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The effect of clinker and limestone quality on the gas permeability, water absorption and pore structure of limestone cement concrete

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Abstract

In this paper the effect of clinker and limestone quality on the air permeability, water absorption and pore structure of limestone cement concrete is investigated. Portland limestone cements of different fineness and limestone content have been produced by intergrinding clinker, gypsum and limestone. Two clinkers with different chemical composition, mineralogical composition and strength development as well as three limestones, differing by their calcite, dolomite, quartz and clay contents, have been used. It is shown that the clinker quality significantly affects the gas permeability and sorptivity of the limestone cement concrete. Limestone cements with high C_3A and alkalis content seem to be more appropriate for improving the permeability properties of concrete. In addition, the effect of the limestone quality on the concrete permeability is not well established. The pore size distribution and more specifically the mean pore size affects the gas permeability and the sorptivity of the concrete. Finally it is concluded that, depending on the clinker quality and the cement fineness, limestone cement concrete, with an optimum limestone content, can give lower gas permeability and water absorption rate as compared with pure cement concrete.

Keywords: Concrete; Limestone cements; Clinker quality; Limestone quality; Gas permeability; Water absorption; Pore structure

1. Introduction

The use of Portland limestone cements seems to have many benefits, both technical and economical [1–5]. In addition, the European Prestandard prEN 197-1 identifies two types of Portland limestone cement containing 6–20% limestone (type II/A-L) and 21–35% limestone (type II/B-L), respectively [6,7]. It is expected that the future world production and use of Portland limestone cement will be significantly extended. The wide use of Portland limestone cement requires a thorough knowledge of the cement and concrete properties.

As far as the cement is concerned, the research work is focused on three areas. The first is the effect of limestone on the cement performance [4,5,8–11]. The second deals with the participation of limestone in the hydration reactions of clinker [12–17], while the third deals with the production process and specifically the co-grinding of clinker and limestone [8,18,19]. Although there is disagreement on many partial topics, the knowledge level is satisfactory and continuously extended.

As far as the limestone cement concrete is concerned, the few available references do not cover the wide area of concrete properties despite their remarkable quality [1,20,21]. Thus, in many areas the literature does not give answers and does not correspond sufficiently to the growing use of Portland limestone cement.

The present work deals with the concrete permeability which is one of the most important parameters influencing the durability of concrete and, ultimately, its performance. In this paper, the effect of clinker and limestone quality on the gas permeability, water absorption and pore structure of limestone cement concrete is investigated. This work is part of a project, developed in our laboratories, concerning the properties of limestone cement and concrete.

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2. Experimental

2.1. Materials and cement production

Two clinkers (C1, C2) with different chemical and mineralogical composition (Table 1) and three limestones have been used. The first (L1) has a higher content of calcite while the second and third samples contain significant amounts of dolomite (L2) and quartz/clay (L3), respectively. All the limestones have a high content of CaO and meet the requirements of the prEN 197-1 (Table 2).

The cements were produced by co-grinding clinker (C1 or C2), limestone (L1 or L2 or L3) and gypsum in a pro-pilot plant ball mill of 5 kg capacity. The gypsum percentage was kept constant (5% per clinker weight), resulting to a SO_3 content of 2.71 and 3.24% in pure cements containing clinker C1 and C2 respectively. The codes of the samples as well as their properties are given in Table 3.

Table 1
Chemical and mineralogical composition of clinkers

Chemical composition (%)			Mineralogical composition (%)		
	C1	C2		C1	C2
SiO_2	21.79	21.75	C_3S	65.15	57.99
Al_2O_3	5.13	5.74	C_2S	13.32	18.60
Fe_2O_3	3.59	2.06	C_3A	7.54	11.74
CaO	66.42	65.04	C_4AF	10.92	6.26
MgO	1.71	2.67	Moduli		
K_2O	0.55	1.24			
Na_2O	0.09	0.22	LSF	95.70	94.26
SO_3	0.52	1.08	SR	2.50	2.79
			AR	1.43	2.79
			HM	2.18	2.20

2.2. Preparation of specimens

The w/c ratio was 0.65, the cement content 300 kg/m^3 and the maximum aggregate size was 15 mm. The concrete mix proportions as well as the aggregate grading are given in Table 4. The slump of the mixes was in the range 110–130 mm (class S3 of EN 206), using plasticizer (Pozzolith 390N) where needed (LC4, LC12). The density of the fresh concrete varies from 2390 to 2375 kg/m^3.

