



Limestone-filled pozzolanic cement

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Abstract

Fillers are specially selected, natural or artificial inorganic materials, which improve the physico-chemical and mechanical properties of the cement such as workability or water retention. They can be inert or have slightly hydraulic, latent hydraulic or pozzolanic properties. They cause no appreciable increase of the water demand of the cement, in addition to not impairing the resistance of the concrete or mortar to deterioration in any way or reducing the corrosion protection of reinforcement. Fillers are normally either limestone or any inert material such as sand. The aim of this investigation is to study the effect of substitution of limestone for Homra in pozzolanic cement. The effect of limestone replacement was studied by the determination of the combined water, free lime contents, bulk density, total porosity and compressive strength. The results show that the addition of limestone reduces the initial and final setting time, as well as total porosity, whereas the free lime and combined water increase with limestone content. It can be concluded that limestone fills the pores between cement particles due to formation of carboaluminate, which may accelerate the setting of cement pastes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Limestone; Homra; Electrical conductivity; Differential scanning calorimeter; Compressive strength

1. Introduction

Cement plants are being built on or close to a limestone quarry, so that the practice of limestone grinding with clinker is obviously cheap. Limestone dust, which is produced in quarrying operations, possesses disposal and environmental problems. There is current interest, however, in the use of limestone as an addition to Portland cements. The addition of a small quantity, up to 5%, of unspecified filler such as limestone has been common practice in many European countries such as France, which has permitted such addition since 1979. Limestone fillers improve physically the denseness of cement composites; furthermore, they are reactive [1]. The consumption of calcite, the formation of carboaluminates, the accelerating effect on the hydration of C_3A , C_3S or CA in the high-alumina cements, the changes in the $C-S-H$ and formation of transition zone between the filler and cement paste, are

all facts specific of the reactivity of limestone fillers. Fillers affect strength by accelerating the cement hydration. This effect is essentially the same for all the fillers, irrespective of their chemical composition [2]. The addition of limestone enhances the rate of hydration as determined by the combined water contents [3].

The substitution of limestone for about 50% gypsum in Portland cement, acts as a filler that leads to affect the particle size distribution, decreases the total porosity and accelerates the rate of hydration of the cement pastes [4]. The effect of partial or full substitution of gypsum in the low-heat Portland cement on the characteristics of the hardened cement pastes up to 90 days was studied. The results show that the substitution of 60% of the gypsum by fine limestone improves the rate of hydration at early ages up to 28 days. In addition, the amount of limestone increases the heat of hydration, as well as the free lime and compressive strength, while the total porosity decreases at early ages.

The addition of limestone filler to neat cement pastes and mortars reduces the diffusion coefficient of chloride ions [5]. This reduction is attributed to the effect of the limestone filler particles on the tortuosity of the system.

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Table 1
Chemical composition of starting materials (wt.%)

Oxide	Ordinary Portland cement (%)	Homra (%)	Limestone (%)
SiO ₂	20.50	74.80	4.37
Al ₂ O ₃	5.05	14.03	0.36
FeO ₃	2.99	5.04	0.29
CaO	62.00	1.25	52.99
MgO	2.07	1.30	0.90
SO ₃	2.40	0.80	0.10
I.L	3.10	–	41.2

Homra is a solid waste material produced from the manufacture of clay bricks. These crushed portions of Homra are not for commercial use and may be considered as a solid waste to the environment. In a previous work, it was found that 20% Homra was the optimum mix composition with higher amount of reacted silica. The electrical conductivity of pozzolanic cement pastes and mortars containing Homra was also studied [6].

The object of the present work is to study the effect from partially up to fully substituted Homra with limestone on the physico-chemical and mechanical characteristics of pozzolanic cement pastes.

