EFFECT OF ULTRA-FINE LIMESTONE ON THE PHYSICO-MECHANICAL PROPERTIES OF CEMENT PASTES

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Abstract

The aim of the present work is to study the effect of limestone and ultra-fine limestone fillers on the physico-mechanical properties of hardened cement pastes. The particle size distribution was determined by laser diffractometer and SEM as well as the mineralogical composition by X- Ray Diffraction (XRD) and Fourier transform Infrared (FT-IR). The OPC was replaced with limestone filler up to 15wt% as well as ultra-fine limestone to form eight mixes. The hydration characteristics of hydrated cement pastes were evaluated by measuring the combined water content, bulk density and compressive strength up to 90 days as well as FTIR and XRD techniques. The results were shown that the coarse limestone filler particles enhance the reaction with C_3A forming calcium carboaluminate hydrates which contain higher amount of combined water content than CSH. Also, the ultra-fine limestone filler particles act as a nucleation site for the precipitation of hydration products and activated the hydration of C_3S and C_2S phases.

Introduction

Fillers are inorganic materials ground to the same fineness as Portland cement. Due to their physical properties, they have beneficial effects on desirable properties on cement hydration. Fillers can be natural materials or processed inorganic mineral materials. Engineering the pore structure is important for designing concrete with specific properties. The pore structure of concrete strongly influences both mechanical behavior and transport properties, which are essential for the durability of the concrete. Addition of micro- and nano-particles to cementitious mixtures may resulted in a more homogeneous and finer pore structure [1].

In the last 25 years, ground limestone has been used in concrete production, not only for the main purposes of lowering the costs and environmental load of cement production, but also to increase the concrete durability. The Canadian Standards Association, CSA and the American Society for Testing and Materials, ASTM allow

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a maximum of 5% addition of limestone to Portland cement in Canada and US, respectively. While, in Europe, the British / European Standard, BS EN 197-1 specifies "Portland limestone cement" allows for 6% up to 35% of the ground limestone.

A number of studies, however, have indicated positive effects of the $CaCO_3$ addition on the hydration of cement and strength development of hardened concrete, especially its accelerating effect on the rate of the hydration. The accelerating effect of the finely ground $CaCO_3$ was observed on the hydration of C_3S [2, 3]. Limestone grains act as nucleation sites for CH and CSH reaction products at early hydration ages, and accelerate the hydration of clinker minerals, especially C_3S, resulting in an improvement in early strength [4].

Improvement of fine-particle packing can considerably enhance stability and workability of fresh concrete [5, 6], as well as increase the density of paste and interfacial transition zone in hardened concrete [7]. Fine limestone filler can improve the rheological properties of cement pastes [8]. Ultra-fine particles cause a retardation of shear thickening, elevation of viscosities and reduction of workability characteristics of fly ash based mortars as a result of strongly accelerated hydration kinetics and the non-spherical shape of the limestone filler [9]. Extremely, ultra-fine limestone filler decreases the initial viscosity of self compacting repair paste compared with plain cement paste [10]. Limestone particles disperse the cement particles more efficiently than silica fume as a result of ionization of SF surface due to the high pH and possible bridging with polyvalent cations like calcium and formation of CSH via a silica gel intermediate. However, silica fume may be have advantageous as stabilizing agent for self-compacting concrete preventing segregation upon standing and reduced form pressure due to a more rapid gel formation [11]. Addition of high volume of ultra-fine limestone filler to self compacting concrete inhibits the induced bleeding of fresh concrete, leads to achievement of the required self-compacting properties at a lower w/b ratio and improves the 28-day compressive strength of concrete mixes due to the filler effect and improved fine-particle packing [12].

This work aims to study the effect of ultrafine limestone on the phsico-mechanical of Portland cement compared with natural micro limestone.

Experimental work

Characterization of raw materials

   The starting materials used in this work were OPC and limestone of Samalout formation, from Beni-Khalid quarries, Minia district, Egypt. The chemical analysis of the starting materials was determined by X- Ray flourcence (XRF) analysis as shown in Table (1). The limestone filler was achieved by grinding limestone powder to pass 90µm sieve. On the other hand ultra-fine limestone filler was achieved by grinding limestone filler in a porcelain ball mill for 24 hours.

Table (1): Chemical analysis of the starting materials, mass%

Oxide	OPC	Limestone Filler
SiO_2	20.88	0.26
Al_2O_3	6.08	0.16
Fe_2O_3	3.18	--
CaO	63.00	54.59
MgO	1.50	0.29
SO_3	1.60	0.05
Na_2O	0.02	0.11
K_2O	0.04	0.03
L.O.I	1.9	43.72

   The XRD pattern of Ultra Fine limestone was recorded on (M/S. Shimadzu Instruments, Japan) diffractometer XRD 7000 with Ni filtered CuKα as a radiation source at 2θ scan speed of 4◦ min^{-1}. XRD pattern of limestone filler is illustrated in Figure (1). The pattern of limestone indicates the calcite is the main mineral.