The concrete specimens were cast in cylindrical steel moulds of 100 mm diameter and 200 mm height. The specimens remained in the moulds for 24 h and were

Table 2
Chemical composition of limestones and chemical requirements of prEN 197-1

Chemical composition (%)				Chemical requirements			
	L1	L2	L3	Permitted constituents	L1	L2	L3
SiO_2	0.61	0.10	8.25	$CaCO_3 > 75\%$	95.3	88.4	84.1
Al_2O_3	0.15	0.16	1.52	MBA < 1.2 g/100 g	0.1	0.1	0.2
Fe_2O_3	0.17	0.02	0.62	TOC < 0.2%	–	–	–
CaO	53.36	49.51	47.09				
MgO	1.47	4.99	0.45				
K_2O	0.02	0.01	0.30				
Na_2O	0.00	0.02	0.06				
LOI	43.54	44.35	37.50				

Table 3
Characteristics of the tested cements

Code	Clinker quality	Limestone quality	Composition (%)		Sp. surf. (cm^2/g)	Compr. strength 28d (N/mm^2)	Paste water demand (%)[a]
			Clinker	Limestone			
LC1	C1	–	100	0	3150	53.8	25.8
LC2	C1	L1	90	10	4010	49.0	25.1
LC3	C1	L1	80	20	4570	46.0	23.3
LC4	C1	L1	65	35	5100	34.0	23.0
LC5	C1	L2	80	20	4490	45.0	23.1
LC6	C1	L3	80	20	4800	49.0	24.0
LC7	C2	–	100	0	3220	44.0	28.7
LC8	C2	L1	90	10	3950	43.5	28.8
LC9	C2	L1	80	20	3960	37.5	28.0
LC10	C2	L1	80	20	4450	39.0	28.1
LC11	C2	L1	80	20	5060	40.0	28.3
LC12	C2	L1	65	35	5150	27.0	28.3
LC13	C2	L2	80	20	4510	36.0	28.2
LC14	C2	L3	80	20	4800	38.0	28.5

[a] Water demand: standard consistency of cement paste.

Table 4
Concrete mix proportions and aggregate grading

W/C	Cement content (kg/m^3)	Aggregate grading (%) size fraction (mm)				
		7–15	3–7	1–3	0.2–1	0–0.2
0.65	300	34	19	14	25	8

then demoulded and placed in water in the curing room for 28 days.

The drying procedure of the specimens is vital, since the gas permeability measurements are very sensitive to the level of moisture within concrete. Besides, the formation of cracks must be prevented. According to literature, oven-drying at 105°C, until a weight change of less than 0.1% over 24 h is observed, seems to be the most suitable curing of specimens prior to gas permeability measurements [22]. The drying period of these specimens was 3–5 days. The porosity and the sorptivity were measured in samples oven-dried at 105°C for 24 h.

2.3. Measuring techniques

A modified commercial triaxial cell for 100 mm diameter samples, operating to maximum cell pressure of 1.7 N/mm^2, was used for the determination of the gas (N_2) permeability of the specimens [23]. The outline of this device is presented in Fig. 1. The gas permeability measurements were carried out for inlet pressure of 0.3, 0.5, 0.7, 0.9 and 1.1 N/mm^2, outlet pressure of 0.1 N/mm^2 and cell pressure of 1.3 N/mm^2.