2. Experimental

The materials used in this contribution were ordinary Portland cement, Homra and limestone. The chemical analyses of these raw materials are shown in Table 1. The surface area of these raw materials are $\cong 3100 \text{ cm}^2/\text{g}$. The mix composition of the investigated mixes are seen in Table 2. The ingredients were homogenized on a roller in a porcelain ball mill with four balls for 1 h to assure complete homogeneity. The mixing and stopping of hydration of the pastes were done as described elsewhere [7]. The mixing of water with the cement pastes was carried out with standard water of consistency [8]. The pastes were molded in 1-in. cubes, cured in a humidity chamber at room temperature, 25°C, for 24 h, then demolded and cured under tap water till the time of testing. The kinetics of hydration were followed by the determination of the free lime [9], as well as chemically combined water contents. The combined water content was determined by the ignition loss of the dried paste on an ignited weight basis minus the amount of water held by free lime and the loss of the anhydrous blend. The compressive strength was determined for each cement paste up to 90 days. The total porosity, ϵ , was calculated by the determination of bulk density d_p , the total water W_t and the evaporable water content W_e of the hardened cement pastes as in the following equation:

$$\epsilon = 0.99W_e * d_p / 1 + W_t$$

In electrical conductivity measurements, the test cell was of the co-axial type, which included concentric inner and outer electrodes mounted on an insulated base plate; the electrodes were polished before the experiment. The cement pastes were placed in the space between the electrodes and the cell was kept in a desiccator at 100% relative humidity during the test period. The measurement begins exactly 3 min after the first contact with water. The electrodes were hooked to RLC meters, model SR 720, 1000 Hz for resistance measurements between the electrodes across the hydration stages of setting and hardening.

3. Results and discussion

3.1. Conductimetry

The electrical conductivity can be used as an effective means of studying the progress of cement hydration and for monitoring structure change occurring with the cement paste and mortar, as well as determining the initial and final setting times [6]. The electrical conductivity is a consequence of movement of charge carriers. The electrical conductivity time curves are shown in Fig. 1. When the cement comes into contact with water, calcium hydroxide is liberated during the hydration process and alkali sulfates present in the cement are completely dissolved contributing K^+ , Na^+ and SO_4^{2-} . The first conductivity peak is controlled by the numbers and mobility of these ions. The initially formed hydration products (C–S–H and ettringite) coat the cement grains, which readily form the electrical insulating layers leading to reduction in the mobility of the ions, i.e. the conductivity decreases (initial set). The second conductivity peak is a consequence of ettringite monosulfate transformation and osmotic pressure development around the cement grains, which leads to an increase in the ionic mobility [10,11]. The sharp decrease in electrical conductivity at later ages of hydration is due to the formation of C–S–H and ettringite, resulting in a marked consumption of the number of ions. It is clear that the maximum height of the first conductivity decreases with addition of 5%, 10% and 20% limestone, as a partial substitution of Homra in cement pastes. While the addition of 15% limestone increases the first conductivity peak. The limestone liberates some Ca^{2+} ions, therefore, the conductivity increases. The free lime content of the sample containing 15% limestone is higher than all mixes at 3

Table 2
Mix compositions of different cements (wt.%)

Mix no.	OPC	Homra	Limestone
I.0	80	20	–
I.5	80	15	5
I.10	80	10	10
I.15	80	5	15
I.20	80	–	20

