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Effect of curing time on the physico-mechanical characteristics of the hardened cement pastes containing limestone

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Abstract

The effect of curing time on the physico-mechanical properties of the hardened Portland cement pastes containing limestone was studied. Five cement–limestone blends were prepared using 0%, 5%, 10%, 15%, and 20% of limestone as a partial substituent of Portland cement. The cement pastes were prepared using the standard water of consistency of 0.255, 0.255, 0.258, 0.261, and 0.263, respectively. The fresh pastes, thus produced, were moulded into $2 \times 2 \times 2$-cm cubes. The pastes were first cured within the moulds at 100% relative humidity for 24 h, then the specimens were demoulded and cured under tap water for 3, 7, 14, and 28 days. At each hydration age, the hardened pastes were tested for bulk density, compressive strength, differential scanning calorimetery (DSC), and X-ray diffraction analysis (XRD). The results obtained were related as much as possible to the mechanical properties of the hardened cement pastes. The inclusion of limestone results in a notable improvement of the mechanical properties of the cement pastes containing limestone. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Curing; Microstructure; Mechanical properties; Physical properties

1. Introduction

The technical and economical aspects regarding the durability, workability, and strength characteristics of limestone-rich cement blends were reported in earlier studies [1]. Sprung and Siebel [2] reported a study on the evaluation of limestone and its suitability for the production of limestone-filled Portland cement. Concrete made with this type of blended cement has a sufficiently high frost resistance if the limestone content in the cement blend is not greater than 20 wt.%. Recently, the effect of limestone substitution on the microstructure of cement mortars was studied [3]. The results showed that the free lime content increases during the hydration of Portland cement and may be due to the leaching of Ca^{2+} from limestone. The effect of substitution of Hamra by limestone in pozzolanic cement was also investigated [4]. The results showed that the addition of limestone reduces the initial and final setting times as well as the total porosity; whereas the free lime and combined water contents increase with increasing limestone content. The physicochemical and thermal characteristics of lime–silica fume pastes were examined at room temperature with respect to the kinetics and mechanism of hydration as well as phase composition of the formed hydrates [5], where five lime–silica fume mixtures having different CaO/SiO_2 molar ratios of 0.8, 1.0, 1.3, 1.7, and 2.0 were hydrated for various time intervals of 0.5, 2, 6, and 24 h and 3, 7, 28, and 90 days. The results showed that the developed strength could be related to the constitution of the lime–silica mixture and the nature of the formed hydrates, where low-lime calcium silicate hydrate (CSH-I) represents the main hydration product of mixes having the initial CaO/SiO_2 ratios of 0.8, 1.0, and 1.3 while the high-lime CSH (CSH-II) represents the main product of the hydrated mixes made with CaO/SiO_2 ratios of 1.70 and 2.0. The changes occuring in the phase composition and microstructure of pozzolanic cement pastes containing activated kaolinite clay were investigated [6]. The results indicated that the thermally activated kaolinite clay prolonged the initial and final setting times and reduced the porosity. The formation of a more dense structure of the hardened paste leads to a high stability towards aggressive ions. In addition, the changes of the mechanical properties of four high-strength concrete caused by the addition of ground blast-furnace slag and silica fume

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were studied [7]. The results indicated that the mechanical properties of high-strength concrete were improved to a great extent at later ages when the cement used in concrete was replaced by slag and silica fume by 25 wt.%. The influence of the combined action of silica fume and limestone on strength development, porosity, pore structure, and morphological features in the system where 15 wt.% of cement was substituted by finely ground limestone was studied [8]. Silica fume was added in amounts of 0, 2, 5, 8, 11, and 15 wt.% on a cement basis, respectively. The results showed that the replacement of Portland cement by 15 wt.% of limestone caused a reduction in the compressive strength. When silica fume was added together with limestone, the mortars containing up to 8 wt.% of silica fume showed a considerable increase in the earlier compressive strength. After 28 days, hydration mortars containing more than 8 wt.% of silica fume show higher strength than mortar containing no silica fume. Also, the results showed that limestone considerably increases the total porosity of mortars. The effect of duration of initial curing on the mechanical properties and the chloride penetration of concrete containing limestone-blended cements were described [9]. Three concrete mixtures containing a Portland and two limestone-blended cements were subjected to three different initial curing regimens (full, wet, and air curing). Results show that the mechanical properties of concrete with limestone-blended cements are less sensitive to an early interruption of the moist curing. Also, curing cessation at 1 day results in a 14–22% of potential strength loss by these cements while this curing condition increases the loss of potential strength for plain concrete by about 32%.

