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Research Article

The size of portlandite crystals in ITZ and its relation with ratios of ingredients and properties of LWAC

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ARTICLE INFO

Article history:

Received 7 July 2022
Received in revised form 28 December 2022
Accepted 28 December 2022
Available online 23 March 2023

Keywords:

Lightweight aggregate concrete, scoria, interfacial transition zone, portlandite, compressive strength, oven-dry density

Doi: 10.24012/dumf.1142093

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ABSTRACT

In this experimental study, nine different lightweight aggregate concrete (LWAC) specimens - in which natural lightweight scoria aggregate was used as coarse aggregate - were prepared for investigating the size of portlandite crystals in their interfacial transition zone (ITZ). Scanning Electron Microscope (SEM) was used to determine the size of portlandite crystals in ITZ of LWAC specimens. The size of portlandite crystals in ITZ of these LWAC specimens was determined quantitatively in order to identify its relation with ratios of ingredients and properties of LWAC that were investigated. It was determined that the size of portlandite crystals in ITZ of nine LWAC specimens is in the range of (0.91-2.047) µm. The size of portlandite crystals in ITZ is found to be increased when the water/cement (W/C) and coarse aggregate/total aggregate (Ac/A) ratios of LWAC get increased. On the other hand, the compressive strength and the oven-dry density of LWAC are found to be decreased when the size of portlandite crystals in ITZ gets increased. The best way to make portlandite beneficial from mechanical, physical and durability points of view is to transform it into so-called secondary hydration products by making it react with materials that have proper chemical properties for this transformation. In this case, the small portlandite crystals dissolve entirely, and the large portlandite crystals become smaller. Lightweight scoria aggregate used in this study is thought to have chemical properties to assist such a transformation in ITZ.

Introduction

Concrete can contain a wide variety of different materials. In basic, it can be regarded as a material that has the filler and the binder components. Aggregate particles are the filler, cement paste is the binder component of concrete. Cement paste holds the aggregate particles together. It can be regarded as a glue [1].

The cement paste is affected by the presence of the aggregate. In the close vicinity of aggregate particles, the cement particles can't pack together efficiently. This narrow cement paste region, typically 10 to 50 µm thick around the aggregate particles, differs from the bulk cement paste [1]. In concrete, this region between cement paste and aggregate is mostly defined as interfacial transition zone (ITZ) among other definitions [2-6].

The components of the hydrated cement paste are some unhydrated clinker grains, pores, and hydration products. Portlandite, calcium silicate hydrate (C-S-H) and calcium sulfoaluminates hydrates are the main hydration products. The volume occupied by these hydration products varies from 20% to 25% for portlandite, 50% to 60% for C-S-H, and 15% to 20% for calcium sulfoaluminates hydrates of total volumes of solids in a completely hydrated cement paste [2].

Although extensive work has been done on the hydrated cement paste, the studies related with portlandite [7-21] have been very limited. The tendency of portlandite is to form large crystals that have hexagonal-prism morphology [2]. During the drying process of cement paste shrinkage occurs. It is believed that portlandite limits the amount of shrinkage [1]. Further, it provides protection to the reinforcing steel that takes place in concrete to avoid from carbonation-induced corrosion via maintaining a high pH in the interstitial water [22].

However, portlandite is the most soluble hydration product. According to numerical simulations, portlandite dissolution increases the porosity of the hydrated cement paste. The material transport properties are negatively affected by this increase in porosity [14]. Also, portlandite has considerably lower surface area compared with C-S-H that limits its strength-contributing potential [2]. And also, its orientation in cement paste provides space for potential crack propagation and therefore a reduction in strength of concrete. In this aspect, portlandite is the weakest point of the hardened high-density systems and restrains their mechanical properties [23].

According to Li and Xu, the lower content of portlandite, the higher content of C-S-H, and the lower porosity in both ITZ and the bulk cement paste have positive effects on transport and mechanical properties of highly resistant concrete [23].

There are larger portlandite crystals in ITZ, than are found in the bulk cement paste [1]. However, there are few studies on the nucleation and growth of these crystals in ITZ [9]. ITZ of around 40 µm covers 20% to 40% volume of cement paste. It has a major role in identifying concrete properties [5]. Size and morphology of the crystals formed within this zone as a result of hydration affect the properties of ITZ. In this regard, the quantitative studies of the features of portlandite crystals in ITZ are essential for the modification of ITZ microstructure.