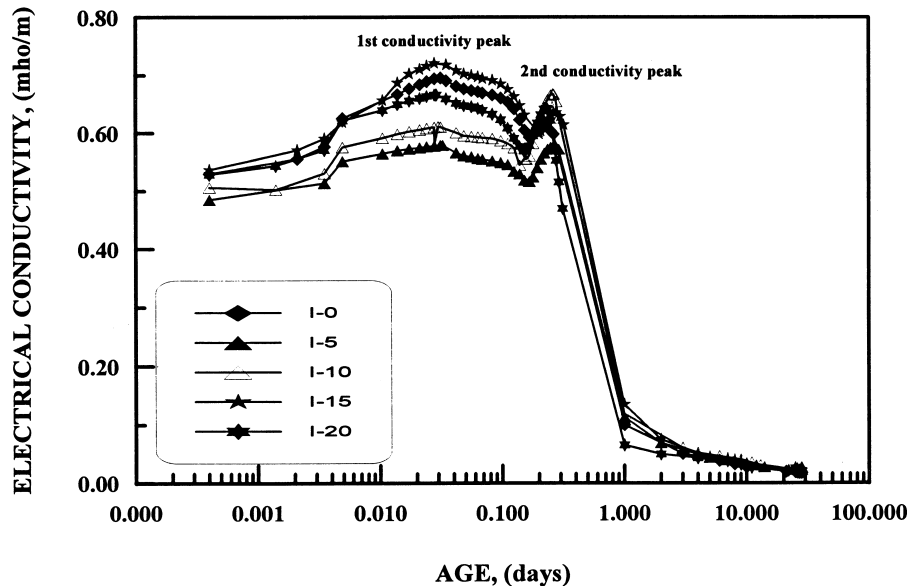


Fig. 1. Electrical conductivity of pozzolanic cement pastes made with limestone as a partial substitution for Homra.

days. The electrical conductivity increases rapidly up to around 45 min, after which there is a slow decrease. After 4 h, the conductivity time curves show gradual increase. The height of second conductivity peak increases with the increase of limestone addition. At 22°C and pH > 12, the SO_4^{2-} groups in the interlayer region of monosulfate are replaced by CO_3^{2-} [12]. This reaction leads to the formation of calcium carboaluminate hydrates. The increase in the sulfate concentration increases the height of the second conductivity peak of cement pastes containing different percentages of limestone. This result indicates that the carbonate anion should be regarded as an important

factor in the hydration of C_3A in the presence of calcium sulfate and lime.

3.2. Setting

The initial and final setting time are plotted as a function of limestone content in Fig. 2. The addition of 5% limestone increases the plasticity of the mix, which needs more water for workability, i.e. the consistency increases from W/C = 0.25 for I.0 (80% OPC and 20% Homra) to 0.265 for I.5 (80% OPC, 15% Homra and 5% limestone). As a result, the initial and final setting time are

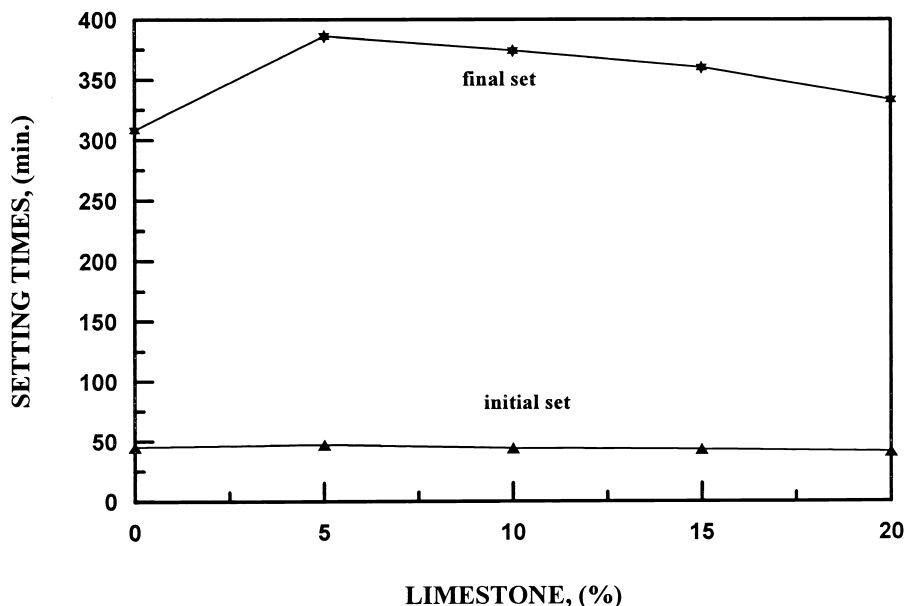


Fig. 2. Setting times of pozzolanic cement pastes made with limestone as a partial substitution of Homra.

elongated. The initial and final setting time are reduced when limestone content increases up to 20%. Limestone enhances the formation of calcium hydroxide at early ages because it provides nucleating sites for its growth. In addition, larger amounts of ettringite are observed at early ages with limestone addition [13]. The effects of limestone are partly physical and partly chemical. Because of its fineness, the material acts as filler between the grains of clinker. Chemically, it reacts with aluminate phase, producing carboaluminate [14]. The final setting time of 20% limestone is longer than 0%. This is mainly due to the decrease of the pozzolanic reaction of Homra. The limestone has no hydraulic properties in comparison with Homra, which is activated by the liberated lime, therefore, the final setting time of cement paste containing 20% limestone is somewhat elongated.