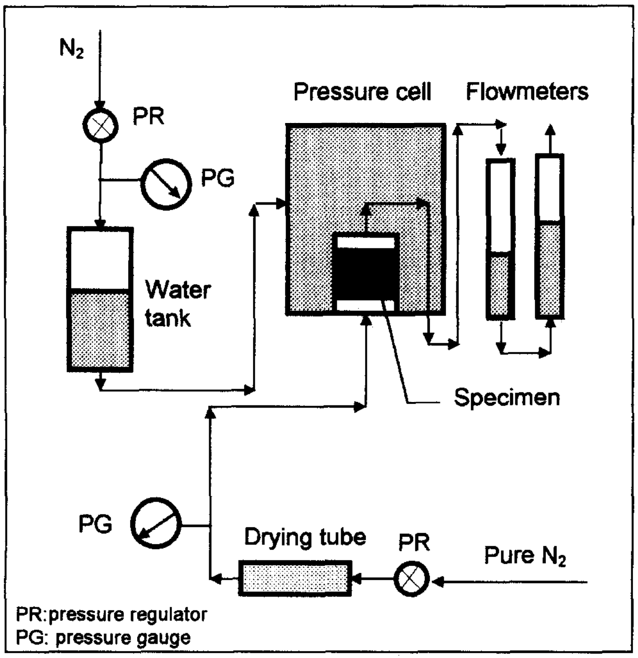

Fig. 1. Outline of the device used for the measurement of gas permeability.

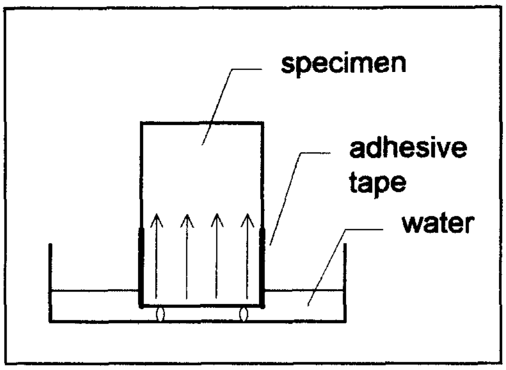

Fig. 2. Schematic diagram of water absorption test.

The sorptivity test was applied to a concrete cylinder of 100 mm diameter and 125 mm height [2,24]. A schematic diagram of water absorption test is given in Fig. 2. The lower part of the sides of the specimens adjoining the inflow face was sealed with adhesive tape. The specimen was rested on rods to allow free access of water to the inflow surface and the tap water level was kept at not more than 5 mm or so above the base of the specimen. The quantity of absorbed water was measured at 10, 20, 30, 45 and 60 min after starting the test.

The concrete pore structure was studied using mercury intrusion porosimetry. More specifically, the porosity of the specimen, as well as its pore size distribution, were measured with a Carlo Erba 2000 Hg porosimeter.

Thin sections of the concrete samples were examined by means of optical microscopy using transmitted ordinary and cross polarized light. This technique has been used in order to examine the homogeneity of the cement paste, the porosity of the samples and the aggregate–paste interface zone.

3. Calculation of gas permeability and sorptivity

The intrinsic permeability (K) is given from the relation [24,25].

$$K = \frac{2\mu L P_2 Q_2}{A(P_1^2 - P_2^2)} \qquad (1)$$

where

K = intrinsic permeability (m^2)
μ = dynamic viscosity (Ns/m^2)
L = specimen thickness (m)
Q_2 = outlet volume rate of flow (m^3/s)
A = cross-sectional area of the specimen (m^2)

P_1 = inlet pressure (N/m^2)
P_2 = outlet pressure (N/m^2)

For the gas permeability tests, the value of K was found at each inlet pressure (0.3, 0.5, 0.7, 0.9 and 1.1 N/mm^2). Due to gas slippage, it is inaccurate to determine the intrinsic permeability as the average of the calculated values of K at the different inlet pressure values. Therefore, a method mentioned in the literature [22–25], was applied in order to correct the taken values of gas permeability. Using regression analysis, the relationship between the gas permeability and the inverse of mean pressure ($1/P_m$ where $P_m = (P_1+P_2)/2)$) was determined. The coefficient b of the resultant equation $K = a(1/P_m)+b$ gives the correct value for gas intrinsic permeability of the sample (K_g). Figure 3 illustrates the relation between the K and $1/P_m$, as well as the followed procedure for the determination of the corrected value of the gas permeability (K_g) concerning the sample LC8.