In this experimental study, nine different lightweight aggregate concrete (LWAC) specimens were prepared for investigating the size of portlandite crystals in their ITZ. Scoria, a natural lightweight aggregate, was used as coarse aggregate in LWAC specimens. The size of portlandite crystals in ITZ of these LWAC specimens was determined quantitatively in order to identify its relation with ratios of ingredients and properties (compressive strength and oven-dry density) of LWAC.

Material and methods

Preparation of LWAC mixtures

Nine LWAC mixtures that were prepared and ratios and proportions of their ingredients are given in Table 1. Properties of cement, physical properties of aggregates and chemical content of scoria aggregate used in LWAC mixtures were given respectively in Table 2, Table 3 and Table 4.

Absolute volume method was used for proportioning the ingredients of LWAC mixtures. Each LWAC mixture was targeted to has high strength and a slump value of minimum 2.5 cm. The recent proportions of ingredients of LWAC mixtures were determined after testing the trial LWAC mixtures that were prepared in accordance with these targets. Polycarboxylate based hyper plasticizer admixture was used in three LWAC mixtures that have W/C ratio of 30%.

Table 1. LWAC mixtures that were prepared and ratios and proportions of their ingredients.

	Ratios and Proportions of Ingredients										
	Ratios of Ingredients		Proportions of Ingredients (in 1000 dm^3 concrete mixture)								
LWAC Mixtures That Were Prepared	Water / Cement (W/C) Ratio by Mass (%)	Coarse Aggregate / Total Aggregate (Ac/A) Ratio by Volume (%)	Cement Mass (kg)	Cement Volume (dm^3)	Coarse Aggregate (Scoria) Mass (kg)	Coarse Aggregate (Scoria) Volume (dm^3)	Fine Aggregate (River Sand) Mass (kg)	Fine Aggregate (River Sand) Volume (dm^3)	Water + Hyper Plasticizer Mass (kg)	Saturation Water Mass of Coarse Aggregate (kg)	Saturation Water Mass of Fine Aggregate (kg)
LWAC 01	30	40	500	160.256	502.134	275.898	1051.169	413.846	143.75 + 6.25	37.310	15.768
LWAC 02	30	50	500	160.256	627.670	344.872	876	344.872	143.75 + 6.25	46.640	13.140
LWAC 03	30	60	500	160.256	753.20	413.846	700.780	275.898	143.75 + 6.25	55.960	10.510
LWAC 04	37.5	40	500	160.256	474.834	260.898	994.019	391.346	187.5 + 0	35.280	14.910
LWAC 05	37.5	50	500	160.256	593.542	326.122	828.350	326.122	187.5 + 0	44.100	12.425
LWAC 06	37.5	60	500	160.256	712.250	391.346	662.681	260.898	187.5 + 0	52.920	9.940
LWAC 07	45	40	500	160.256	447.534	245.898	936.869	368.846	225 + 0	33.256	14.053
LWAC 08	45	50	500	160.256	559.417	307.372	780.725	307.372	225 + 0	41.565	11.711
LWAC 09	45	60	500	160.256	671.300	368.846	624.580	245.898	225 + 0	49.880	9.370

Table 2. Properties of cement used in LWAC mixtures.

Properties of Cement Used in LWAC Mixtures (Normal Early Strength Portland Cement)					
Strength Properties		Physical Properties		Chemical Properties	
Compressive strength (2 days)	31.0 MPa	Specific weight (g/cm^3)	3.12	Insoluble residue (%)	0.55
Compressive strength (7 days)	39.5 MPa	Volume constancy (mm)	1.2	SO_3 (%)	2.38
Compressive strength (28 days)	46.5 MPa	Specific surface area (cm^2/g)	3395	Cl (%)	0.0085
		Setting start (hour)	2.15	Ignition loss (%)	2.65
		Setting ending (hour)	3.35		

Table 3. Physical properties of aggregates used in LWAC mixtures.

Aggregates Used in LWAC Mixtures	Physical Properties						
	Maximum Particle Size (mm)	Particle Size Distribution	Bulk Density (Mg/m^3)	Particle Density (Mg/m^3)	Shape Index	Water Absorption (24 h) (%)	Moisture Content (%)
River sand (fine aggregate)	4	Appropriate for ASTM C 330	1.707	2.538	-	2.538	1.96
Scoria (coarse aggregate)	16		0.864	1.819	10	10.884	0.89

Table 4. Chemical content of scoria aggregate used in LWAC mixtures.