3.3. Combined water

The combined water contents increase with curing time, this is attributed to the progress of hydration and to increasing the amount of hydration products. The chemically combined water contents are represented as a function of curing time, as well as limestone content in Fig. 3. The addition of limestone to Homra pozzolanic cement increases the combined water contents at all ages. The combined water content increases with limestone up to 10 wt.% and then decreases at 15 wt.%, as well as at 20 wt.%. The mix containing 10 wt.% Homra and 10 wt.% limestone (I.10) is considered as the optimum mix composition at which the maximum amount of reaction can occur (i.e. higher chemically combined water content). It has also higher bulk density and lower amount of free lime than the other limestone pozzolanic cement. This is due to the fact that limestone activates Homra to

react with liberated lime thus forming more hydration products. The increase of combined water content is due to the addition of limestone filler that may be due to the formation of rims of C–S–H surrounding C_3S particles and increases the rate of hydration of C_3S [13]. The results indicate that the carbonate anion should be regarded as an important factor in the hydration of C_3A in the presence of calcium sulfate and $Ca(OH)_2$ [12]. It is shown that in the presence of CO_3^{2-} , the possible phase assemblages in the system are $C_3A \cdot Ca(OH)_2 \cdot 18H_2O$, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, $C_3A \cdot CaSO_4 \cdot 12H_2O$ and $C_3A \cdot CaCO_3 \cdot 12H_2O$. The presence of CO_3^{2-} prevents the reaction of ettringite formed in the early hydration stages with C_3A to monosulfate at the end of the induction period. The concentration of ettringite remains almost unchanged and the crystallization of hemihydrate, monocarbonate or both is observed [12,15]. These phases have higher combined water contents in comparison with the hydrated calcium silicates. It is noticed that 15 and 20 wt.% limestone decrease the combined water contents of the hardened pastes more than the 10 wt.%. This is due to the decrease of Homra content, which reacts with lime liberated from the hydration of OPC forming C–S–H that affects the combined water content.

3.4. Free lime

The variations of free lime contents of limestone-filled pozzolanic cement pastes are plotted as a function of curing time in Fig. 4. The free lime contents were corrected to 100% of OPC in each mix. This means that the amount of CaO liberated from pure OPC. The Homra pozzolanic cement pastes (I.0), with 20 wt.% Homra increases up to 7 days and then decreases with curing time. This is due to the pozzolanic reaction of Homra.

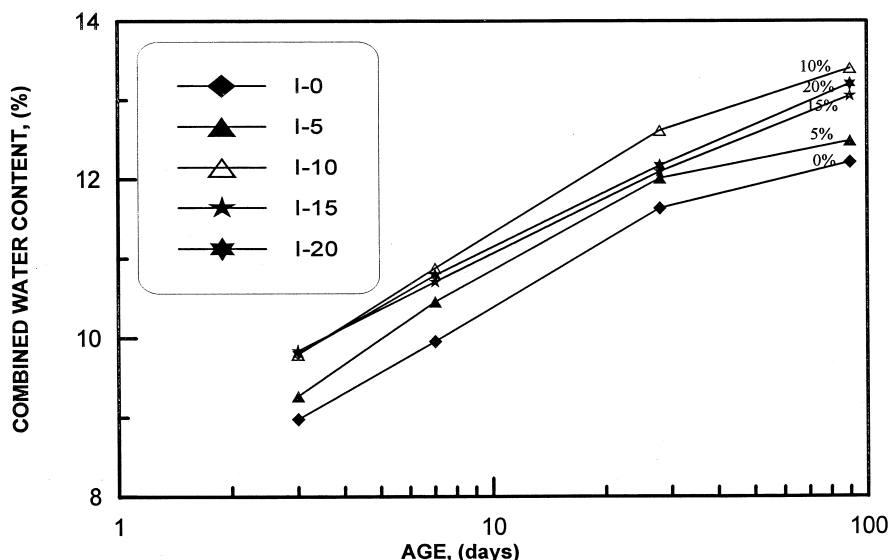


Fig. 3. Chemically combined water contents of hardened cement pastes containing limestone instead of Homra.