   The particle size distribution and scan electron microscope (SEM) photograph of ultra-fine limestone are illustrated in Figures (2) and (3). The morphology of the particles was characterized using SEM (JEOL JSM 6360 DLA, Japan). The particle size distribution was analyzed by L4 submicron particle size analyzer, He-Ne Laser beam, Florida, USA. These illustrations indicate that the grain size of particles was in the range 98-3258 nm. It can be seen from Fig. 3(a, b) that the ultra fine limestone has practical size smaller than that of normal limestone.
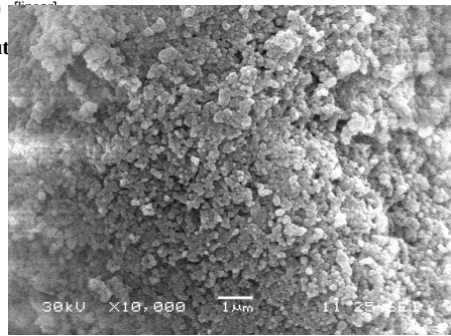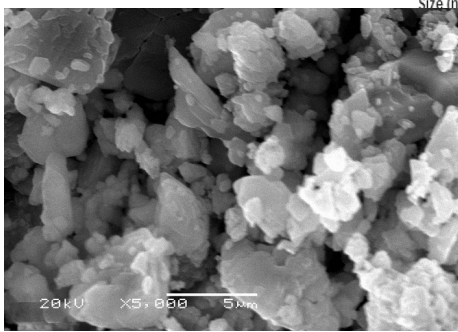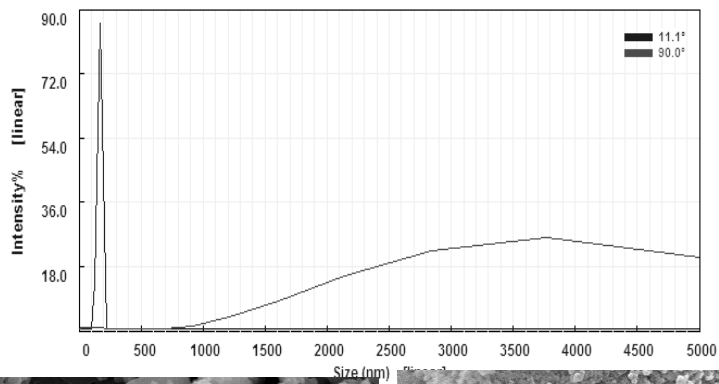
INTENSITY

2θ
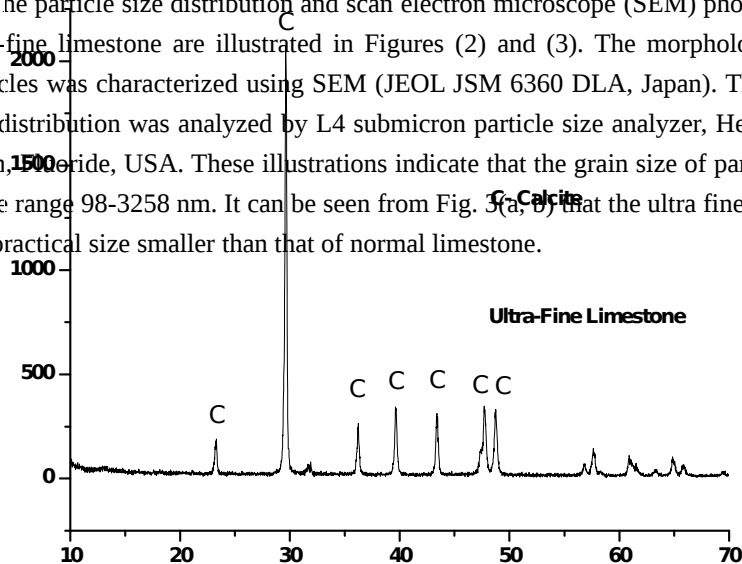
Figure (1) XRD pattern of ultra-fine limestone

Different Angle SDP Set 1 Intensity Analysis Results for Repetition 1

SDP Results Summary

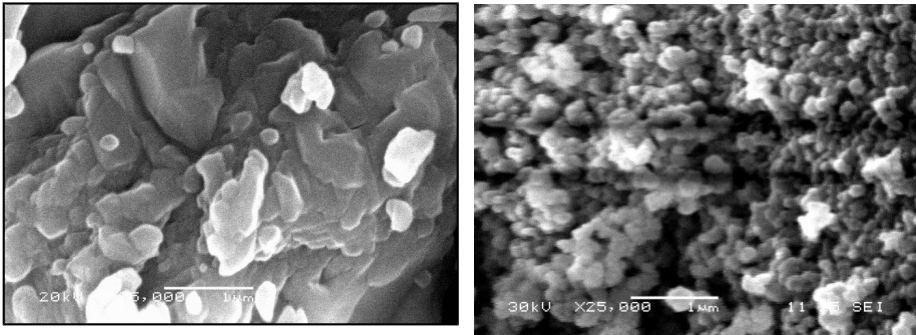| Angle	Parameter SDP Range (nm)	Calculated Results					
		Size (nm)	%amt (nm)	Std.Dev (nm)	Mean Size (nm)	Mean SD (nm)	%Dust
11.1°	1.0-5000.0	160.5	100.00	16.4	160.5	16.4	1.551
90.0°	1.0-5000.0	58.5	3.99	46.6	3130.6	1568.0	20.490
		3258.4	96.01	1281.9			