Chemical Content of Scoria Aggregate Used in LWAC Mixtures	Ratios (%)
SiO_2 (total)	45.06
Al_2O_3	13.34
Fe_2O_3	12.80
CaO	12.05
MgO	7.41
SO_3	0.36
Na_2O	2.88
K_2O	1.32

River sand aggregate was entirely dried in the oven before used in LWAC mixtures. It is suggested to keep lightweight aggregates in water during ten minutes before using them in concrete mixtures. However, it was thought that this period of time wouldn't be sufficient due to high cement content used in LWAC mixtures and ambient temperature of 30-35 °C at the time of LWAC production. Therefore, before used in LWAC mixtures, scoria aggregate was kept in water during thirty minutes after entirely dried in the oven. Saturation water of aggregates was added to LWAC mixtures subsequently.

Preparation of test specimens and determination of the compressive strength and oven-dry density

Test specimens were prepared in order to determine the compressive strength and oven-dry density of prepared LWAC mixtures in the hardened state. In this regard, moulds for test specimens were prepared, moulds were filled with LWAC mixtures that were prepared and then compacted (by vibrating table), surfaces of them were leveled and finally test specimens were cured. These operations carried out according to procedures given in TS EN 12390-1 [24] and TS EN 12390-2 [25].

In this study, 27 test specimens (three for each of the nine LWAC mixtures) were prepared in 150x300 mm sizes and in the form of cylinders for the compressive strength tests and also 27 test specimens in 100x100x100 mm sizes and in the form of cubes for the oven-dry density tests.

It was seen that there is no consensus in literature on the curing time and testing age of LWAC test specimens. In this study, LWAC test specimens were cured in lime-saturated water during 56 days. Later on, they were kept in the laboratory under environmental conditions at the end of 90th day.

The compressive strength of these test specimens was determined according to instructions given in TS EN 12390-3 [26] and TS EN 12390-4 [27], and the oven-dry density of test specimens was determined according to instructions given in TS EN 12390-7 [28].

Preparation of SEM specimens and determination of the size of portlandite crystals in ITZ

In this study, images obtained from Scanning Electron Microscope (SEM) were used to determine the size of portlandite crystals in ITZ. For this, 100x100x500 mm sized beam specimens were prepared at first. Considering the fact that ITZ and scoria aggregate may interact within time, the prepared beam specimens were kept in the laboratory under environmental conditions for one year. The 10x25x50 mm sized SEM specimens (Figure 1) were obtained from these beam specimens. SEM specimens were polished, wiped with methyl alcohol to obstruct further hydration, coated with gold for conductivity and dried in an oven.

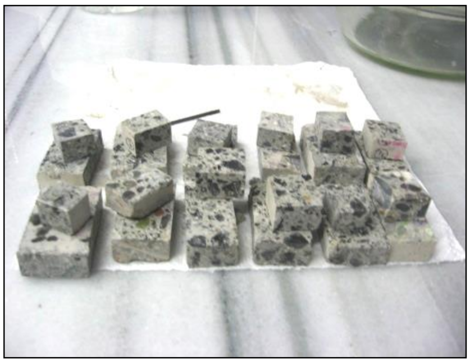


Figure 1. Preparation of SEM specimens.

In able to determine the size of portlandite crystals in ITZ, 6 Secondary Electron Images (SEIs) were taken from each SEM specimen. Thus, 54 SEIs at 10000x magnification ratio were taken in total. Quantitative data related with the size of portlandite crystals was obtained from SEIs by direct measurement. The size of each portlandite crystal was measured in two perpendicular directions and was determined by taking average of these two sizes. The size of portlandite crystals in ITZ of each SEM specimen was determined by taking the average of the measured sizes of the largest three portlandite crystals in ITZ.

Results and discussion

The size of portlandite crystals in ITZ of LWAC

The size of portlandite crystals in ITZ of LWAC specimens is given in Figure 2, and the images of portlandite crystals in Figure 3.

