduction in high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys, and fly ash, a by-product of the burning of coal in thermal power stations [16]. **Figure 9** shows that the particles in a typical fly ash vary from <1 μ m to about 100 μ m in diameter with more than 50% by mass less than 10 μ m. In addition, compared to Portland cement and fly ash, silica fume shows finer particle size distribution by two orders of magnitude with a mean particle diameter of about 0.1 μ m.



Figure 9. Particle size distribution of cement, fly ash, and silica [1].

Superplasticizers and water-reducing admixtures are important to increase the strength, which were developed in the 1970s and have found wide acceptance in the concrete construction industry. The surfactant imparts a strong negative charge when adsorbed on cement particles, which leads to lower the surface tension of the surrounding water and greatly improves the fluidity of the system [1]. The mechanism of action is shown in **Figure 10** and can be summarized as follows: when the cement particles (which have a mixture of positive and negative charges) are mixed with water, they coalesce into flocks resulting in trapping a considerable amount of mixing water and therefore reducing the fluidity. To solve this, adding the superplasticizer (which constitutes a negative ionic group) will form a negative charge on the cement

particles after adsorbing onto them. Now, the cement particles repel each other and become more dispersed, releasing the trapped water and increasing the fluidity [17].



Figure 10. Diagrammatic representation of plasticizers' action [17].

3.2. Pore structure

It is well known that the pore structure of cementitious material is a significant characteristic because it affects properties such as strength and durability due to their dependence on material porosity, permeability, and pore size distribution [18]. The typical sizes of the voids in hydrated cement paste are shown in **Figure 11**.



Figure 11. Dimensional range of pores in a hydrated cement paste [1].

Just and Middendorf [19] stated that by using low w/c ratio and adding microsilica, density increases and the average air voids' diameter decreases. Furthermore, decreasing the diameter of the pores may lead to regularly formed air voids, resulting in increasing compressive strength for the same densities. Therefore, understanding the pore parameters is important for producing a product with a high strength to weight ratio and good properties.

3.3. Interfacial transition zone (ITZ)

Concrete may be considered to consist of three phases: a cement paste, the aggregate, and the interfacial transition zone (ITZ) between them. In the ITZ, the structure of the cement paste is different from that of the bulk paste in terms of morphology, composition, and density. Compared to the bulk paste, the ITZ has less unhydrated cement, less C-S-H, large crystals of calcium hydroxide, greater concentration of ettringite, and higher porosity (lower density) [20]. As in the bulk paste, calcium, sulfate, hydroxyl, and aluminate ions are produced by the dissolution of calcium sulfate and calcium aluminate compounds. These ions combine to form ettringite and calcium hydroxide, which, due to the high w/c ratio, become larger in the vicinity of the aggregate resulting in more porous framework than in the bulk cement paste or unfoamed matrix [1]. The microstructure of an interfacial transition zone in concrete is presented schematically in **Figure 12**.



Figure 12. Schematic diagram of ITZ in concrete [1].

Quantitative characterization of the ITZ between the aggregate and the cement paste in concrete confirms that it arises due to the packing of cement grains (1–100 μ m) against the larger aggregate particles. In other words, this difference in size means that each aggregate particle is a mini "wall," disrupting the normal packing of the cement grains and leading to accumulation of smaller grains in the zone close to the aggregate while larger grains are found further out (see **Figure 13**). This packing leads to a more porous zone, and the deposition of hydration products, especially calcium hydroxide, tends to fill this zone [21].



Figure 13. Schematic diagram showing "wall" effect of aggregate: (A) imaginary case and (B) reliable case [21].



Figure 14. Effects of the ITZ on mechanical properties of concrete [21].

The ITZ, about 50 µm thick, plays a role in the stiffness, strength, and permeability of cementitious materials containing aggregate due to its generally lower density and strength compared to bulk cement paste. When the material is subjected to loads, microcracks may appear within the ITZ due to its weakness leading to the quasi-brittle nature of concrete [22] (see **Figure 14**). This explains the phenomenon that the components of concrete (aggregates and hydrated cement paste) usually remain elastic until failure during a uniaxial compression test, while concrete shows inelastic behavior at levels higher than 70% of ultimate strength [1].

The quality of the bond between the paste matrix and aggregates is influenced by the shape, size, mineral composition, surface roughness, surface moisture content, and porosity of aggregates as well as water/cement ratio [22].

In a study on the effect of water/cement (w/c) ratio, aggregate size, and age on the microstructure of the interfacial transition zone between the normal weight aggregate and the bulk cement paste, it was concluded that the w/c ratio plays an important role in controlling the microstructure of the ITZ and its thickness. In addition, at the same w/c ratio and age, reducing the aggregate size tends to reduce the porosity and increase the content of unhydrated (UH) particles in the region surrounding the aggregate. Moreover, at the same w/c ratio (0.55), they reported that the ITZ is more porous compared to the bulk paste at 180 days than at 7 days due to deficiency of UH content in the ITZ compared to bulk paste at an early age [23].