Figure (3): SEM photographs of limestone (a) and ultra-fine limestone (b) filler

Fourier transform Infrared (FT-IR) spectra were measured using a Perkin Elmer 880 FT IR spectrometer by incorporating samples in KBr (1: 99 mg) disks to confirm the characteristic vibration bands. Figure (4) represents the FTIR spectra of ultra-fine limestone filler. The data illustrate that the ultra-fine limestone sample composed mainly form $CaCO_3$ (calcite) as indicated from the presence of the main bands around 876, 1428 and 3616 cm^{-1}. The first two bands are due to the v_2 and v_3 CO_3^{2-} of $CaCO_3$ while the third band is due to the OH$^-$ of free and hygroscopic water [13].
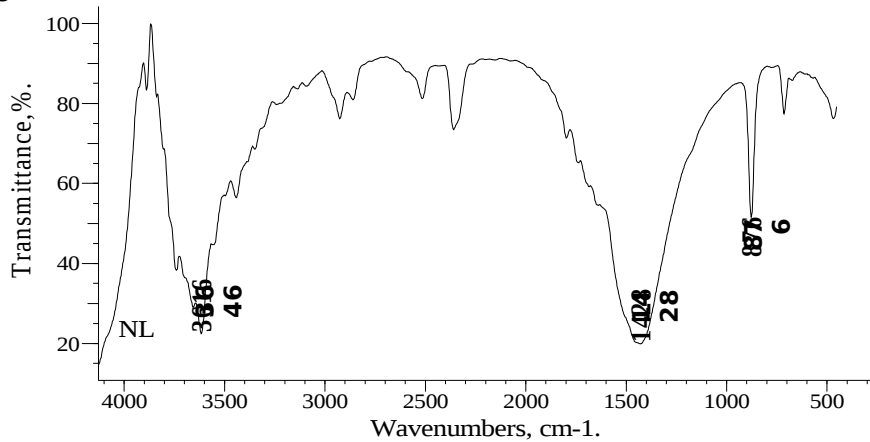
Figure (4): FTIR analysis of ultra-fine limestone filler

Preparation of cement pastes

Eight mix of filled cements containing 2.5, 5, 10 and 15 % limestone as well as ultra-fine limestone fillers in addition to OPC were prepared as shown in Table (2). Each dry mix was homogenized in porcelain ball mill using four balls for one hour on a mechanical roller to obtain complete homogeneity. All dry mixes were molded into 2x2x2 cm cubes using the standard water of consistency according to ASTM Designation C 187-98 [14]. The specimens were demolded after 24h casting and cured up to 90 days under tap water. Bulk density was determined from weights of hydrated paste cubes both in air and suspended in water according to Archimedes principle [15]. The determination of compressive strength of hardened cement pastes was carried out according to ASTM designation: C 109-80 [16] using compressive strength machine. After the compressive strength determination, the broken pieces of each cube were used for stopping the hydration by microwave drying technique [17]. The combined water (Wn), was determined from the ignition loss of dried samples at 1000 °C.

Table (2): Mix composition of investigated filled cements, wt %

Symbol	OPC	Ultra-fine Limestone	Limestone
C	100	00	00
UL1	97.5	2.5	00
UL2	95	5	00
UL3	90	10	00
UL4	85	15	00
L1	97.5	00	2.5
L2	95	00	5
L3	90	00	10
L4	85	00	15

Results and discussion

Combined water content

Figure (5) illustrates the combined water content of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days. The combined water content increases in comparison with OPC for all hydrated cement pastes with curing time. The combined water contents values of limestone cement pastes are higher than those of OPC as well as ultra-fine limestone filled cement pastes at all hydration ages. This may be due to nucleation site for the precipitation of hydration products and activated the hydration of C_3S and C_2S phases of ultra-fine particles limestone [4]. Whereas coarser limestone particles enhance the reaction with C_3A forming calcium carboaluminate hydrates which contain higher amount of combined water content than CSH [18].
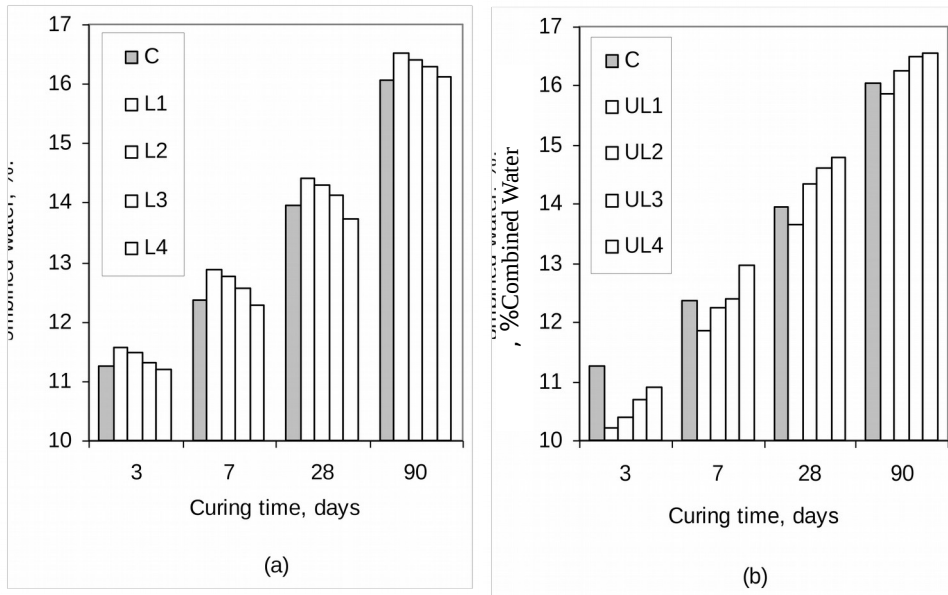