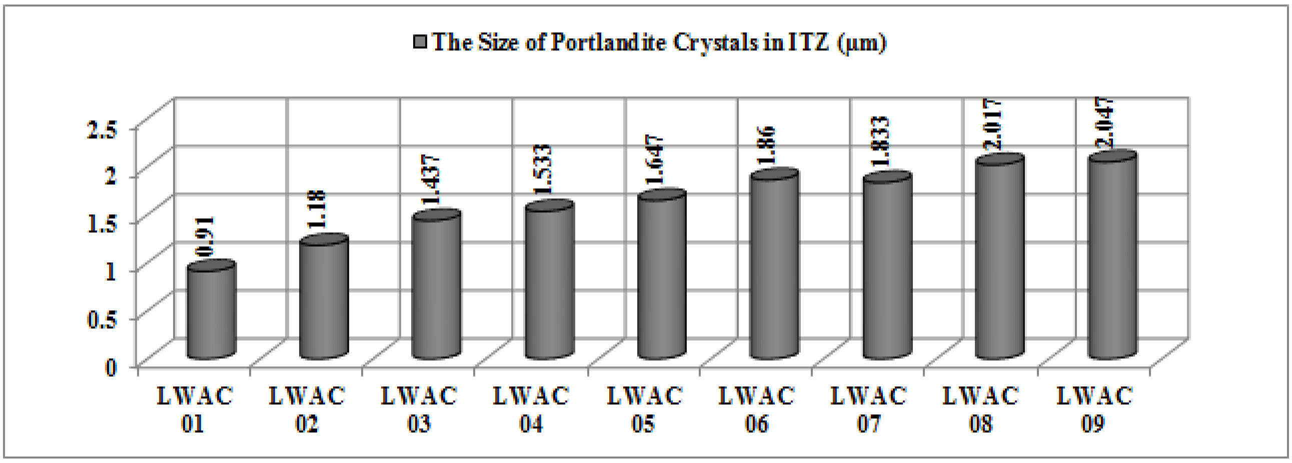
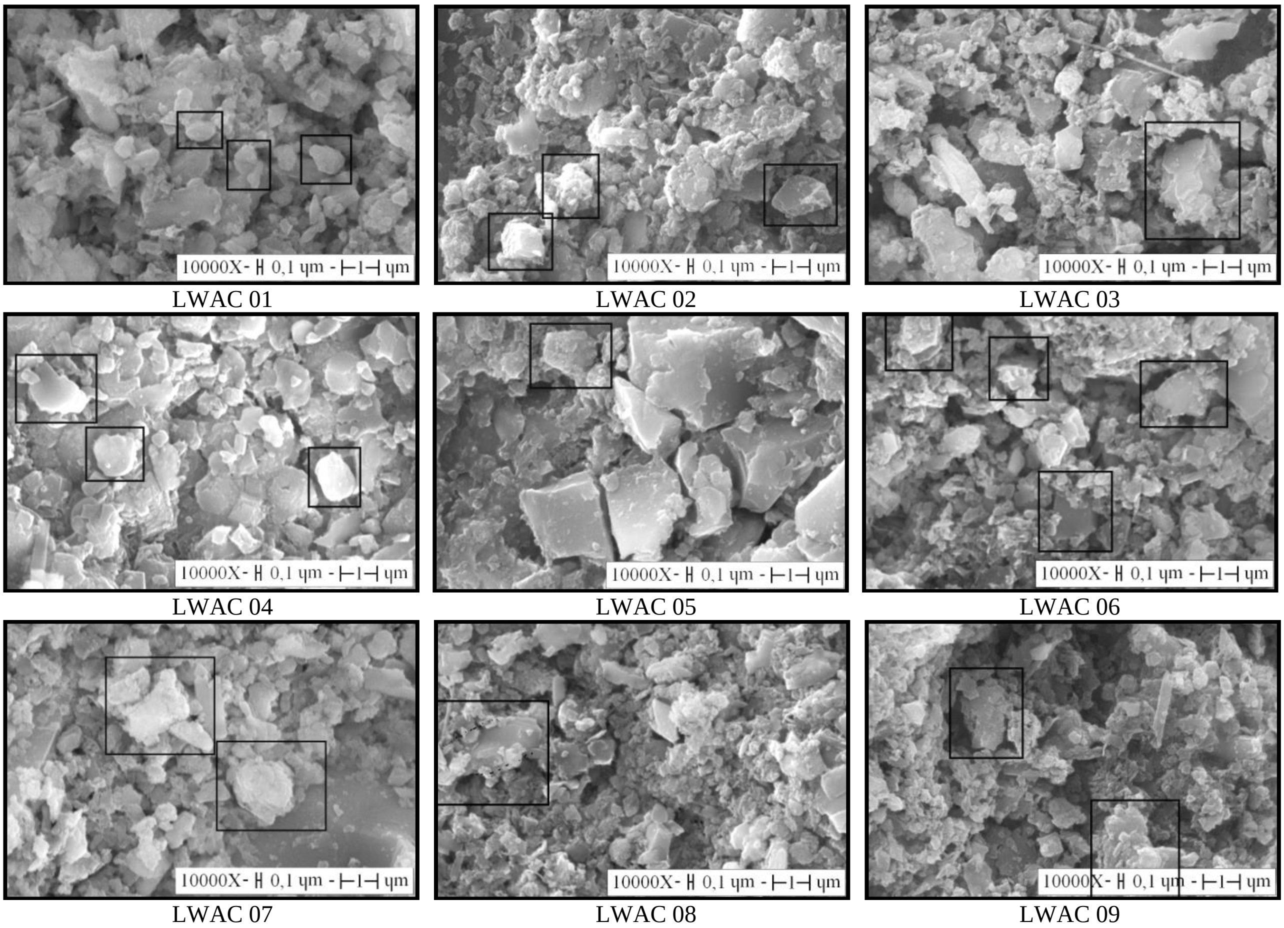