The sorptivity test determines the rate of capillary-rise absorption by a concrete specimen. It has been shown that there exists a relation of the form [2,24]

$$\mathrm{i} = St^{0.5}$$

where

i = increase in mass (g/mm^2) since the beginning of the test per unit of cross-sectional area in contact with water; as the increase in mass is due to the ingress of water, 1 g is equivalent to 1 mm^3, so that **i** can be expressed in mm
t = time at which the mass is determined (min)
S = sorptivity (mm/min$^{0.5}$)

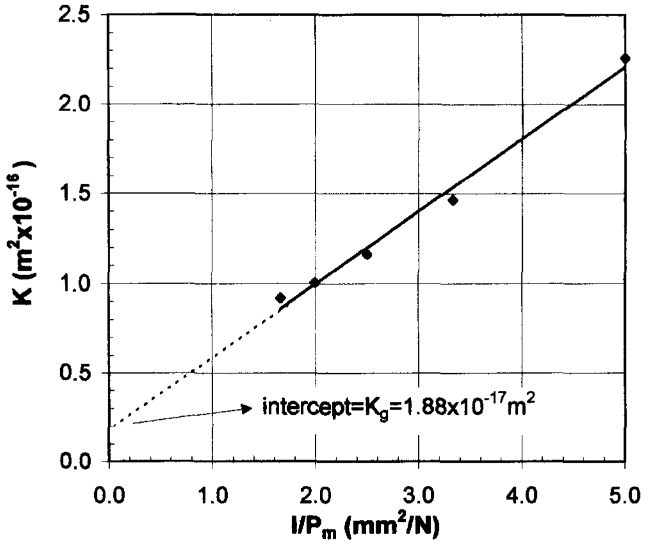

Fig. 3. Relation between the intrinsic permeability (K) and the inverse of mean pressure ($1/P_m$) for sample LC8. Followed procedure for the determination of the corrected value of gas permeability (K_g).

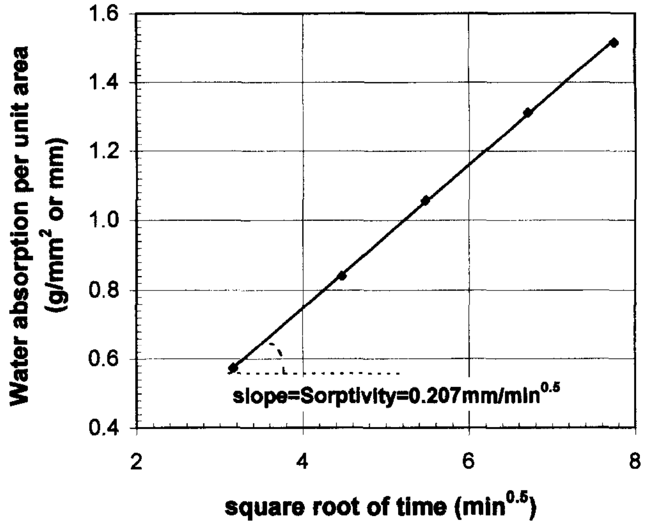

Fig. 4. Relation between water absorption per unit area and time for sample LC3. Sorptivity determination.

The above relation (2) shows that the cumulative water absorption (per unit area of the inflow surface) **i** increases as the square root of elapsed time t. Therefore the sorptivity S is defined as the slope of the **i** against $t^{0.5}$ and is determined using regression analysis. Figure 4 illustrates the relation between water absorption per unit area and time as well as the sorptivity calculation procedure concerning the sample LC3.