Figure (5): Combined water content of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days

Bulk density

Figure (6) illustrates the bulk density of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days. The bulk density increases with curing time for all hydrated cement pastes as a result of hydration of clinker phases. As the hydration progresses, hydration products fill

some of pores that tend to decrease the porosity and increase the bulk density of hardened cement paste. The bulk density values of ultra-fine limestone blended cement pastes are higher than those of OPC and limestone blended cement pastes at all curing time. This is mainly attributed to the additional CSH phase formed as a result of hydration of C_3S and C_2S phases precipitates on the surfaces of ultra-fine particles of limestone as well as fills some of pores of hardened cement paste leads to increasing the bulk density [1, 4, 7]. It was noticed that the bulk density of limestone as well as ultra-fine limestone filled cement pastes decreases with filler content due to the dilution effect of filler materials.

Total porosity

Figure (7) illustrates the total porosity of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days. The total porosity decreases with curing time for all hydrated cement pastes as a result of hydration of clinker phases. As the hydration progresses, hydration products fill some of pores decreasing the total pore volume ratio of hardened cement paste. The total porosity values of ultra-fine limestone filled cement pastes are lower than those of OPC and limestone filled cement pastes at all ages of hydration. This agrees with the bulk density results, because, as bulk density of hardened cement pastes increases, the total porosity decreases. The total porosity of limestone as well as ultra-fine limestone blended cement pastes are increased with filler content this is mainly due to the dilution effect of filler materials to the cement.

Compressive strength

Figure (8) illustrates the compressive strength of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days. The compressive strength increases with curing time for all hydrated cement pastes with the progress of hydration and formation of more cementing materials. The compressive strength values of ultra-fine limestone filled cement pastes are higher than those of OPC and limestone cement pastes at all ages of hydration. This may be due to the effect of ultra-fine limestone filler as activated the hydration of C_3S and C_2S and enhance the formation of additional amounts of CSH. On the other hand, limestone filler is favored the formation of calcium carboaluminate hydrates which are contain higher amount of water that has inversely effect on the bulk density and

compressive strength hardened cement pastes [19, 20]. The compressive strength of ultra-fine limestone blended cement pastes decreases with filler content due to the dilution of cement. While coarser limestone filler show reverse effect i.e. compressive strength of limestone filled cement pastes improved with increasing the filler content as a result of the presence of coarse limestone particles which improves the binding nature and compressability of hardened limestone blended cement pastes[1,18]. Figure (9) shows the relative compressive strength of filled hardened cement pastes with limestone and ultrafine limestone filler. At early ages, the hydrated cement pastes of normal limestone filler has been lower relative strength than the reference. While, the strength of the ultra fine limestone filler is higher than the reference OPC mortar. However, at later ages the advantage of the acceleration process has disappeared, and the strength remain below those of the reference [21]. On the other hand the UL1 (2.5%) has the highest value of relative strength.
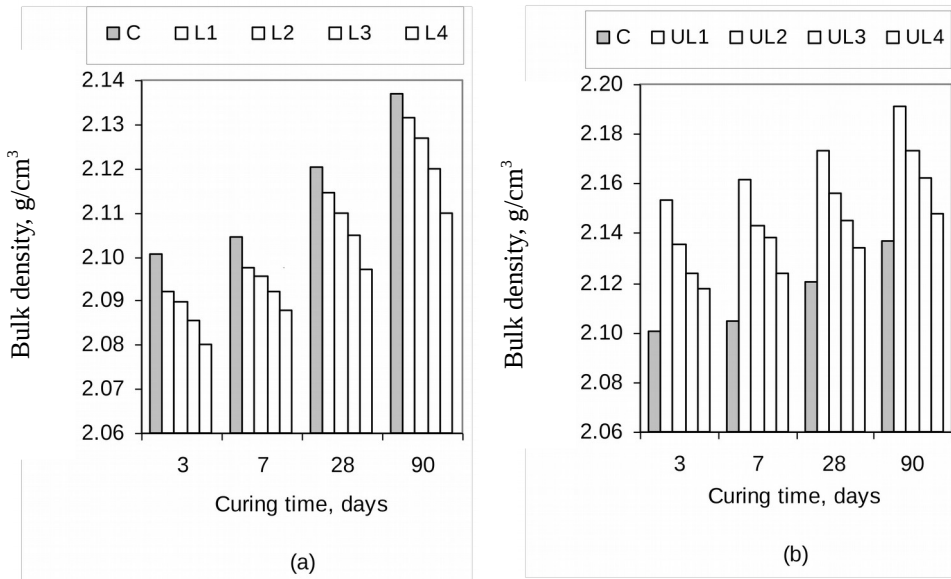