Figure 2. The size of portlandite crystals in ITZ of LWAC specimens.



LWAC 01 LWAC 02 LWAC 03
LWAC 04 LWAC 05 LWAC 06
LWAC 07 LWAC 08 LWAC 09

Figure 3. The images of portlandite crystals in ITZ of LWAC specimens.

The size of portlandite crystals is around 1 µm in well-hydrated bulk cement paste. According to Jiang [29], the amount and size of portlandite crystals in ITZ is more than those of in bulk cement paste. Some admixtures that are used in concrete can decrease the size of portlandite crystals in ITZ. It has been stated the size of portlandite crystals to be (3-4) µm in ITZ of concrete containing ground granulated blast-furnace slag produced by Gao et al. [30], and to be 2 µm in ITZ of concrete containing nanoparticles of TiO_2 produced by Ren et al. [31].

In this study, it was determined that the size of portlandite crystals in ITZ of LWAC specimens is in the range of (0.91-2.047) µm. There isn't any orientation of portlandite crystals in ITZ. Portlandite crystals, morphologically, is similar to a cube with rounded edges, and in the form of pebble stone.

In order to explain these satisfactory small values obtained in this study with respect to the size of portlandite crystals, the sequence of ITZ's hydration development must be followed from the time concrete is placed: At the beginning of the hydration, ettringite and portlandite are formed in ITZ, as in the bulk cement paste. These crystalline products in ITZ consist of relatively larger crystals. In the next stage of hydration, C-S-H and smaller crystals of ettringite and portlandite are formed and the space between the large ettringite and portlandite crystals starts filling by them. In later process of hydration, chemical reactions between the aggregate (siliceous aggregate or limestone) and the cement paste may form new hydration products (C-S-H or carboaluminate hydrates) in the pores of ITZ. Such chemical reactions reduce the concentration of the portlandite in ITZ [2].

Scoria aggregate particles have a rich silica and alumina content. In this study, considering the fact that ITZ and scoria aggregate may interact within time, the prepared beam specimens that SEM specimens removed from were kept in the laboratory under environmental conditions for one year. In this long term, scoria aggregate particles must have reacted with portlandite crystals to form so-called secondary hydration products. In this case, small portlandite crystals dissolve entirely, and large portlandite crystals become smaller.

Relation of the size of portlandite crystals in ITZ with the ratios of LWAC ingredients

Relation of the size of portlandite crystals in ITZ with the ratios of LWAC ingredients is given in Figure 4.