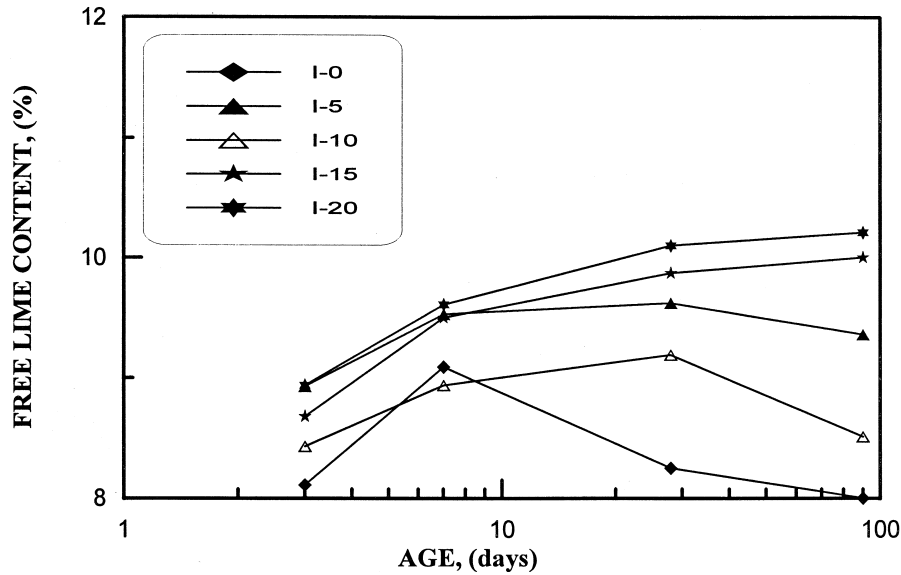


Fig. 4. Free lime contents of hardened cement pastes containing limestone instead of Homra.

Homra reacted with lime liberated from the hydration of OPC, forming additional C-S-H. Both C-S-H increase the compressive strength. The addition of 10 wt.% limestone increases the free lime up to 28 days, then decreases at 90 days with addition of 15 and 20 wt.% limestone the free lime increases up to 90 days. This is due either to the decrease of Homra content which reacts with lime liberated or to the leaching of lime (Ca^{2+}) from the limestone present in the pastes leading to increase of free lime content [3]. The results illustrate that the limestone accelerates the rate of hydration of OPC, i.e. increases the combined water contents of pozzolanic cement pastes. It can be said that, the increase of limestone content increases free lime content. The mix

I.10 (80% OPC, 10% Homra and 10% limestone) shows lower free lime content than mix I.5 (80% OPC, 15% Homra and 5% limestone). This may be due to the fact that 10 wt.% limestone activates Homra to react with liberated lime thus forming more hydration products. This mix is the optimum mix, which has also higher combined water content.

3.5. DSC

Figs. 5 and 6 show the DSC thermograms of hardened filled pozzolanic cement pastes hydrated up to 90 days. Fig. 5 illustrates the DSC thermograms of mix I.10 hydrated for 3, 7, 28 and 90 days. There are three main