Figure (6): Bulk density of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days
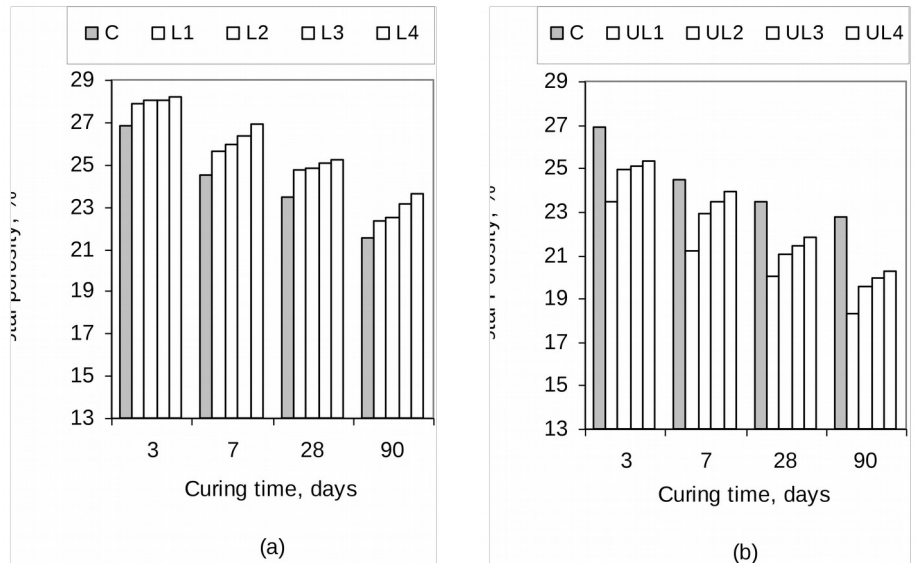
Figure (7): Total porosity of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days.
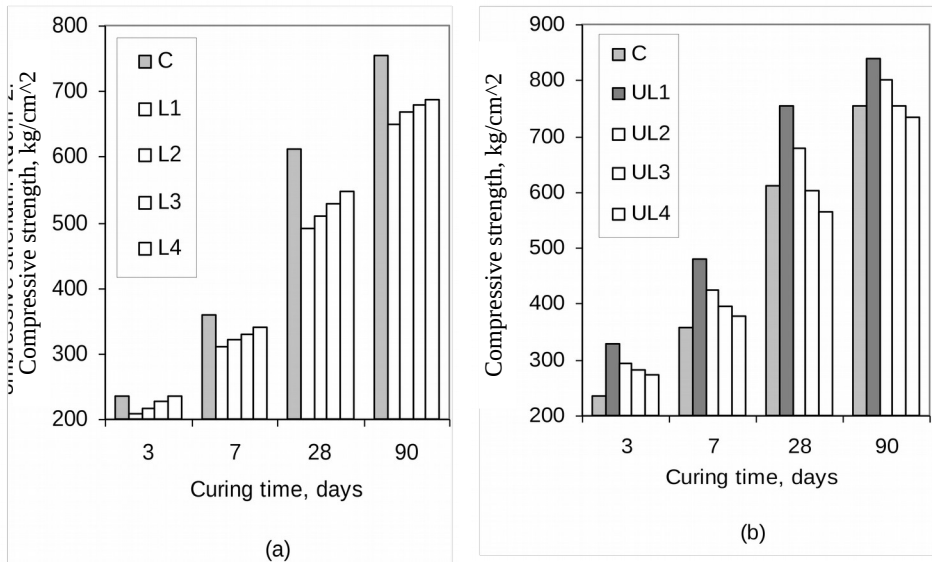

Figure (8): Compressive strength of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days
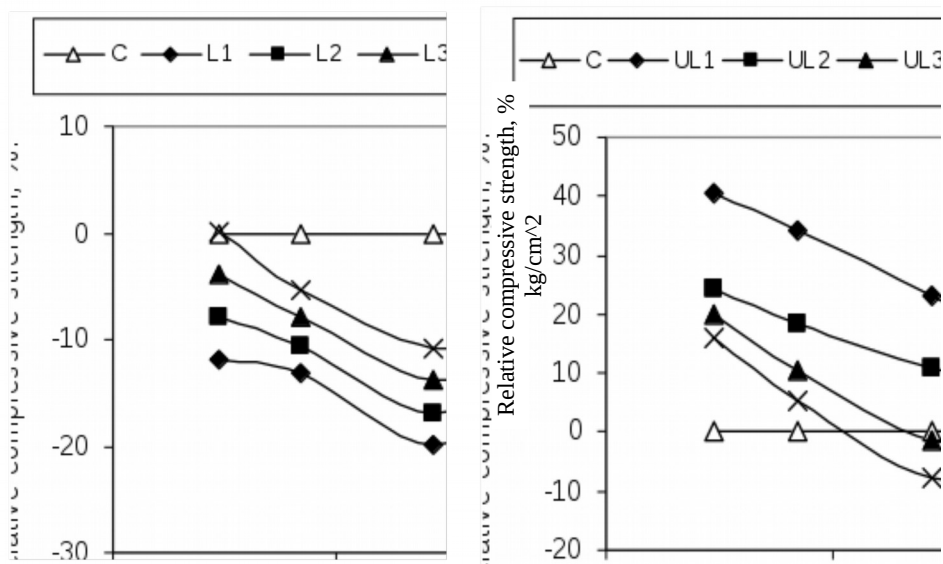
Figure (9): Relative compressive strength of filled cement pastes containing limestone (a) and ultra-fine limestone (b) as a function of curing time up to 90 days

