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An analysis of the properties of Portland limestone cements and concrete

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Abstract

In this paper the main factors affecting the properties of Portland limestone cements are discussed while the hydration behavior of limestone cements is examined. In addition, the intergrinding process, concerning the production of the limestone cements, is studied. Finally the properties and the behavior of limestone cement concrete as well as the corrosion behavior of limestone cement mortar are investigated. It is concluded that the fineness of clinker and limestone is strongly connected with the limestone content and the fineness of the cement. The limestone cements indicate satisfactory strength and generally demand less water than the relative pure cements. The limestone addition improves the clinker reactivity and the exploitation of its hydraulic potential. The Portland limestone cements indicate competitive concrete properties and improve the corrosion performance of the concrete.

Keywords: Portland limestone cement; Intergrinding; Cement properties; Hydration; Concrete properties; Corrosion

1. Introduction

The use of Portland limestone cements seems to have many benefits, both technical and economical [1–3]. In addition, the European Standard EN 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 [4]. It is expected that the future world production of Portland limestone cement will be continuously increased. The wide use of 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 one is the effect of limestone on the cement performance [3,5–8]. The second one deals with the participation of limestone in the hydration reactions of clinker [9–19], while the third one with the production process and specifically the intergrinding of clinker and limestone [5,20–22]. Although there is a disagreement in many partial topics, the knowledge level is satisfactory and continuously extended.

As far as the limestone cement concrete is concerned, the few available references are focused on two areas. The first one is the effect of limestone on the concrete properties and behavior [23–29]. The second one deals with the "thaumasite problem", correlated with the use of limestone cement concrete and calcareous aggregates. Recent research work shows that Portland limestone cement pastes are susceptible to the thaumasite formation, due to sulfate attack at 5 °C, after only a few months exposure to sulfate solutions [30–35].

In this paper the main factors affecting the properties of Portland limestone cements are evaluated, while the hydration behavior of the limestone cements is examined. In addition, the intergrinding process, concerning the production of the limestone cements, is studied. Finally the properties and the behavior of limestone cement concrete as well as the corrosion behavior of limestone cement mortar are investigated. This work is a part of a project, developed in our laboratories, concerning the properties of limestone cement and concrete.

2. Intergrinding of clinker and limestone

Ordinary Portland clinker of industrial origin and limestone of high calcite content ($CaCO_3$: 95.3%) were

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Table 1
Chemical and mineralogical composition of clinker

Chemical composition (%)		Mineralogical composition (%)	
SiO_2	21.79	C_3S	65.15
Al_2O_3	5.13	C_2S	13.32
Fe_2O_3	3.59	C_3A	7.54
CaO	66.42	C_4AF	10.92
MgO	1.71	*Moduli*	
K_2O	0.55	LSF	95.70
Na_2O	0.09	SR	2.50
SO_3	0.52	AR	1.43
		HM	2.18

used (Tables 1 and 2). Four clinker/limestone mixtures, containing 10%, 20%, 30% and 40% limestone, respectively, were ground to four different fineness each one in a pro-pilot plant ball mill (16 samples CL*i-j* of Table 3).

In order to determine the particle size distribution of clinker and limestone after their intergrinding, a sedimentation method (Andreasen apparatus) was used. A sample of each mixture was well dispersed in absolute ethyl alcohol. At predefined time intervals samples were withdrawn using a pipet. The selected time intervals correspond to particle sizes less than 32, 16, 8 and 4 μm. The alcohol was removed by drying and the limestone content was determined by measuring the loss of ignition (LOI) at 1000 °C. Finally, the particle size distribution of clinker and limestone was computed.

The Rosin–Rammler distribution was used for describing the particle size distribution of the interground samples. The values of the uniformity factor (n) have been computed (Table 3). It is seen that the increase of the limestone content, as well as the increase of the cement fineness, leads to wider particle size distribution.