2. Experimental

The materials used in this investigation were ordinary Portland cement (OPC, with fineness of 3050 cm^2/g) and limestone (fineness of 3500 cm^2/g). The chemical oxide composition of starting materials used is shown in Table 1. The OPC contains a fixed gypsum content of 5%. The practical size analysis of both OPC and limestone is given in Table 2. The OPC has been partially substituted by limestone with ratios of 0, 5, 10, 15, and 20 wt.%. The cement pastes were prepared using the standard water of consistency of 0.255, 0.255, 0.258, 0.261, and 0.263. The fresh pastes were moulded in 2 × 2 × 2-cm steel moulds. The pastes were first cured within their moulds at 100% relative humidity for 24 h, then the specimens were demoulded and cured under tap water for 3, 7, 14, and 28 days. After the predetermined curing time, the hydration of cement was stopped by grinding in acetone–methanol mixture [10]. The changes in the mechanical and physical properties of the specimens due to curing were examined for compressive strength, bulk density, differential scanning calorimetery (DSC), and X-ray diffraction analysis (XRD).

Table 1
The chemical composition (%) of the starting materials

Oxide	OPC	Limestone
CaO	62.78	51.45
SiO_2	20.22	5.42
Al_2O_3	5.34	0.59
Fe_2O_3	3.20	0.2
MgO	2.26	1
SO_3	2.38	0.17
Na_2O	0.29	0.24
K_2O	0.11	0.02

Table 2
Data of the grain size analysis in weight percentage of OPC and limestone

	Size fraction (in μm)				
Sample name	1000–500	500–250	250–125	125–63	< 63
OPC	0.12	16.52	59.3	23.66	0.4
Limestone	1.56	66.32	27.44	4.58	0.08

3. Results and discussion

Fig. 1 shows the water of consistency and setting times of cement pastes containing different proportions of limestone. The results show that the water of consistency increases with increasing limestone content in the cement blend. This result is related to the relatively high water absorption capability of limestone. Evidently, addition of limestone is associated with a notable decrease in the setting times (initial and final) as shown in Fig. 1. This result is mainly due to the formation of increased amounts of calcium carboaluminate hydrates, which have a high rate of formation at the early ages of the hydration process.

Fig. 2 shows the variation of bulk density with increasing time of hydration of the cement pastes containing different proportions of limestone. Evidently, the bulk

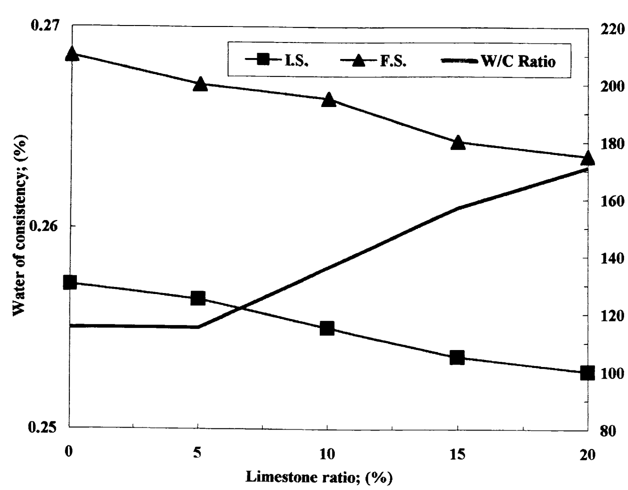

Fig. 1. Water of consistency and setting times of cement pastes containing different proportions of limestone.

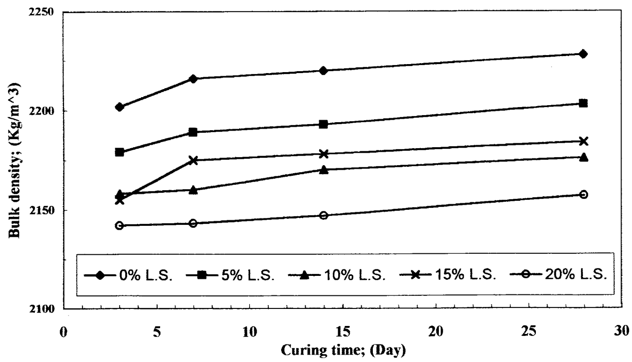

Fig. 2. The variation of bulk density with curing time for cement pastes containing different proportions of limestone.