FT-IR Spectra

Infrared spectra of hardened filled cement paste (UL1) containing ultra-fine limestone as a function of curing time up to 90 days are seen in Figure (10). It is shown that sharply band at 3646 cm^{-1} related to the OH stretching vibration of calcium hydroxide [13]. Its intensity increases with curing time up to 28 days as a result of acceleration effect of ultra-fine limestone on the hydration of C_3S. On the other hand the bands of cement hydration products are shifted to lower frequency with curing time and reached to 976 cm^{-1}, that characteristic band to the CSH [23]. The appearance of absorption band at 1462 cm^{-1} is due to the presence of $(\nu_3)CO_3^{-2}$ as well as 876 cm^{-1} (ν_2). Also, there is monocarboaluminate detected in the spectra by (ν_2) CO_3^{-2} 875 cm^{-1} [22]. The presence of broad band near 2900-3550 cm^{-1} is due to stretching band $(\nu_1+\nu_2)$ of H_2O that increases with curing time as a progress of hydration reaction. In addition, the band at 1650 cm^{-1} is related to the bending (ν_2) of H_2O and indicates the formation of CSH [23].

IR spectra of hydrated filled cement pastes with ultra-fine limestone up to 15% (UL1-UL4) curing for 90 days are shown in Figure (11). It can be shown that, the intensity of portlandite band slightly decreases with ultra-fine limestone content.

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While the intensity of band at 3646cm^{-1} in UL1 hydrated filled cement is higher than that of other hydrated filled (UL2-UL4). This is attributed to the role of filler act as a nucleation surface to the precipitation of hydration products that increases the rate of hydration of cement clinker. On the other side, the monocarboaluminate detected in the spectra by (ν_2) CO_3^{-2} 876 cm^{-1} [22] increases with ultra- fine limestone content, as a result of formation of more monocarboaluminate[20]. Also, the spectra shows the broad band near 2900-3550 cm^{-1} is due to stretching vibration band ($\nu_1+\nu_2$) of H_2O that increase in UL1 more than other filled cement pastes.
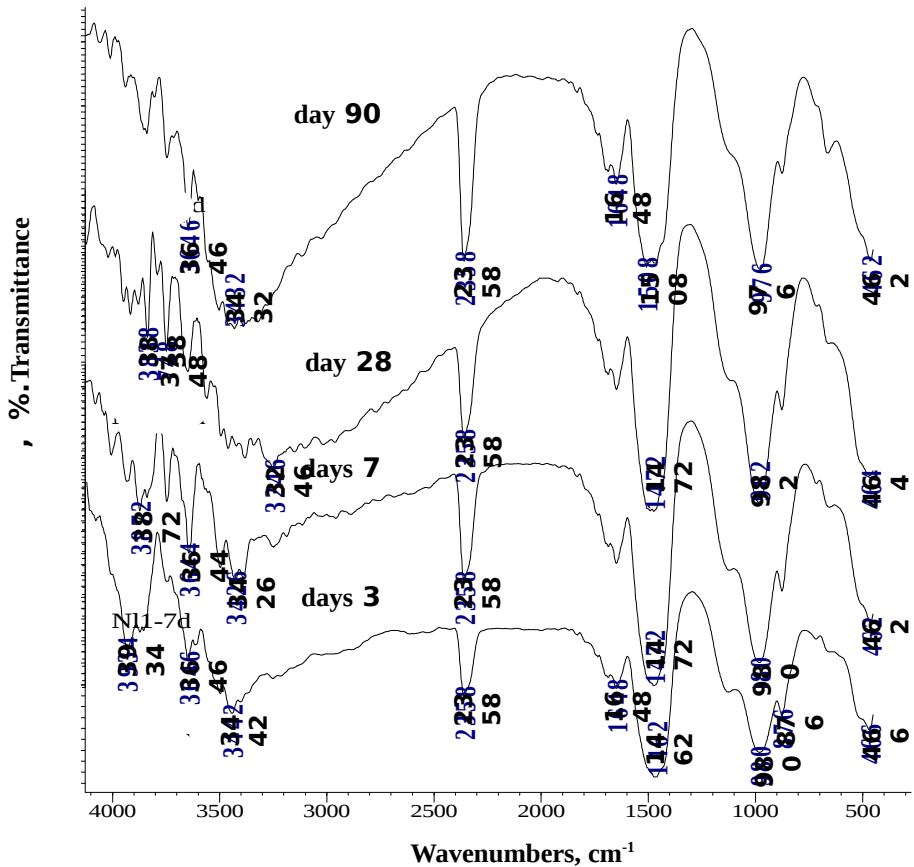