The particle size distribution of the clinker is significantly different than that of the mixture. The limestone is concentrated in the fine fractions (<8 μm), while the clinker is concentrated in the coarser fractions. Fig. 1 presents limestone and clinker contents of the different size fractions. It is seen that the limestone content in the fraction with size less than 4 μm is 24.8% and the clinker content is 75.2%. It must be noticed that the initial sample contains 20% limestone and 80% clinker. However, the size fraction greater than 56 μm contains only 12% limestone.

According to data given in Table 3, the increase of the mixture fineness influences the clinker fineness but not to a significant degree. In addition, a limestone content over 30% obstructs the grinding of both clinker and limestone. The samples containing 40% limestone have reduced clinker and limestone finenesses, compared with those containing 30%.

All the above results show that the particle size distribution of the Portland limestone cements, as well as the finenesses of clinker and limestone, is strongly connected with the limestone content and the fineness of the mixture. In order to produce a Portland limestone cement of desired properties, the grinding to higher fineness (compared with the pure cements) is the easy way, but the proper one is to define the optimum fineness level, taking into account the limestone content and the grinding properties of the components.

3. Properties of Portland limestone cements

Portland limestone cements were produced by intergrinding of clinker (Table 1), limestone (Table 2) and gypsum in a pro-pilot plant ball mill of 5 kg capacity. The composition and the properties of the cements tested are given in Table 4.

Fig. 2 shows the influence of limestone content on the strength development of CL-c-45. It is observed that the addition of 10% limestone does not significantly alter the compressive strength at any age of samples having fineness up to 3800 cm^2/g. Further increase of the cement fineness leads to the production of limestone cements having compressive strength lower than the pure ones. In general, the influence of the fineness on the compressive strength is stronger for limestone addition up to 10%.

Table 4 also presents the cement paste water demand, the setting time and the expansion of the tested samples. The limestone cements, despite their higher fineness, generally demand less water than the relative pure cements. In limestone cements containing 10% limestone, there is a reduction of water demand from 26% to 25%. The increase of the limestone content to 20% and 35% causes a decrease of the water demand to 23.5–22.8%. The effect of limestone on the paste water demand of cements can be attributed to the different particle size distributions of the samples. Limestone cements despite their higher fineness have wider particle size distributions – lower value of uniformity factor (n) of the Rosin–Rammler distribution–compared with Portland cements (Table 4). This is due to the intergrinding of an easy-ground material such as limestone with the clinker.

Table 2
Chemical composition (%) of limestone

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
0.61	0.15	0.17	53.36	1.47	0.02	0.00	43.54

