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Characterization of micro- and nano- modified cementitious system using micro analytical techniques

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ABSTRACT

The influence of incorporation of micro and nano sized particles such as fly ash, silica fume, nanosilica and nanoalumina on the hydrated cementitious system is studied. The transformation in the hydrated products due to these additions are analyzed using X ray diffraction and scanning electron microscopy. Further, transition in the pore structure owing to the formation of hydrated products are evaluated through nitrogen adsorption/desorption (NAD) technique method and image analysis. The pore structure is characterized by the total pore volume and pore size distribution using NAD method and pore area fraction from image analysis. It is found that the micro and nano additions do not always improve the microstructure by reducing the pores, sometimes (in case of addition of nano materials/silica fume) increase the size of the pores by pore widening phenomena. Neverthless, it is realized that the nano alumina addition helps in filling the pores only at later ages.

1. Introduction

The main properties of concrete such as strength and durability are affected by the constituents and proportion of the materials in the mix and degree of particle packing [1–4]. The dense particle packing achieved by incorporating different size of the particles influences the physico mechanical properties of concrete at fresh as well as hardened states. There are contradictory statements regarding the particle size distribution and its relation to mechanical and durability properties. It is reported that the reduction in particle size generally results in increased rate of hydration which in turn results in early high strength [1–4]. According to the reported literature [5,6], early age strength is varied between 1 and 28 days depending upon the type of additions used. However, in the study by Wang et al. [7] neither the formation of larger amount of hydration products nor high rate of hydration which leads to higher compressive strength was reported. But the porosity and pore size distribution which are affected by the packing density of cement paste [7] play a major role in strength achievement. Also it is reported that cement particles of size larger than 45 μm have good filling effect but are difficult to hydrate resulting in less strength development [8,9]. However, Mehta [10] reported that under durability considerations, coarser material behaves better than finer ones. It is evident that there is no generalized statement regarding the relationship between particle size and durability or strength improvement of cementitious system. In this study, to investigate the role of incorporation of various micro/nano materials with different fineness on pore size reduction, in this study, cement, fly ash, silica fume, nanosilica and nanoalumina having different median sizes are chosen. The advantage of physical and chemical properties of fly ash, silica fume, nanosilica and nanoalumina reported in literature are of importance and are briefly discussed.

1.1. Fly ash (FA)

The effect of fineness of fly ash (FA) on pore size and microstructure of hardened cement pastes are extensively discussed [11,12]. As FA possesses relatively smaller size particles compared to cement, it is capable of increasing the compressive strength of cement paste during early and later stages of hydration due to its efficient pore filling capacity during hydration. The hydration process of FA particles known as pozzolanic reaction is slower than that of cement grains and continues for years after reacting with pore solution [13–16] thus reducing the pores over a period of time.

1.2. Silica fume (SF)

Silica fume (SF) improves the bond between the paste and aggregate [17–19] because of its smaller size. Incorporation of SF

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in cement therefore improves the compressive strength of cement paste [20,21]. Moreover, silica fume reacts with calcium hydroxide to produce more calcium silicate hydrates and calcium aluminosilicate hydrates making the mix denser thus reducing the porosity [22]. High pozzolanic activity of silica fume is due to the presence of high content of amorphous silicon dioxide apart from its small spherical size [23].

1.3. Nanosilica and nanoalumina

One of the widely used nano materials in cementitious composite is nano silica (NS) and is reported [24,25] that nano silica increases the compressive strength and reduces the permeability. Nanosilica (NS) can act as extraordinary filler material to cement voids because of its high surface to volume ratio. The rate of cement hydration is highly dependent on the surface area of nanosilica, which acts as nucleation site for the precipitation of CSH-gel. The performance enhancing properties of nanosilica are due to dual actions: (i) filling capability of voids of micro size between the cement particles thus improving packing and creating a less permeable structure (ii) forming additional calcium silicate hydrate during hydration by reacting with portlandite [26]. Moreover, NS can provide large number of binding sites to free lime and salts which can prevent the formation of efflorescence effectively [27] which would cause the reduction of pores.

Nanoalumina is another nanosized material which can be employed in cement and concrete. It is reported that the addition of even small quantities of nanoalumina (nanosized particles of alumina, Al_2O_3) increases the mechanical properties of both ordinary portland and belite cement pastes [28,29]. However, it is reported that the addition of nanoalumina does not help in the improvement of pore reduction [28].

Hence, micro and nano additions used in cement act as a filler, would not only improve the physical structure, they also provide nucleation sites for hydration products and altering the microstructure of cement. The unique physical and chemical properties of individual materials used in this study contribute to the pore filling effect owing to their size and pozzolanic activity.