Figure (10) : FT-IR spectra of filled cement paste (UL1) containing ultra-fine limestone as a function of curing time up to 90 days.
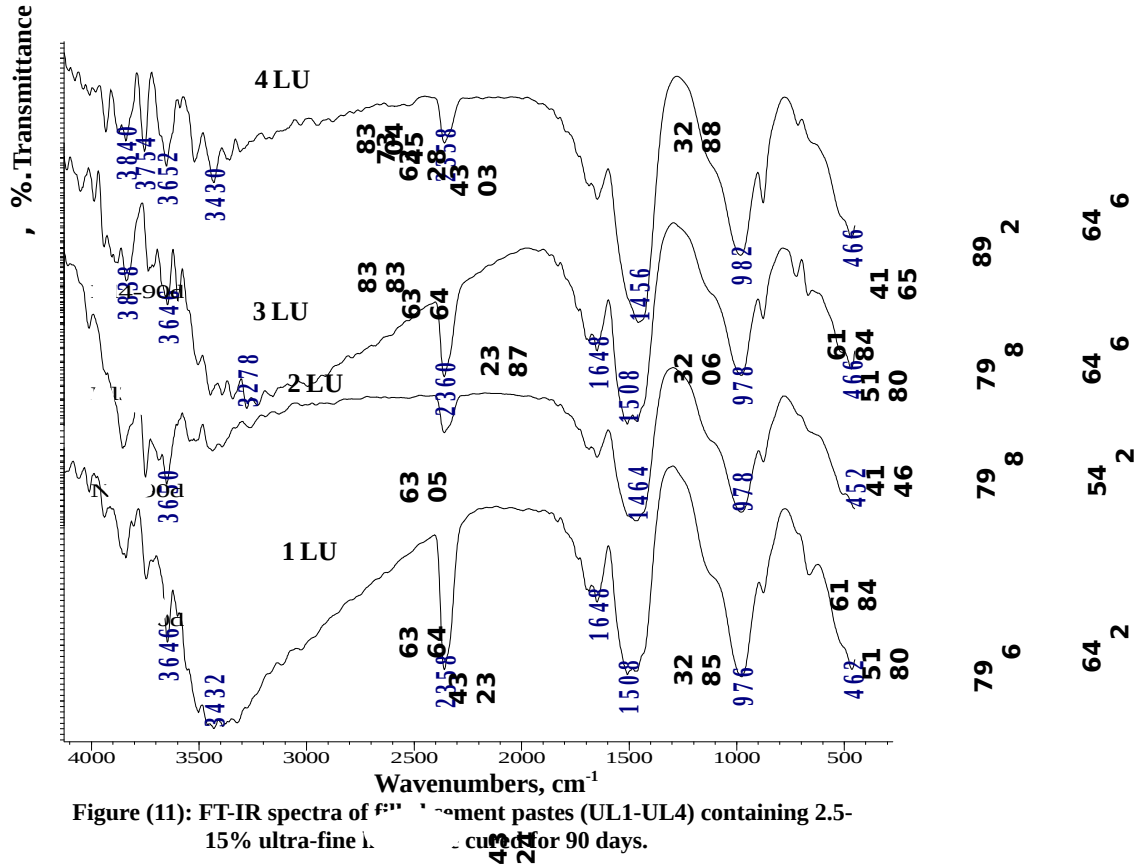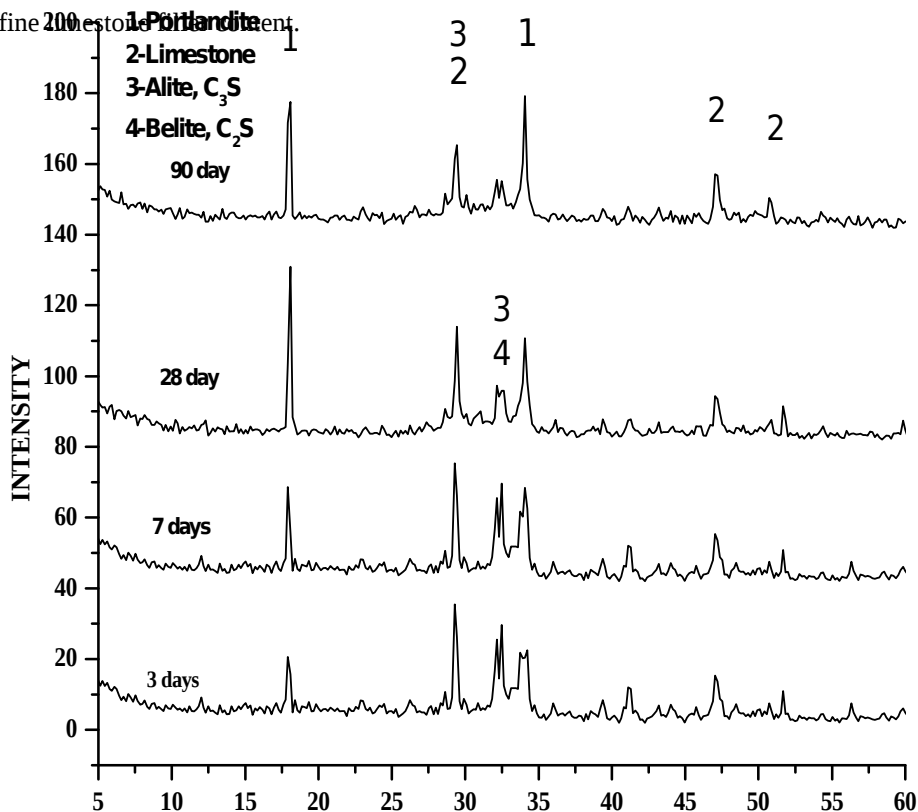
Figure (11): FT-IR spectra of filled cement pastes (UL1-UL4) containing 2.5-15% ultra-fine limestone cured for 90 days.