Table 3
Particle size distribution (passing %) of clinker, limestone and mixture

d (μm)	CL10-A[a] ($S = 2830$ g/cm^2, $n = 0.97$)[c]			CL10-B ($S = 3580$ g/cm^2, $n = 0.95$)			CL10-C ($S = 4050$ g/cm^2, $n = 0.80$)			CL10-D ($S = 4420$ g/cm^2, $n = 0.76$)		
	C	L	CEM[b]	C	L	CEM	C	L	CEM	C	L	CEM
56	86.53	92.11	87.10	91.39	95.28	91.80	91.14	95.56	91.60	91.68	96.49	92.20
32	73.68	82.74	74.60	73.75	81.92	74.60	72.35	82.46	73.40	73.79	85.81	75.10
16	46.71	56.48	47.70	52.87	61.76	53.80	54.06	65.95	55.30	55.19	70.93	56.90
8	27.77	35.94	28.60	31.16	39.18	32.00	37.68	49.41	38.90	38.90	53.60	40.50
4	14.76	20.07	15.30	17.44	22.79	18.00	23.45	32.57	24.40	26.74	38.33	28.00
d (μm)	CL20-A ($S = 3220$ g/cm^2, $n = 0.90$)			CL20-B ($S = 3890$ g/cm^2, $n = 0.84$)			CL20-C ($S = 4360$ g/cm^2, $n = 0.79$)			CL20-D ($S = 4800$ g/cm^2, $n = 0.75$)		
	C	L	CEM	C	L	CEM	C	L	CEM	C	L	CEM
56	84.42	91.01	85.10	87.40	93.14	88.00	86.28	93.16	87.00	87.61	94.83	88.40
32	73.51	83.17	74.50	73.12	82.42	74.10	72.65	83.69	73.80	72.64	85.97	74.10
16	51.61	62.18	52.70	54.44	64.54	55.50	57.18	69.79	58.50	59.43	75.52	61.20
8	32.15	41.39	33.10	37.50	47.06	38.50	40.59	53.11	41.90	42.93	58.14	44.60
4	20.10	26.91	20.80	23.76	30.79	24.50	25.77	35.63	26.80	27.15	38.52	28.40
d (μm)	CL30-A ($S = 3850$ g/cm^2, $n = 0.88$)			CL30-B ($S = 4780$ g/cm^2, $n = 0.80$)			CL30-C ($S = 5210$ g/cm^2, $n = 0.76$)			CL30-D ($S = 5690$ g/cm^2, $n = 0.70$)		
	C	L	CEM	C	L	CEM	C	L	CEM	C	L	CEM
56	81.90	89.64	82.70	83.82	91.21	84.60	85.95	93.06	86.70	87.16	94.71	88.00
32	73.96	83.99	75.00	74.27	84.05	75.30	72.30	83.67	73.50	72.17	85.95	73.70
16	53.66	64.69	54.80	57.29	67.81	58.40	60.97	73.58	62.30	62.74	78.58	64.50
8	35.47	45.43	36.50	39.45	49.42	40.50	42.76	55.46	44.10	44.42	59.53	46.10
4	23.31	30.95	24.10	24.73	32.02	25.50	27.33	37.44	28.40	28.72	40.25	30.00
d (μm)	CL40-A ($S = 4310$ g/cm^2, $n = 0.85$)			CL40-B ($S = 5410$ g/cm^2, $n = 0.68$)			CL40-C ($S = 5900$ g/cm^2, $n = 0.69$)			CL40-D ($S = 6500$ g/cm^2, $n = 0.67$)		
	C	L	CEM	C	L	CEM	C	L	CEM	C	L	CEM
56	77.31	82.21	79.30	82.13	87.01	84.10	86.10	90.32	87.80	86.96	91.65	88.90
32	62.64	69.44	65.40	67.94	74.77	70.70	70.26	77.07	73.00	70.92	77.89	73.80
16	47.89	55.05	50.80	55.17	62.42	58.10	57.51	64.70	60.40	59.84	67.72	63.10
8	26.93	32.76	29.30	37.54	44.12	40.20	40.25	47.09	43.00	40.76	48.84	44.10
4	13.50	17.44	15.10	23.44	28.29	25.40	25.76	30.83	27.80	26.93	33.87	29.80

[a] CL*i*-*j*: C: clinker, L: limestone, *i*: limestone content (%), *j*: grinding time (A = 35 min, B = 50 min, C = 65 min, D = 85 min).
[b] CEM: mixture (cement).
[c] *S*: specific surface (Blaine), *n*: uniformity factor of RR distribution.

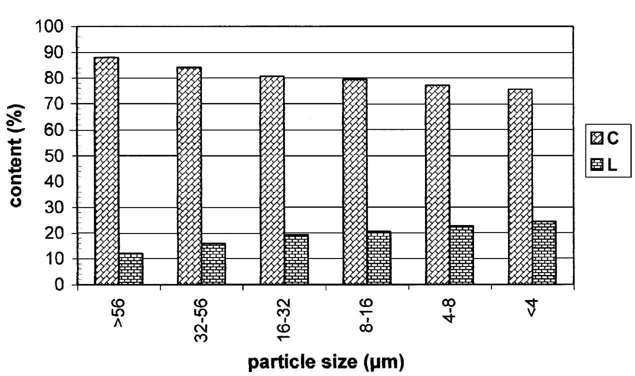

Fig. 1. Limestone (L) and clinker (C) content in different size fractions after their intergrinding (mixture fineness: 3890 cm^2/g, limestone content: 20%).