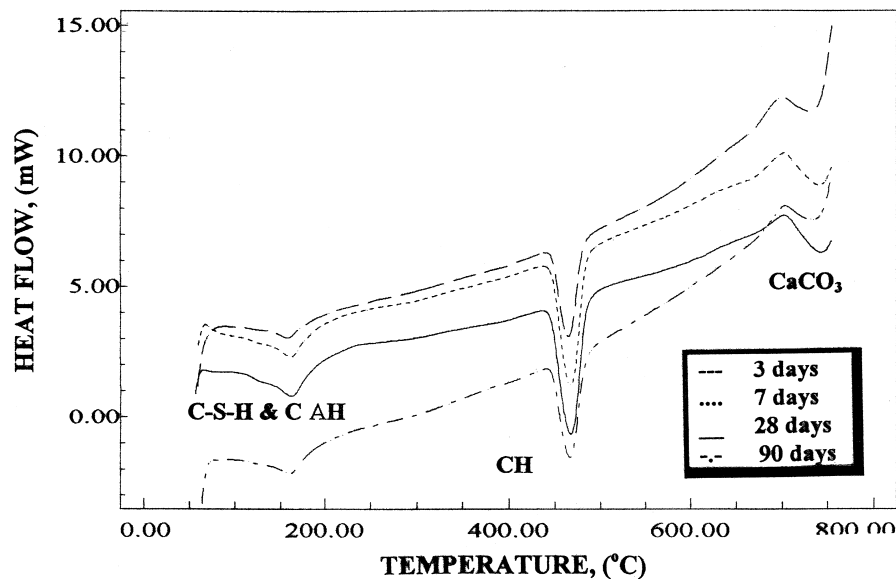


Fig. 5. DSC thermograms mix I.10 hydrated for 3, 7, 28 and 90 days.

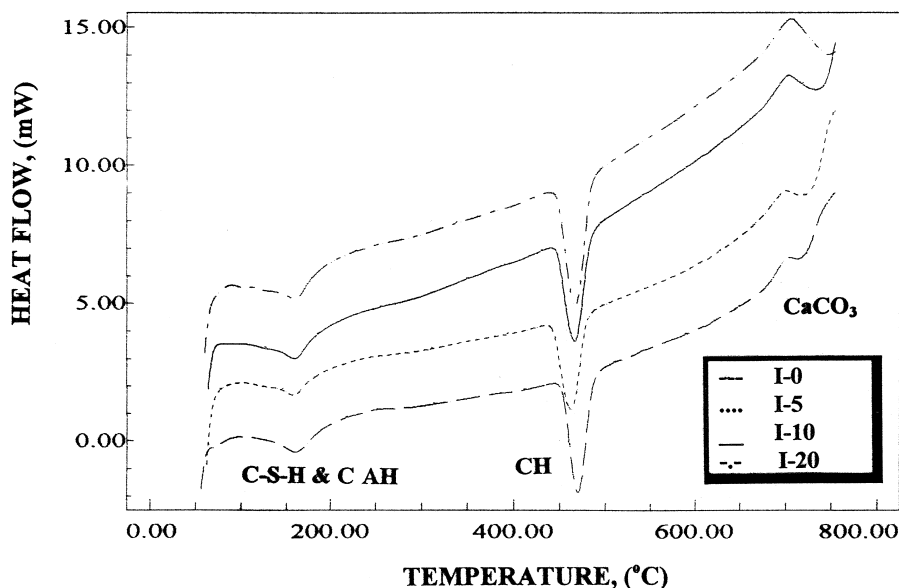


Fig. 6. DSC thermograms of mix I.0, I.5, I.10 and I.20 hydrated for 90 days.

endothermic peaks. The first peak is located at 160°C, which are due to loss of water from C–S–H, calcium sulfoaluminate and calcium carboaluminate hydrates. The second peak, which is located at about 465°C, is attributed to the dehydroxylation of calcium hydroxide. The last endothermic peak appearing at 720°C represents the decarbonation of calcium carbonate. It is clear that the enthalpy of $\text{Ca}(\text{OH})_2$ phase increases with the increase of curing time up to 28 days from 431 to 726 mJ, then decreases to 486 mJ at 90 days. This is due to the pozzolanic reaction of Homra with $\text{Ca}(\text{OH})_2$. The enthalpy of calcium carbonate phase decreases from 431.99 mJ at 3 days to 230 mJ at 90 days. The decrease in CaCO_3 may be due to the

formation of hemihydrate and monohydrate. Fig. 6 shows the thermograms of hardened filled pozzolanic cement pastes namely I.0, I.5, I.10 and I.20 hydrated up to 90 days. The enthalpy of $\text{Ca}(\text{OH})_2$ increases from 406 to 582.73 mJ. The increase of the amount of limestone content increases the free lime content.