4. Results and discussion

Table 5 presents the intrinsic gas permeability (K_g), the sorptivity (S), the total porosity (P) and the mean pore size (d_m) of the tested specimens. The results given in Table 5 are the average values of three

Table 5
Gas permeability, sorptivity, porosity and mean pore size of the tested samples

Code	K_g (m^{2}x10^{-17})	S (mm/min$^{0.5}$)	P (%)	d_m (μm)
LC1	1.08	0.153	17.1	0.142
LC2	1.05	0.171	10.1	0.117
LC3	2.40	0.193	10.0	0.153
LC4	4.51	0.257	12.7	0.242
LC5	1.50	0.193	15.7	0.186
LC6	1.05	0.178	15.1	0.152
LC7	2.60	0.203	15.6	0.141
LC8	1.93	0.208	15.0	0.116
LC9	2.25	0.223	14.0	0.194
LC10	1.59	0.218	13.5	0.153
LC11	1.15	0.204	14.9	0.151
LC12	3.17	0.275	16.9	0.254
LC13	1.45	0.220	15.0	0.150
LC14	1.41	0.234	15.0	0.153

different specimens. Figures 5 and 6 present the effect of limestone content on the studied concrete properties. Figure 7 presents the effect of cement fineness on the concrete properties.

In general, concrete, based on cements containing clinker C1 and limestone up to 20%, exhibits higher or similar gas permeability values compared with the pure cement concrete. On the contrary, the relative samples, containing clinker C2, have lower gas permeability than the pure one. The addition of 35% limestone in the cement causes a definite increase of the concrete permeability. These samples, also, present lower compressive strength at 28 d. As far as the effect of the limestone quality is concerned, limestone L3 seems to

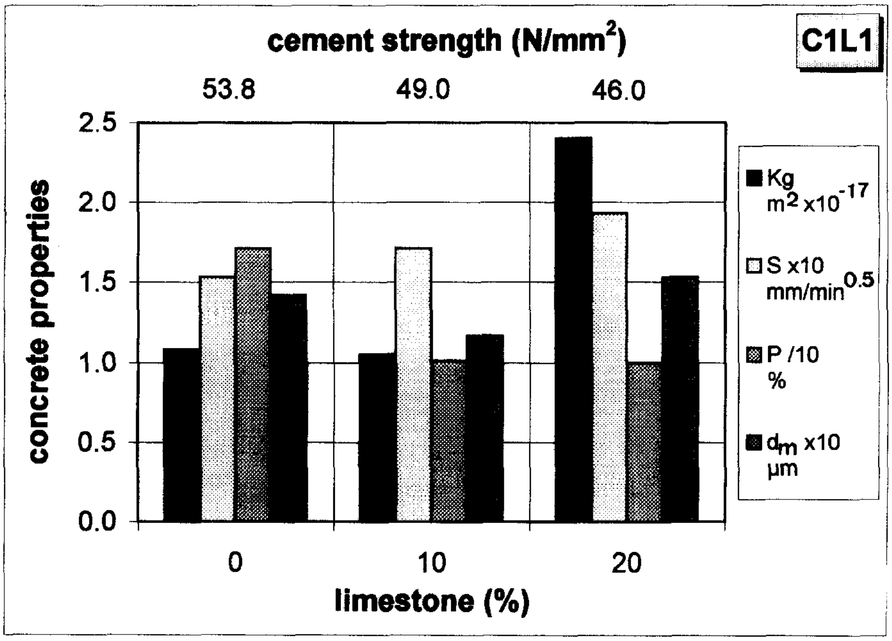

Fig. 5. The effect of limestone content on concrete properties (samples: LC1, LC2, LC3).