The initial and final setting times of limestone cements (Table 4) are similar to those of the Portland cements. The soundness of the limestone cements (Table 4) is satisfactory. The expansion measured according to the Le Chatelier process varies from 0.5 to 1.5 mm while the limit according to EN 197-1 is 10 mm.

4. Hydration of Portland limestone cements

Limestone cements containing 0%, 10%, 20% and 35% w/w limestone were examined (samples C-45, CL-10-45, CL-20-45 and CL-35-45 of Table 4). The properties of the studied cements are given in Table 4.

Pastes were prepared by mixing solid and carbon dioxide-free distilled water in polyethylene vials subjected

Table 4
Composition and properties of Portland limestone cements

Sample[a]	Fineness		n[b]	Compressive strength (N/mm^2)				Paste water dem. (%)	Setting time (min)		Exp. (mm)
	S_b (cm^2/g)	Residue at 32 μm (%)		1 d	2 d	7 d	28 d		Initial	Final	
Portland cements											
C-38	2830	29.0	1.06	11.4	20.6	36.1	50.2	26.0	160	215	
C-45	3150			14.5	24.7	40.6	53.8				
C-52	3390	21.2	0.99	16.6	28.6	42.2	57.2	25.7	130	190	
C-60	3710	20.2	0.96	19.0	31.0	46.9	58.2	25.7	110	145	0.5
Portland limestone cements											
CL-10-38	3320	26.4	0.96	11.4	20.8	39.1	49.5	25.4	145	190	
CL-10-45	3830	22.3	0.95	15.0	25.9	44.0	53.3	25.0	145	195	
CL-10-52	4060			14.5	24.6	41.3	54.1				
CL-10-60	4410	19.1	0.92	14.6	25.3	44.1	55.0	25.1	120	170	1.0
CL-20-38	3990	27.5	0.89	10.9	20.6	36.2	44.6	23.5	105	180	
CL-20-45	4330	24.5	0.84	11.0	21.4	37.6	45.9	23.2	110	180	
CL-20-52	4670			12.8	22.5	37.9	45.6				
CL-20-60	4830	23.1	0.79	13.2	24.0	39.0	46.6	23.4	115	185	0.5
CL-35-38	4790	26.6	0.77	7.8	15.4	27.6	34.3	22.9	105	165	
CL-35-45	5150	22.6	0.78	7.5	15.9	27.2	33.5	22.8	100	165	
CL-35-52	5430			8.6	15.8	26.4	35.2				
CL-35-60	5850	19.5	0.81	9.1	17.1	28.9	35.9	23.1	90	150	1.0

[a] Limestone cement: CL-c-t, C: clinker, L: limestone, c: limestone (%), t: grinding time (min).
[b] n: Uniformity factor of RR distribution.

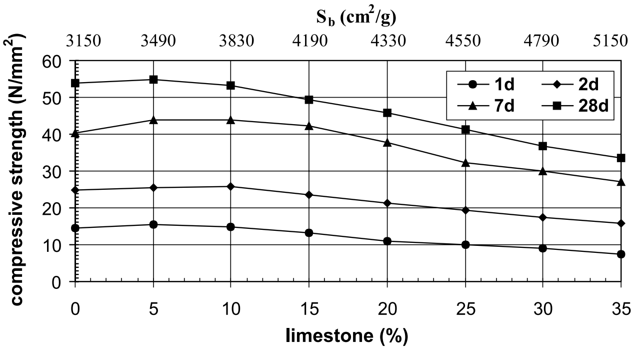

Fig. 2. Influence of limestone content on cement strength development (grinding time: 45 min).

to rotation from time to time. The water-to-cement ratio used is 0.3. After periods of 1, 2, 7 and 28 days, the samples were dried in vacuum for 24 h and subjected to X-ray diffraction.