4. Microstructure of high performance concrete

The following requirements should be considered in producing HPC: (i) low w/c ratio; (ii) fine aggregate; (iii) large quantity of mineral additives, silica fume and fly ash; (iv) high dosage of superplasticizer; and (v) high-pressure steam curing [6].

It should be noted here that before discussing the factors influencing some of the important engineering properties of concrete, strength, and durability, an understanding of the essential features of its microstructure would be helpful.



Figure 15. Microstructure of high performance concrete: C-S-H gel becomes denser with dense ettringites in the form of pike and flower [24].

The type, size, amount, shape, and distribution of phases in a solid constitute its microstructure at a microlevel. The microstructure of concrete can be described in the following three aspects: (i) hydrated cement paste, which represents the hydration products of cement and water reaction, and the main product of this reaction is the calcium silicate hydrate (C-S-H) gel; (ii) pore structure, which refers to the gel pores, capillary pores, and voids; and (iii) interfacial transition zone (ITZ), which represents the boundaries between the cement paste and the aggregate particles [6].

It was suggested that C-S-H exhibited from different microscopic shapes: (a) needle shape crystals with a size of 0.5–2 μ m long and <0.2 μ m wide; (b) plate-like crystals; (c) irregular hexagonal panel crystals; and (d) dense C-S-H paste (see **Figure 15**) [24].

In terms of the volume of capillary voids in the hydrated cement paste, it decreases with deceasing the w/c ratio or with increasing the age of hydration. Moreover, in the presence of aggregate, the microstructure of hydrated cement paste in the vicinity of large aggregate particles (ITZ) is usually very different from that of bulk paste or mortar in the concrete. This ITZ is the weakest region in concrete due to its higher porosity resulting from the poor packing of cement particles [1].

To improve the concrete performance, the following three aspects should be considered [6]:

- Strengthening the hydrated cement paste: this can be achieved by adding the mineral additives, which help in generating a crystalline C-S-H gel with lower gel porosity, compared to a conventional amorphous C-S-H gel, resulting in reducing the gel porosity in addition to the reduction in capillary porosity.
- Lowering the porosity: this can be achieved by filling the empty spaces in cement paste, resulting in lowering the pore connectivity as well and then reducing the total paste porosity.
- Toughening the ITZ: this can be done by using a superplasticizer to reduce the w/c ratio and improving the particle packing in this zone by adding the mineral admixture.

In addition to the microstructure evolution, chemical changes, and attention should be paid to the rheological properties of freshly mixed cement paste. This is due to the flocs phenomena, which causes from entrapping large quantities of mixing water by anhydrous particles of cement. Thus, the resulted microstructure of high performance concrete, the crystalline products of hydration, and the volume, size, and shape of pores would be different compared to the traditional concrete [1].

Compared to a traditional concrete, the addition of silica fume and fly ash leads to reduce the pore proportion in the enlarged ITZ, reduced CH crystals and ettringites, as well as with this addition, a denser C-S-H gel has been noticed [6]. **Figure 16** displays the hydrated cementitious products in cement mortars, impregnated with nano silica, silica fume, and fly ash [25]. From this figure, it was observed that small and large crystals are dispersed in the ordinary Portland mix and sometimes in fly ash and silica fume mixes. While, compared to these three mixes, the texture of the hydration products of nano silica mix is denser and more compact without large crystals of CH.



Figure 16. SEM images of the mortar specimens after 28 days of curing: (a) ordinary Portland cement (control group), magnification ×5000; (b) nano silica, magnification ×15,000; (c) silica fume, magnification ×5000; and (d) fly ash 10, magnification ×5000 [25].

From the above information, it can be concluded that the microstructure of high performance concrete (HPC) is more homogenous than that of normal concrete (NC) due to the physical and chemical contribution of the additives (SF and FA) as well as being less porous due to reduced w/c ratio with the addition of a superplasticizer. As concrete has a highly heterogeneous and complex microstructure, it is very difficult to reliably predict its behavior from constituting realistic models of its microstructure. However, knowledge of the microstructure of concrete and its relationships to the material properties is useful for enhancing these properties.

5. Effect of microstructure on strength and durability

High performance concrete (HPC) consists of cement, water, fine sand, superplasticizer, fly ash, and silica fume. Additionally, to have ultrastrength and ultraductility, quartz flour and fiber may be added, respectively [6].

It is important to understand how concrete performance is linked to its microstructure.

The main source of strength in concrete is the adhesion between the solid products of hydrated cement paste. This adhesion can be attributed to the van der Waals forces of attraction with a degree of adhesive depends on the extent and the nature of the solid surfaces involved. Some of hydrated products, such as C-S-H crystals, calcium sulfoaluminate hydrates, and hexagonal calcium aluminate hydrates, possess vast surface areas and adhesive capability. Therefore, they tend to adhere strongly to each other and at the same time to solids with low surface areas such as lime, anhydrous cement particles, and aggregate particles (fine and coarse) [1].