XRD Analysis

Figure (12) illustrates the XRD patterns of hardened filled cement paste (UL1) containing ultra-fine limestone. The portlandite, cement clinker phases (C_3S and C_2S) as well as calcite (Calcium carbonate) components are present. The intensity of portlandite lines increases with curing time up to 90 days due to the hydration of clinker phases especially C_3S and β-C_2S. Also, the hydration products (CSH and C_4AH_{13}) lines appear at all curing times. On the other side, the intensity of ultra-fine limestone lines decreases with curing time. This is mainly due to reaction between hydration products and calcium carbonate to form other products [20].

The XRD patterns of hardened filled cement pastes (UL1-UL4) with 2.5-15wt% of ultra-fine limestone cured for 90 day are shown in Figures (13). The peaks of portlandite decrease with ultra-fine limestone content. This may be attributed to the acceleration effect of ultra-fine limestone as well as the low clinker content and dilution effect of ultra-fine limestone. It can say that the ultra-fine limestone filler has good acceleration properties on the cement especially with low content (2.5 wt %, UL1) [24]. On the other side the intensity of calcite peaks increases with ultra-fine limestone content.

Figure(12): XRD pattern of filled cement paste(UL1) containing ultra-fine limestone as a function of curing time up to 90 days.
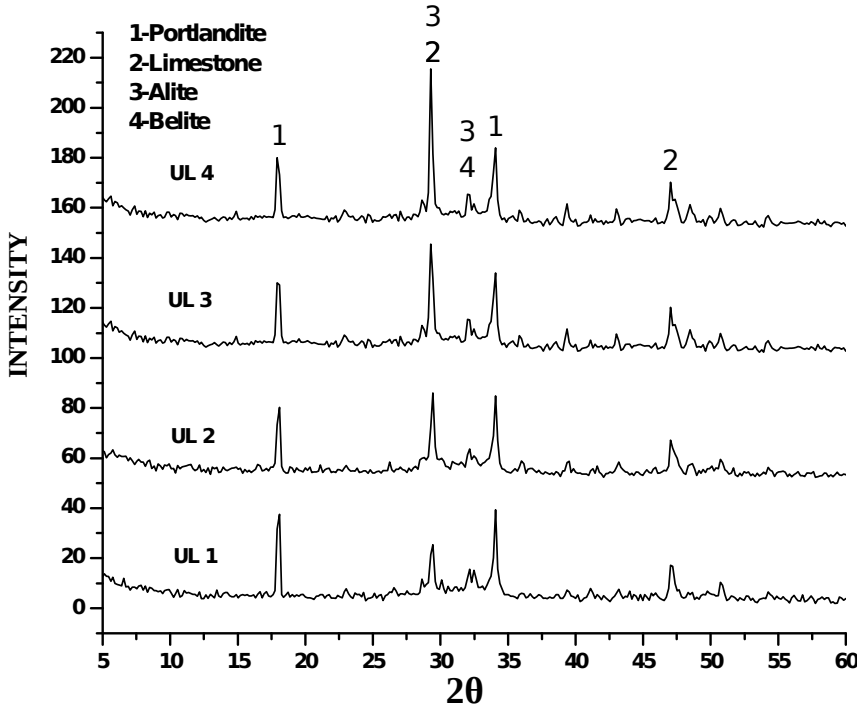
**Figure (13): XRD pattern of filled cement pastes (UL1-UL4) containing 2.5- 15%
ultra-fine limestone cured for 90 days.**

Conclusions

From the above results, we can be concluded that:

1- Addition of ultra-fine lime stone particles act as nucleation site to accelerate the cement hydration process. This process results in the enhancement of strength.

2- Hardened cement pastes containing ultra-fine limestone filler exhibit higher bulk density, lower total porosity and improved compressive strength values than both OPC and coarse limestone blended cement pastes.

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3- Mechanical properties such as compressive strength of hardened cement pastes are remarkably improved by the additions of limestone. While, the effect of ultra-fine limestone addition is very marked.

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