Thermogravimetric analysis (TGA) was used for the determination of non-evaporable water and calcium hydroxide content in dried cement pastes, using a TA Instruments Thermal Analyst 3000. The samples (~50 mg) were heated over the range 20–900 °C at a constant rate of 15 °C/min in an atmosphere of carbon dioxide-free nitrogen, flowing in 90 cm^3/min.

Table 5 shows the hydration products in the C-45 and CL-35-45 pastes. In C-45 pastes, ettringite is gradually transformed into monosulfate. In CL-35-45 pastes, the formation of ettringite is delayed and monocarboaluminate is preferably formed instead of monosulfate. Calcium aluminate hydrates ($3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O$ and $Ca_2Al_2O_5 \cdot 8H_2O$) are detected in C-45 pastes but not in limestone pastes, probably because of the dilution of the samples by limestone.

Concerning the CH and non-evaporable water determinations (Table 6), the higher content of bound water, in the pastes made from limestone cements, indicates that limestone improves the clinker reactivity and the exploitation of its hydraulic potential. This effect may be related to the structure modification of the hydration products as well as to the nucleating action of the finely ground limestone. The increase of $Ca(OH)_2$ content in pastes of limestone cement indicates an acceleration of calcium silicates hydration, especially in cement containing 10% limestone.

5. Properties of limestone cement concrete

The composition and properties of the tested cements are given in Table 7. Portland limestone cements were produced by intergrinding of clinker, limestone and gypsum in a pro-pilot plant ball mill of 5 kg capacity. The cements LC1–LC4 contain 0%, 10%, 15% and 20% limestone, respectively, and have the same 28d compressive strength (48–51 N/mm^2, strength class 42.5R of EN 197-1). The cement LC5 contains 35% limestone (32.5R of EN 197-1).

The concrete production was carried out in a mixer of 50 l capacity. The mix proportions and the aggregate grading are given in Table 8.

The concrete properties of the tested cements are given in Table 9. The mixes with limestone cement,

Table 5
Hydration products in samples C-45 and CL-35-45

Hydration products	1 d		2 d		7 d		28 d	
	A[a]	B[a]	A	B	A	B	A	B
$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O$	√	Little	√	√	√	√	√	√
$Ca_3Al_2O_6 \cdot CaSO_4 \cdot 13H_2O$	Little		√	√	√	√	√	√
$Ca_4Al_2O_6 \cdot CO_3 \cdot 11H_2O$				√		√		√
$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O$					√		√	
$Ca_6Al_2O_6(OH)_6 \cdot 32H_2O$					√		√	
$Ca_2Al_2O_5 \cdot 8H_2O$							√	

[a] A: C-45, B: CL-35-45.

Table 6
Non-evaporable water and $Ca(OH)_2$ content in limestone cement pastes

Sample	Non-evaporable water (%)			$Ca(OH)_2$ (%)		
	2 d	7 d	28 d	2 d	7 d	28 d
C-45	18.72	23.72	24.44	9.43	14.55	16.05
CL-10-45	21.75	24.46	24.78	9.10	20.59	19.80
CL-20-45	20.22	26.62	27.75	8.95	18.52	18.35
CL-35-45	19.01	28.65	29.36	9.98	16.03	16.13

Table 7
Characteristics of the tested cements

Sample	Composition (%)		Sp. surf. (cm^2/g)	Compressive strength (N/mm^2)			
	Clinker	Limestone		1 d	2 d	7 d	28 d
LC1	100	0	2600	11.9	21.3	35.3	51.1
LC2	90	10	3400	11.2	20.9	36.3	47.9
LC3	85	15	3660	12.9	22.7	37.7	48.5
LC4	80	20	4700	14.9	24.3	38.0	48.1
LC5	65	35	5300	9.8	17.0	26.2	32.9

Table 8
Concrete mix proportions and aggregate grading

Sample	W/C	Cement (kg/m^3)	Aggreg. (kg/m^3)	Aggregate grading (%)					
				Size fraction (mm)					
				30–15	15–7	7–3	3–1	1–0.2	<0.2
LC1–LC4	0.70	270	~1940	30	22	8	15	15	10
LC5	0.62	330	1905	30	22	8	15	15	10