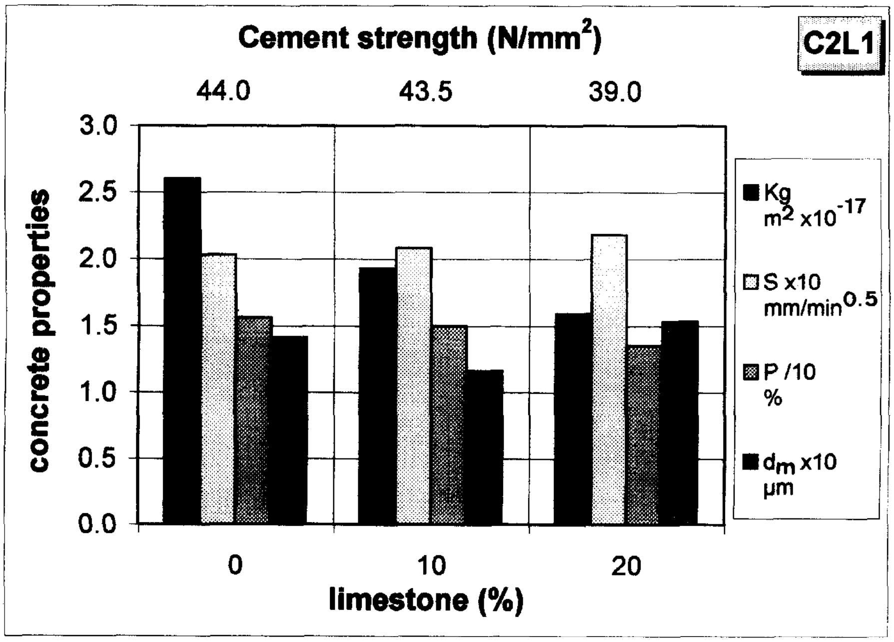

Fig. 6. The effect of limestone content on concrete properties (samples: LC7, LC8, LC10).

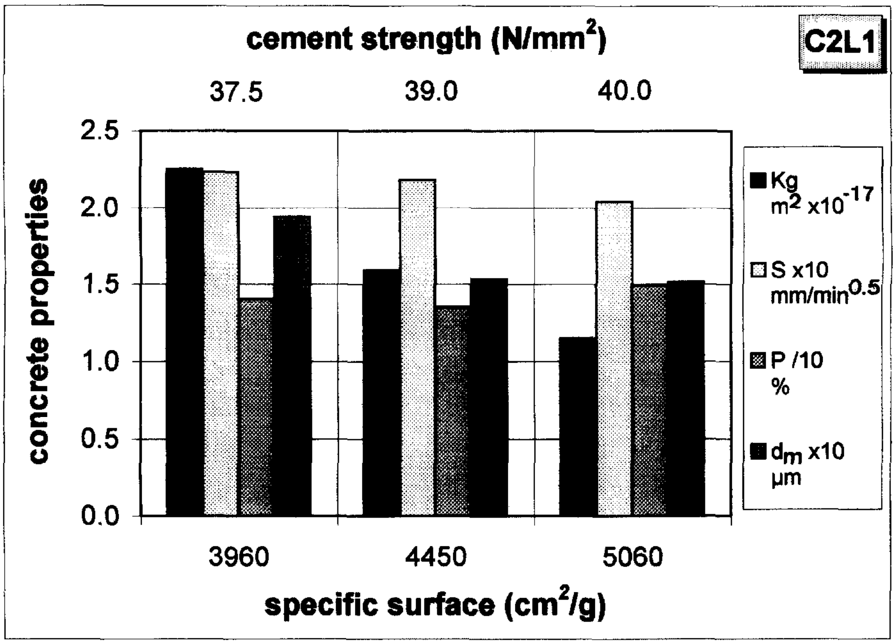

Fig. 7. The effect of cement fineness on concrete properties (samples: LC9, LC10, LC11)

improve the permeability of the samples based on clinker C1, while no differentiation is observed when clinker C2 is used. Finally, as expected, the increase of the cement fineness decreases the concrete permeability.