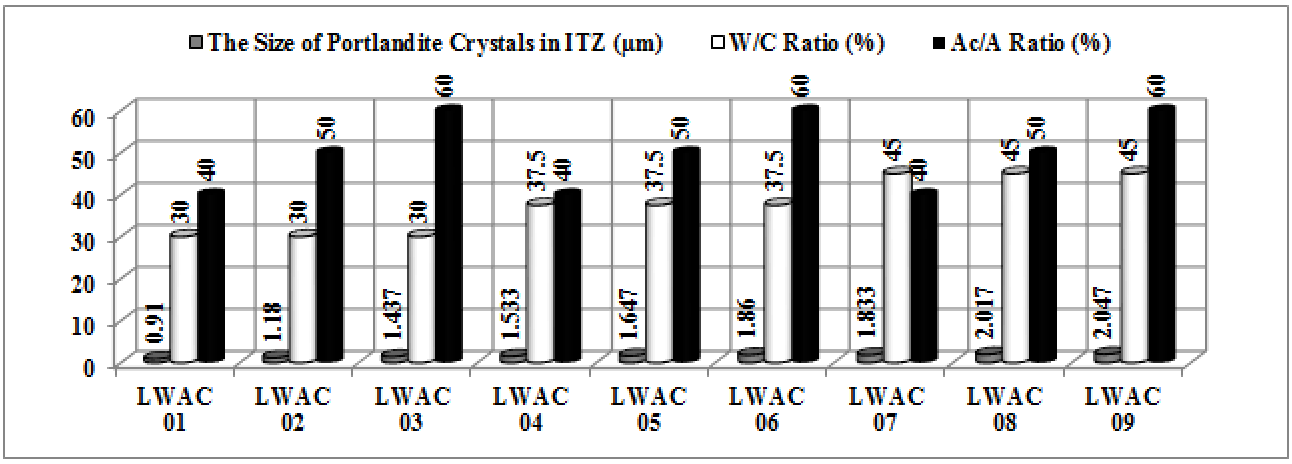


Figure 4. Relation of the size of portlandite crystals in ITZ with the ratios of LWAC ingredients

The size of portlandite crystals in ITZ is found to be increased when the W/C ratio of LWAC gets increased. Increase in W/C ratio of LWAC from 30% to 45%, increased the size of portlandite crystals in ITZ by 71% on average. The increase in the size of portlandite crystals comes true as follows: During cement hydration, hydration products grow outward from the surface of cement particles. When hydration products from two close cement particles contact, they stop growing in that particular direction. Portlandite forms as crystals with a wide range of shapes and sizes, depending primarily on the amount of space available for growth [1]. According to Richardson, there is a lot of space when the W/C is high (Figure 5). Thus, hydration products can grow unhindered and large crystals are formed. In contrast, in low W/C paste the growth of hydration products is hindered and water availability for hydration becomes limited [22].

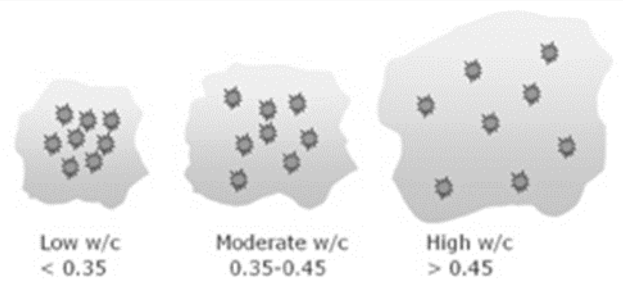


Figure 5. Schematic representation of water and cement particles for low, moderate and high W/C ratios [32].

In this study, hyper plasticizer made it possible to produce LWAC that has a low W/C ratio (30%). Hyper plasticizer increases the dispersion of cement particles by electro-steric repulsion. Electro-steric repulsion includes both electrostatic repulsion and steric hindrance (Figure 6). Surface tension is decreased when hyper plasticizer adsorbed by particles. Thus, it is possible to reduce W/C ratio, enhance workability, improve segregation resistance, and increase homogeneity of concrete with hyper plasticizer. The size of portlandite crystals in ITZ of LWAC specimens produced with hyper plasticizer is seen to be considerably small due to low W/C ratio.

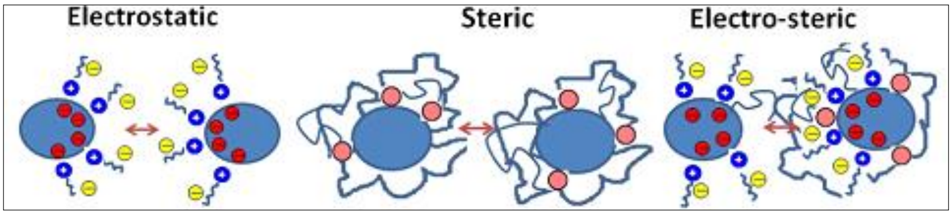


Figure 6. Schematic representation of electrostatic, steric, and electro-steric repulsion [33].