density increases gradually with increasing time of hydration for all Portland cement–limestone mixtures up to 28 days. This is due to the increase in the amounts of the hydration products, which are deposited within the pore system with a consequent increase in the bulk density, which causes a decrease in the total porosity. Therefore, the values of bulk density for all hardened cement pastes increase with increasing curing time. The results of Fig. 2 also show that with increasing limestone content from 0% to 10%, the total porosity increases with a notable decrease in the values of bulk density. This effect results in an increase in the degree of hydration of Portland cement as a result of opening of the total pore system with increasing limestone replacement. On replacement of Portland cement by 15% limestone, however, there appeared an increase in the bulk density, which is associated with a decrease in the total porosity. This is accompanied by a notable decrease in the degree of hydration. At 20% replacement of Portland cement by limestone, the normal expected behavior takes place with an increase in the total porosity and consequent decrease in the bulk density; therefore, the degree of hydration shows a further increase.

Fig. 3 shows the compressive strength of cement pastes containing different proportions of limestone as a function of curing time. The results indicate that the compressive strength increases with the increasing of curing time for all pastes with some exceptional cases, where a reduction in the compressive strength values was observed after 28 days of hydration. As the curing time increases, more hydration products and more cementing materials are formed and deposited within the pore system. This leads to an increase in compressive strength of most of the cement pastes. The marked decrease in the strength of the hardened paste containing 15% limestone after 28 days of hydration is mainly attributed to a sort of pore opening with a slight increase in the bulk density (cf. Fig. 2). Therefore, the increased degree of hydration, as representing the main binding centers in the hardened pastes, as well as the partial opening of the pore system of the pastes containing limestone represent the two factors operating in opposite directions in affecting the strength characteristics of the hardened pastes. The net effect of these two factors may cause either an

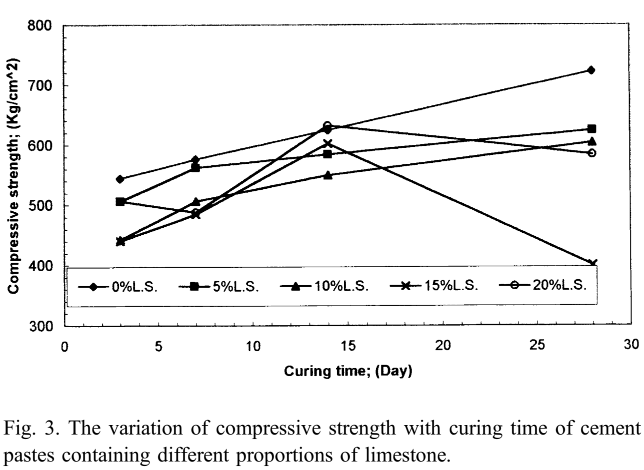

Fig. 3. The variation of compressive strength with curing time of cement pastes containing different proportions of limestone.

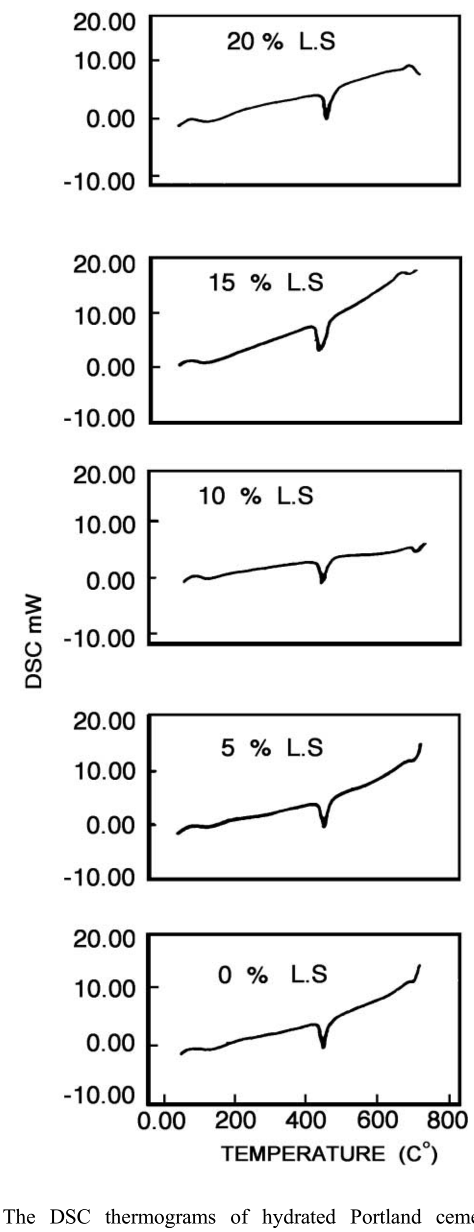

Fig. 4. The DSC thermograms of hydrated Portland cement pastes containing different proportions of limestone after 28 days of hydration.