The sorptivity of the cements, containing up to 20% limestone, varies from 0.153 to 0.193 mm/min$^{0.5}$ when clinker C1 is used and from 0.203 to 0.234 mm/min$^{0.5}$ when clinker C2 is used. In these samples, the increase of the limestone content causes a slight increase of the sorptivity. Significant higher values are measured in cements containing 35% of limestone. The effect of the limestone quality on the water absorption rate cannot be well established according to the measurements presented in Table 5.

The concrete based on limestone cements, generally, has lower porosity than the pure ones. This is more clear in samples containing clinker C1. In any case, there is no obvious relationship between the porosity and the gas permeability as well as the sorptivity of the samples. The mean pore size seems to be affected by the limestone content. The cements containing 10% of limestone have lower mean pore size compared with the pure ones. Further increase of the limestone content causes a relative increase of the mean pore size. The cements containing 35% limestone indicate extremely high values of mean pore size. The mean pore size does not seem to be related to the limestone quality while it is positively affected by the fineness of the cement (LC9–LC11).

The Pearson correlation analysis ($\alpha = 0.05$) showed that K_g and S are correlated with the mean pore size while no correlation is established between K_g, S and percentage porosity (Table 6). This is due to the existence of pores of different kinds, some of which contribute to the permeability and some of which do not.

The examination of the samples by means of O.M. has led to the pictures presented in Fig. 8. The images are selected to be representative as far as the condition of the cement paste and the interface of paste–aggregate are concerned.

In all samples, the cement paste appears to be uniform in colour. It indicates that water is well distributed resulting in a homogeneous mixture. Besides, the entrained air is uniformly distributed in the form of small rounded bubbles [Figs 8(a) and (b)].

In the samples made from clinker C2 and having limestone content over 10%, precipitation of hydration products on the aggregate surface takes place, as it is indicated by the white line in Figs 8(c) and (d). The XRD analysis of limestone cement pastes confirms the formation of ettringite and carboaluminate hydrates, but it is not possible to determine the exact nature of the precipitated compounds. As this participation is not observed in the relative samples based on clinker C1 [Fig. 8(e)], it is probably attributed to the higher content of C_3A in clinker C2.

Table 6
Pearson product–moment correlation's matrix ($r_c = 0.457$, $\alpha = 0.05$)

	Porosity	Mean pore size
Gas permeability (K_g)	−0.18	0.60
Sorptivity (S)	0.17	0.75

In the sample LC4 (C1, 35% L1), large air voids entrapped in concrete are observed as irregular, angular and white areas [Fig. 8(f)]. This is probably due to the fact that the cement fineness has been