Furthermore, the size of portlandite crystals in ITZ is found to be increased when the Ac/A ratio of LWAC gets increased. Increase in Ac/A ratio of LWAC from 40% to 60%, increased the size of portlandite crystals in ITZ by 30% on average. The increase in the size of portlandite crystals comes true as follows: In the production of LWAC, sand was used in dry state and scoria aggregate was used after kept in water for 0.5 hour. Saturation water of aggregates was added to LWAC mixtures subsequently. The amount of saturation water of scoria aggregate is much more than the amount of saturation water of sand. When the Ac/A ratio of LWAC gets increased, the increased mixture water was accumulated around (especially beneath) the scoria aggregate that had substantially saturated due to being kept in water for 0.5 hour (Figure 7). Thus, the W/C ratio of ITZ was increased. Increase in W/C ratio of ITZ, must have increased the size of portlandite crystals in ITZ at the beginning of hydration.

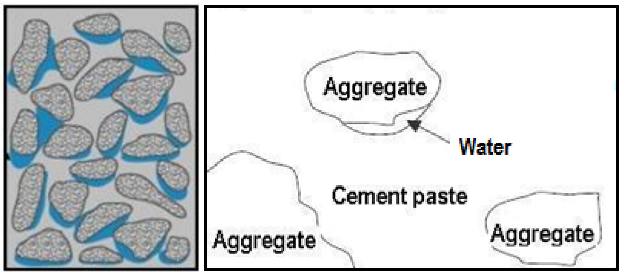


Figure 7. Schematic representation of water accumulation around the aggregate particles [2, 34].

Relation of the size of portlandite crystals in ITZ with LWAC properties

Relation of the size of portlandite crystals in ITZ with LWAC properties is given in Figure 8.

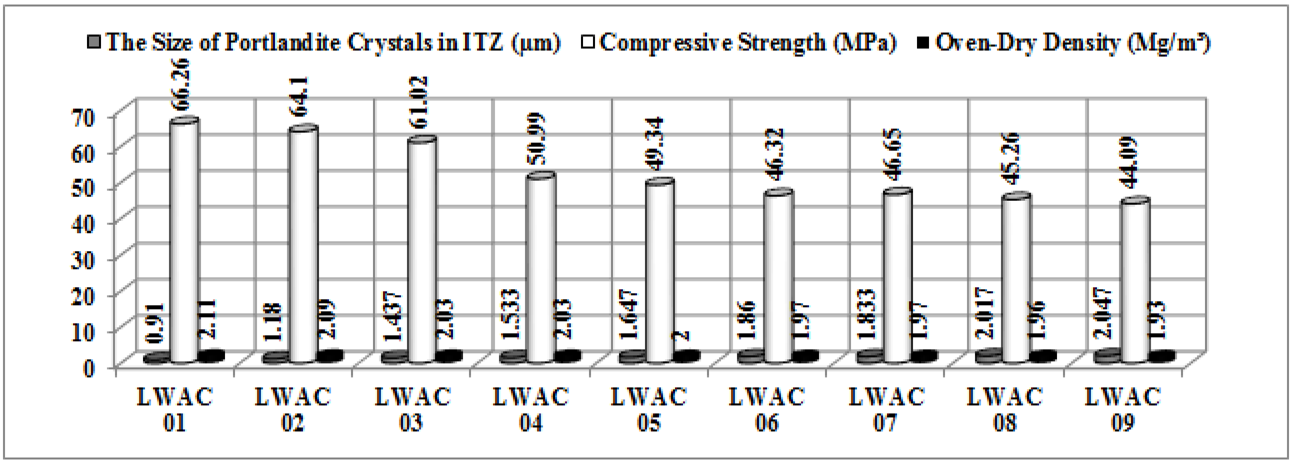


Figure 8. Relation of the size of portlandite crystals in ITZ with LWAC properties.

The compressive strength and the oven-dry density of LWAC are found to be decreased when the size of portlandite crystals in ITZ gets increased. In this context, there are inversely proportional relations between the size of portlandite crystals in ITZ and LWAC properties that were investigated.