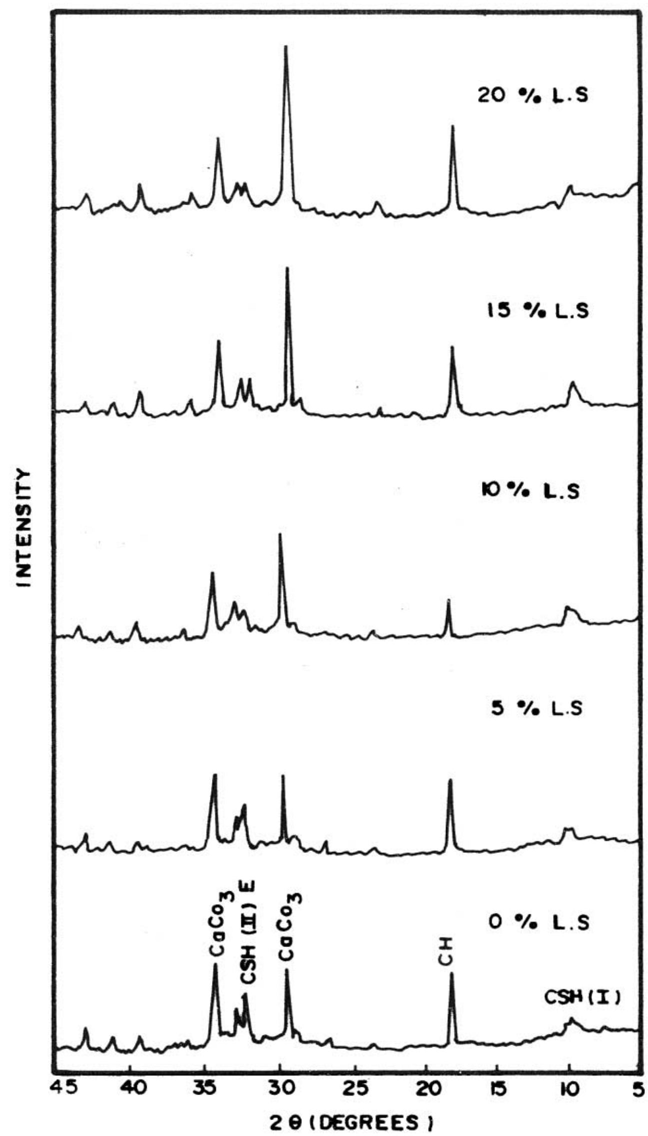

Fig. 5. The results of XRD analysis of hydrated Portland cement pastes containing different proportions of limestone after 28 days of hydration.

increase or a decrease in the strength values with increasing time of hydration.

The effect of limestone replacement on the various physicochemical properties of Portland cement paste could be clearly distinguished from the results of the DSC thermograms shown in Fig. 4. Obviously, the intensities of the main endothermic peaks characterizing the hydration products, namely, CSH and calcium hydroxide (CH), are decreased with increasing limestone replacement up to 10%, a result that is mainly associated with the relatively low stability of the formed hydrates for the hardened pastes containing 10% limestone. On further limestone replacements to 15% and 20%, the main characteristic peaks of cement hydrates (CSH and CH) appeared with relatively high intensity values. This effect is related to the relative increase in the total porosity of the hardened pastes containing 15% and 20% of limestone.

Fig. 5 shows the results of XRD analysis of hydrated Portland cement pastes containing different proportions of limestone after 28 days of hydration. The results indicated the formation of microcrystalline CSH, mainly as CSH-I and CSH-II, as well as the free lime, $Ca(OH)_2$, released as a result of cement hydration, as representing the main hydration products identified. The peaks characterizing limestone, $CaCO_3$, appeared also in the diffraction patterns.

4. Conclusions

The main conclusions derived from this study can be summarized as follows:

1. The standard water of consistency of Portland cement paste increases slightly with increasing limestone content of the paste.
2. Addition of limestone is associated with a notable decrease in the initial and final setting times.
3. The partial substitution of Portland cement with limestone results in an increase in the total porosity and consequent decrease in the bulk density of the pastes except for the paste containing 15% limestone.
4. The results of DSC are in good agreement with the results of bulk density and total porosity.

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