3.6. Porosity and bulk density

The total porosity and bulk density of limestone pozzolanic cement pastes cured for 3, 7, 28 and 90 days are presented in Figs. 7 and 8. The total porosity for all cement pastes decreases with curing time, whereas the

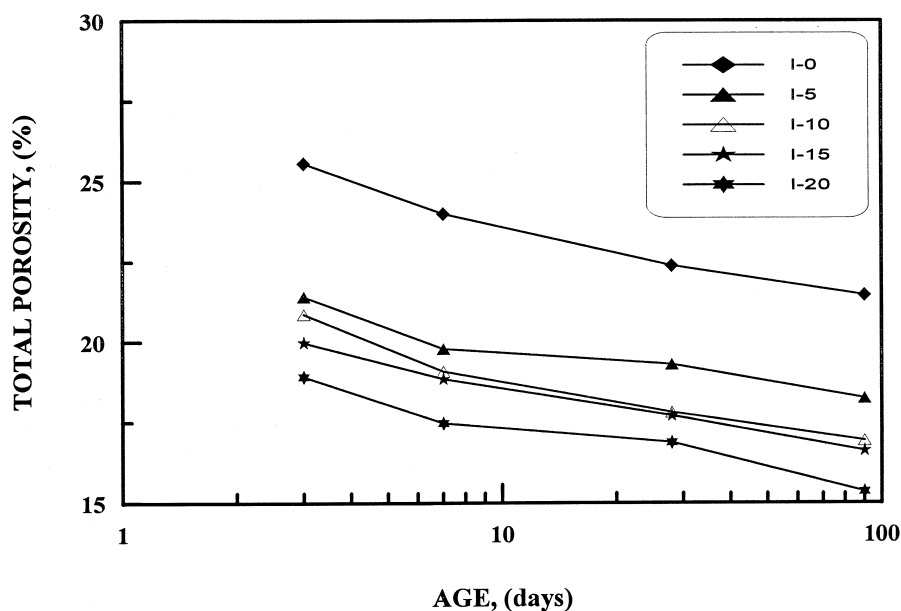


Fig. 7. Total porosity of hardened cement pastes containing limestone as a partial substitution for Homra.

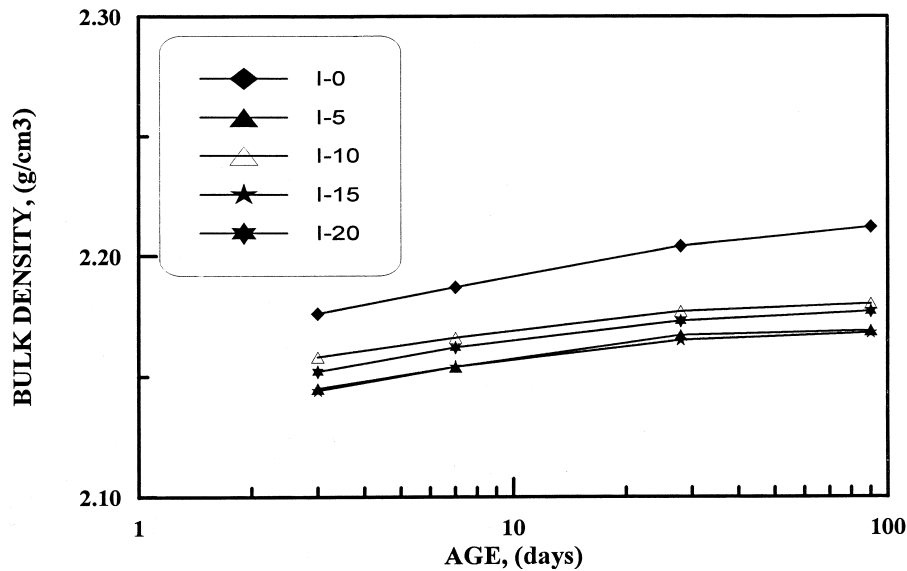


Fig. 8. Bulk density of hardened cement pastes containing limestone as a partial substitution for Homra.