ITZ behaves as the “weak link in the chain” beside the bulk cement paste and the aggregate particles in concrete. The strength and density of ITZ have direct effects on the strength and density of concrete [1]. The van der Waals forces of attraction are the principal source of strength in the solid products of ITZ (Figure 9). The degree of the adhesion between two solid surfaces depends on the extent and nature of the surfaces. Larger solid products of ITZ have lower surface area and weaker van der Waals forces of attraction accordingly. Thus, they possess less adhesion capacity. Besides, larger solid products of ITZ form a more porous framework [2]. For these reasons, the compressive strength and oven-dry density of concrete are found to be decreased when the size of solid products of ITZ gets increased.

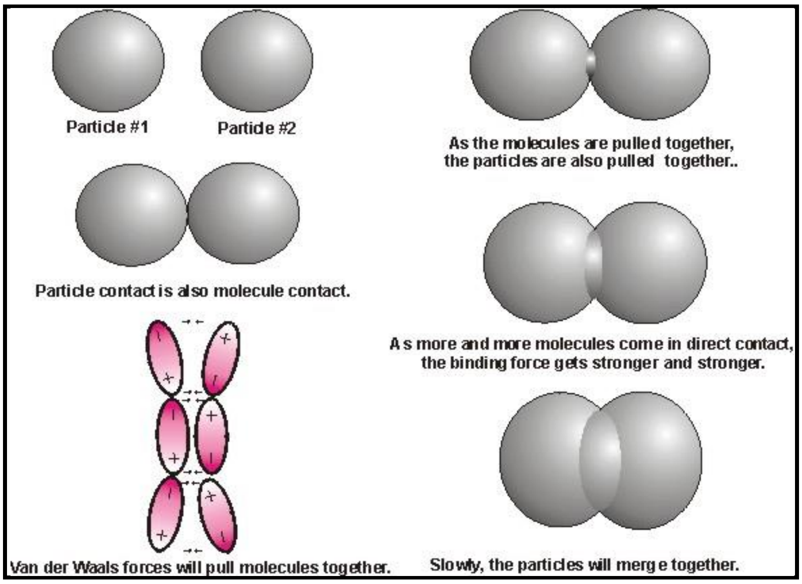


Figure 9. Van der Waals forces of attraction [35].

Conclusions

In this experimental study, it was determined that the size of portlandite crystals in ITZ of nine LWAC specimens is in the range of (0.91-2.047) µm. There isn’t any orientation of portlandite crystals in ITZ of concrete specimens. Portlandite crystals, morphologically, is similar to a cube with rounded edges, and in the form of pebble stone.

The size of portlandite crystals in ITZ is found to be increased when the W/C and Ac/A ratios of LWAC get increased. Increase in W/C ratio of LWAC from 30% to 45%, increased the size of portlandite crystals in ITZ by 71% on average. Hyper plasticizer made it possible to produce LWAC that has a low W/C ratio (30%). Thus, the size of portlandite crystals in ITZ of LWAC specimens produced with hyper plasticizer decreased considerably. Similarly, increase in Ac/A ratio of LWAC from 40% to 60%, increased the size of portlandite crystals in ITZ by 30% on average.

On the other hand, the compressive strength and the oven-dry density of LWAC are found to be decreased when the size of portlandite crystals in ITZ gets increased. In this context, inversely proportional relations have determined between the size of portlandite crystals in ITZ and LWAC properties that were investigated.

Portlandite tends to form as large crystals amongst the other hydration products. Larger crystals have lower surface area and weaker van der Waals forces of attraction accordingly. Thus, they possess less adhesion capacity and form a more porous framework. Also, portlandite is the most soluble hydration product. The best way to make portlandite beneficial from mechanical, physical and durability points of view is to transform it into so-called secondary hydration products by making it react with materials that have proper chemical properties for this transformation. In this case, the small portlandite crystals dissolve entirely, and the large portlandite crystals become smaller. Lightweight scoria aggregate used in this study is thought to have chemical properties to assist such a transformation in ITZ. The small values related with the size of portlandite crystals obtained from this experimental study support this judgment.

According to the researchers, any further research should include quantitative examination of ITZ chemically and in terms of other morphological issues in order to better understand ITZ microstructure.

Ethics committee approval and conflict of interest statement

There is no need to obtain permission from the ethics committee for this article prepared.

There is no conflict of interest with any person in this article prepared. All authors declare that they have no conflict of interest.

Authors' Contributions

All authors contributed equally.

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