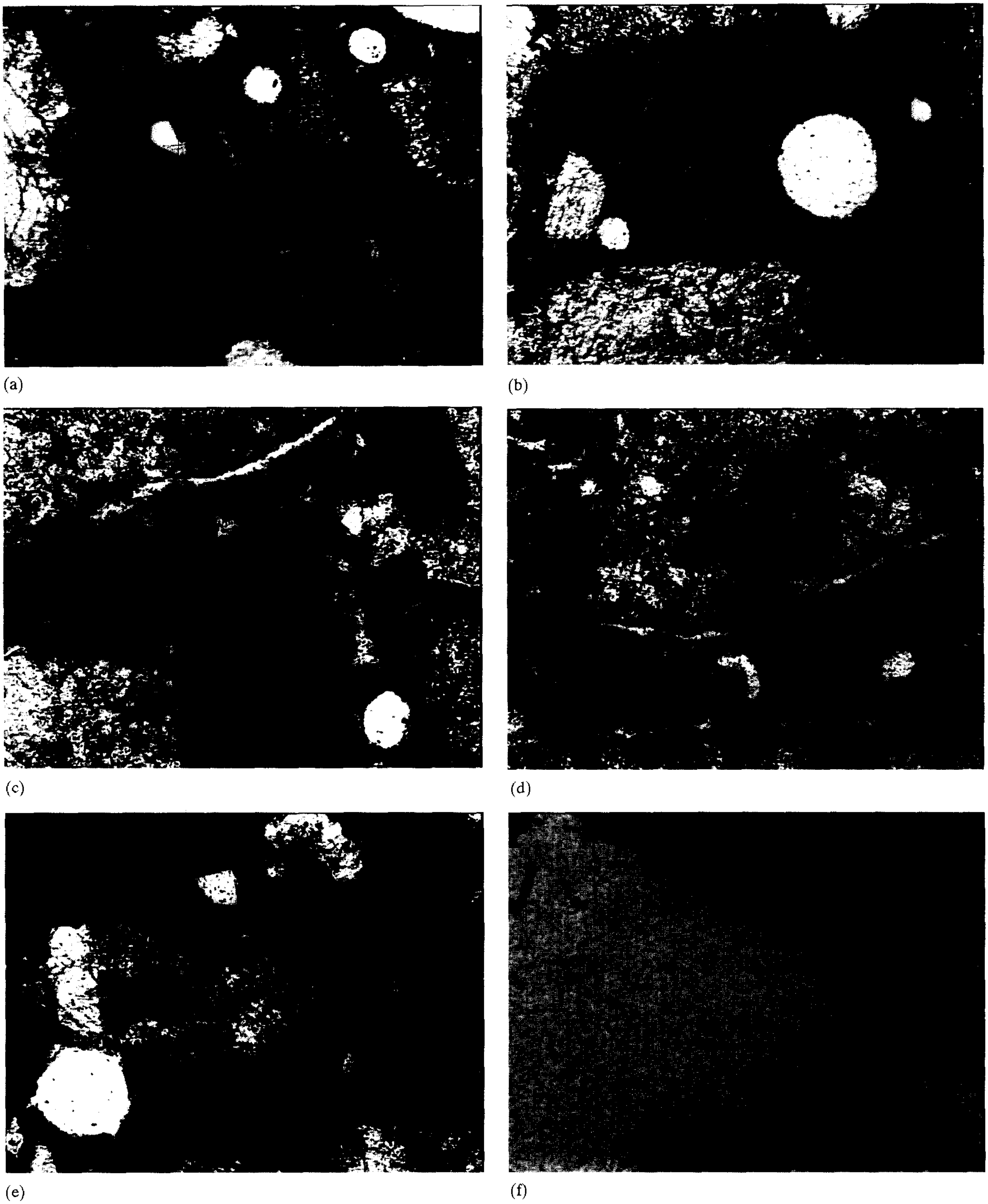

Fig. 8. Thin sections of concrete samples. (a) LC1(× 5); (b) LC2(× 5); (c) LC10(× 10); (d) LC13(× 10); (e) LC6(× 10); (f) LC4(× 10).

increased while the size distribution of aggregates was kept constant.

With the exception of the above remarks, the samples appear to have a similar picture. It seems that, although O.M. provides very useful information on the structure of the concrete, the observed features cannot be directly related to the gas permeability of the samples.

5. Conclusions

The following conclusions can be drawn from the present study:

- The clinker quality affects significantly the gas permeability and sorptivity of the limestone cement concrete. The effect of the limestone quality on the concrete permeability is not well established.
- Limestone additions can improve the permeability properties of the concrete, especially in cements having high C_3A content.
- The pore size distribution, and more specifically the mean pore size, affects the gas permeability and the sorptivity of the concrete.
- In concrete containing cement with clinker of high C_3A value, hydration products precipitate on the aggregate surface but it does not affect the permeability properties of the concrete.

In any case, it is concluded that, depending on the clinker quality and the cement fineness, limestone cement concrete, with an optimum limestone content, can give lower gas permeability and water absorption rate compared with pure cement concrete.

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