bulk density increases. This is due to the filling up of a part of the available pore volume with the hydration products, as the hydration proceeds. Limestone addition decreases the total porosity, due to the formation of a dense structure and crystallization of a highly polymerized calcium silicate hydrate [16]. The bulk density decreases with the increase of limestone content. The mixture with 10 wt.% limestone has higher bulk density than the other limestone-filled pozzolanic cement pastes. This is due to higher chemically combined water content, lower free lime content, i.e. more hydration products. With the increase in limestone content, the total porosity decreases. It can be concluded that limestone fills the pores between the cement particles. The porosity de-

creases as limestone ratio increases. This result is due to the filler effect of limestone.

3.7. Compressive strength

The compressive strengths of hardened cement pastes are illustrated as a function of hydration ages in Fig. 9. It is clear that the compressive strength increases with curing time for all hardened cement pastes. The addition of limestone reduces the compressive strength of the hardened cement paste. Increase of the amounts of limestone dilutes the pozzolanic reaction. As a result of this, the compressive strength at 90 days shows a dilution effect. The strength development depends primarily on the formation of

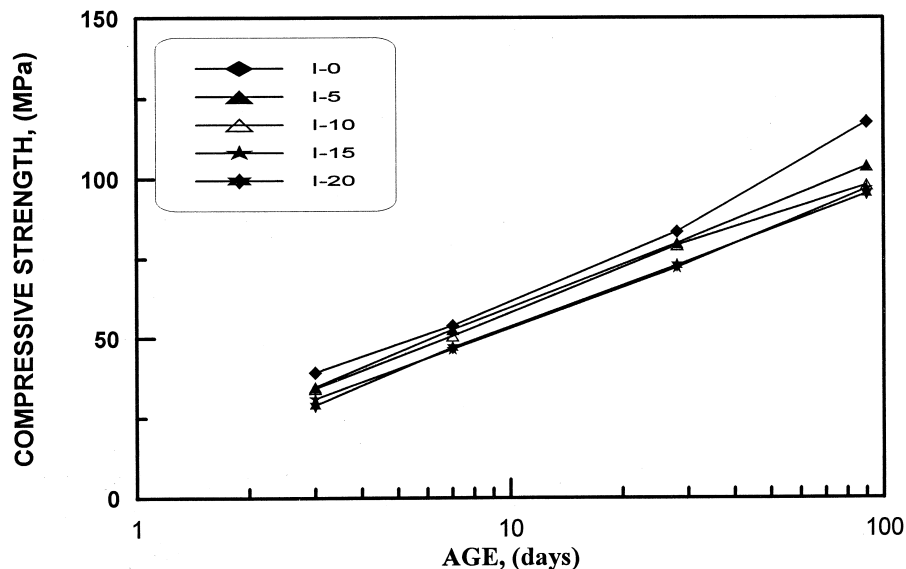


Fig. 9. Compressive strength of hardened cement pastes containing limestone instead of Homra.

hydrated calcium silicate as the main hydration product, which is precipitated into the water filled spaces to form a more compact body. This is mainly attributed to crystallization of the initially formed hydrates, having strong binding forces and/or their transformation into other hydration products having weaker binding forces.

4. Conclusion

From the above finding, it can be concluded that:

1. Limestone is an important factor in the hydration of C_3A , as well as C_3S and β - C_2S in the presence of $CaSO_4$ and lime.
2. Limestone fills the pores between the cement particles due to the formation of carboaluminate phases.
3. Limestone addition leads to an increase of the lime liberated from the cement pastes.
4. The replacement of OPC by 20 wt.% of Homra increases the compressive strength.

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