When fly ash (amorphous alumina silicate with varying amount of calcium) is added to concrete mixture and in the presence of cement and water, products of pozzolanic reaction, between the silica glass (SiO₂) in the fly ash composition and the calcium hydroxide (Ca(OH)₂), which released by the hydration of cement, fill the interstitial pores reducing the pore connectivity and then the microstructure porosity. In addition, in the absence of a source of calcium hydroxide, some fly ash will display cementitious behavior. Thus, more C-S-H will produce by a reaction between this fly ash, with higher amount of calcium, and water (see **Figure 17**) [26].



Figure 17. Left: hydration products of Portland cement; middle: lime is formed a by-product of hydration; right: the pozzolanic reaction products fill the interstitial spaces [26].

Depending on the type of mix, cement type, silica fume amount, use of water reducer agents, aggregate type, and curing regimes, the addition of silica fume to a concrete mix will increase its strength by between 30 and 100% of that of the conventional mix [26]. This strength enhancement is due to a reaction of C-S-H gel formed by conventional hydration, with the silica fume at high temperature, which forms a dense phase crystalline hydrate resulting in enhancing the aggregates-cement interfaces and improving the strength. Additionally, it is found that the silica fume, in combination with superplasticizer, improved the bonding between the paste and the aggregate due to the formation of dense microstructure in the ITZ. It was suggested that the addition of water-reducing agent can help increase the density of the microstructure, by reducing its porosity, and thus improve the properties of concrete [6].

As the various phases in the hydrated cement paste are neither uniformly distributed nor uniform in size and morphology (microstructural inhomogeneity), series effects on mechanical properties and durability can be raised.



Figure 18. Hydration, pozzolanic, and filler effects of cementitious pastes with silica fume [28].

To achieve the high strength requirements (generally higher than 50 MPa), only reducing the capillary porosity is not enough, but also a substantial reduction in the total porosity should be achieved by reducing the gel porosity. This substantial porosity reduction is required to change the C-S-H structure from porous to more crystalline phase, i.e., change in concrete microstructure [6].

When added to the cement paste, pozzolanic materials play an important role leading to enhance the mechanical and durability properties. The most important effect on microstructure is the change in pore structure by the reduction in the grain size, which resulted, chemically, from the pozzolanic reactions (pozzolanic effect) and, physically, from the obstruction of pores by the action of the finer grains (filler effect) [27]. **Figure 18** shows the pozzolanic, physical, and hydration effects of cement pastes with silica fume [28].

Relative comparisons between the pozzolanic and the filler effects of concrete mixes are shown in **Figure 19**. On average, from this figure, it can be seen that, at higher age (91 days), the pozzolanic effect was more significant in the lower strength (35 MPa), whereas the filler effect was more effective in the higher strength (65 MPa). However, at both 28 and 91 days, the physical effect exceeded that of Pozzolan for mixture containing 50% Pozzolan and with 65 MPa strength. In general, from the findings, it was observed that the pozzolanic and physical effects have increased as the mineral addition increased. Meanwhile, for the same strength value, the filler effect was higher than that of Pozzolan.



Figure 19. Total, filler, and pozzolanic effect performance indexes related to reference concrete (**a**) at 28 and 91 days and (**b**) 35 and 65 MPa strength levels [27].



Figure 20. Influence of water/cement ratio and degree of hydration on permeability and strength [1].

In term of durability, it is well known that durability problems of concrete are related to its resistance to water and chemical ion penetration. The liquid penetration may lead to steel reinforcement corrosion, alkaline-silica reaction, and freeze-thaw damage. Therefore, a key factor influencing the durability of concrete is its permeability, which is primarily related to pore structure of cement paste in terms of pore size, volume, and connectivity. Since that the prestructure is a function of the water/cement ratio and the degree of hydration, the permeability is a function of them as well [6] (see **Figure 20**), and it is noted that the shaded area represents the typical capillary porosity range in hydrated cement paste.

It was discussed that the ITZ is a weakest zone, which is strengthened and being less porous with the inclusion of mineral admixtures resulting in improving the concrete microstructure. This improvement, reducing porosity and pore connectivity, leads to reduce the permeability and finally improve the durability.

In summary, it can be seen from the above information that inclusion of additives (individually or in combination) helped in improving the strength and durability concrete. This is due to the additional reduction in porosity of cement paste and an improved interface between it and the aggregate by (i) a substantial reduction in mixing water (using a superplasticizer); (ii) forming calcium silicate hydrate (C-S-H) from a pozzolanic reaction of fly ash with the lime produced from the hydration of cement and water; and (iii) acting as fine filler (silica fume).

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