In cementitious material, the study of distribution of pores is complicated because of the continuous transformation of pore structure during different stages of curing as a result of alteration in the formed hydration products. Moreover, during hydration the complexity is attributed to the presence of broad variation in the size of pores ranging from micro ($\leqslant$2 nm) to meso (2–50 nm) pores according to IUPAC classification [30]. Pores of size greater than 10 μm are likely to affect properties such as compressive strength [31,32] and permeability characteristics and hence pores of these sizes are of importance in pore structure analysis. There are many experimental techniques available to study and measure the pore structure. The most widely used methods include the mercury intrusion porosimetry (MIP) and nitrogen adsorption/desorption (NAD). The interpretation of MIP is misleading because, unless a break-through pressure is attained mercury cannot enter the interior pore space. Hence, the pore size found from MIP measurement is finer than the reality [33]. On the otherhand, it is observed in adsorption method that the value measured with nitrogen adsorption is lesser than that measured with water vapor. This difference in measurement is justified as the nitrogen molecules are bigger than water molecules and are excluded from pores with small openings [34].

1.4. Review of pore structure models

To improve the understanding of the pore system in cement based materials, various researchers introduced several concepts [35–37] in the past few decades. Among the reported studies, pioneering work by Powers and Brownyard [37] paved the way for the exploration of structure by establishing relationships between structure and properties. It is understood that when water is mixed with cement, hydration process starts immediately and begins to alter the microstructure of cement paste system. During the hydration process of cement, as a part of microstructure development, porosity arises as a result of air mixed into the cement, vaporization of free water and generation of hydrates [38–40]. According to IUPAC [41], sizes of pores are classified as macropores (radii greater than 50 nm), mesopores (radii 2–50 nm), and micropores (pore radii less than 2 nm), and each kind is characterized by distinctive type of adsorption isotherms. Microstructure includes various sizes of pores in varied numbers in the hydrated cement and this can be measured by means of advanced techniques like gas adsorption [42,43], mercury intrusion porosimetry [44], nuclear magnetic resonance (NMR) [45], small angle scattering etc. Among all the methods, gas adsorption using nitrogen is used widely to measure the surface area, pore size, pore size distribution etc. The mechanism of adsorption by the porous material have an effect on the adsorption hysteresis and helps in the identification of type and size of the pores present in the system. Generally, two cases of pore filling (micropore and mesopore) can be distinguished from the adsorption isotherms. Micropore filling is observed as a result of adsorbent-adsorbate forces and mesopore filling is the result of adsorbate–adsorbate forces.

1.4.1. Surface adsorption

Since the aperture of the micropore is only a few molecules in diameter, the potential fields of the contiguous pore walls are overlapped with one another [46,47]. This intensifies the interaction between the adsorbent and the gas molecule, resulting in a dramatic increase in adsorption quantity even at low relative pressures (P/P_0) and thereafter it flattens after reaching the saturation pressure. Thus, the corresponding adsorption isotherms of microporous materials have a steep, positive initial slope and followed by a long horizontal line over a broad range of relative pressures. The nitrogen and water vapor adsorption techniques are widely used in the determination of specific surface of hydrated cements. Calculation of specific surface is based on BET method, which is a widely used and established approach for determining the specific surface area of solid materials using Eq. (1) as suggested by Brunauer et al. [35].

$$\frac{p}{v.(p_0-p)} = \frac{1}{v_m.C} + \frac{C-1}{v_m.C}.\frac{p}{p_0} \tag{1}$$

where v is a volume of the adsorbed substance (water or nitrogen) and p and p_0 are equilibrium pressure and saturation pressure on a free surface respectively, v_m is the volume of the adsorbent which is adsorbed on the sample in case of monolayer adsorption and C is a constant which characterizes the interaction between sample and adsorbed gas (a large value of C indicates a large interaction). The volume of the adsorbent in case of monolayer adsorption v_m can then be calculated using Eq. (2):

$$v_m = \frac{1}{A+1} \tag{2}$$

where A is the slope of the straight line plotted between $p/[v.(p_0-p)]$ vs p/p_0. The specific surface S_{BET} was then calculated from the known area occupied by one molecule of the adsorbed substance. (the value s_m is assumed as 0.114 nm^2 for the molecule of water and 0.162 nm^2 for the molecule of nitrogen [48]) using Eq. (3):

$$S_{BET} = \frac{v_m.N_A.s_m}{V} \tag{3}$$

where N_A is Avogadro's number, V is molar volume.