Table 9
Concrete properties

Sample	Slump (mm)	Flow (mm)	Unit weight (kg/m^3)	Compressive strength (N/mm^2)	
				7 d	28 d
LC1	130	460	2400	26.65	31.85
LC2	120	440	2395	21.90	27.40
LC3	120	420	2400	22.45	27.30
LC4	110	420	2394	22.05	28.00
LC5[a]	110	400	2390	21.60	26.55

[a] Plasticizer (Pozzolith 390N).

although their higher fineness, indicate a satisfactory workability. The slump of the mixes was in the range 110–130 mm (class S3 of EN 206). A plasticizer (Pozzolith 390N) was used in concrete containing cement with 35% limestone (LC5). Concerning the compressive strength, all the mixes belong to the class C20/25 of EN 206.

6. Corrosion behavior of limestone cement mortar

The cements of Table 7 have been used for the relative tests. The W/C ratio was 0.50 and the calcareous sand:cement ratio was 3:1. Prismatic specimens ($80 \times 80 \times 100$ mm^3) were constructed and four cylindrical steel bars (12×100 mm^2) were embedded in each one. Each bar has a properly attached copper wire. Both, the top surface of all specimens and the part of steel bars which protrudes over the concrete, are covered with an epoxy glue to protect the bars from atmospheric corrosion.

The specimens were partially immersed in a 3 wt% NaCl solution, up to a height of 25 mm, in order to accelerate the corrosion process. After immersing all specimens in the corrosive solution, the following measurements were carried out: (a) gravimetric mass loss of the rebars after 9 and 12 months exposure, (b) mean carbonation depth, after 9 and 12 months, using phenolphthalein indicator, anointed across a vertical section of the specimen and (c) porosity of the specimens, after 9 months exposure, using a Carlo Erba 2000 Hg porosimeter. It must be noted that the advanced investigation of steel rebars corrosion with strain gauges is the subject of a future study [36].

Fig. 3 presents the mass loss of rebars (average value of four specimens), expressed as mg/cm^2 of surface of the rebars. There is an explicit decrease of corrosion in specimens with limestone. The mass loss of rebars decreases as the limestone content increases up to 20%. It must be noticed that the corrosion rate of LC4 is three times lower than LC1 (0.030 mg/cm^2 month against 0.093 mg/cm^2 month). The mass loss of specimens with

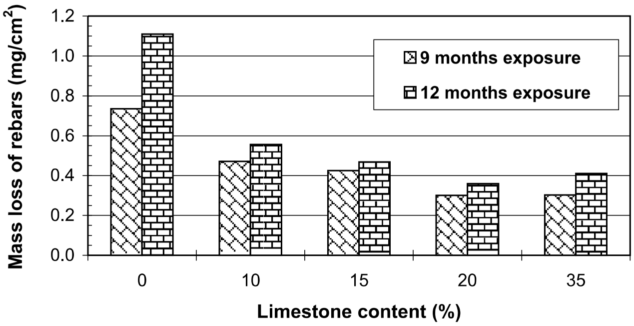

Fig. 3. The effect of the limestone content on the mass loss of rebars.

20% and 35% limestone is the same, in the frame of statistical analysis.

Concerning the carbonation depth, all types of Portland limestone cements used did not show any carbonation after exposure times of 9 and 12 months. The Portland cement specimen had a carbonation depth of 3–5 mm. In addition, the specimens with limestone had lower porosities compared with those of the Portland cement specimen (LC1: 15.3%, LC2: 11.6%, LC3: 12.2%, LC4: 12.5%, LC5: 13.1%).

Thus, the corrosion behavior of the limestone cement concrete may be attributed to the lower total porosity and the negligible carbonation depth. The above phenomena lead to a significant reduction of the corrosion potential resulting in reduced mass loss of the used rebars.

7. Conclusions

The following conclusions can be drawn from the present study:

- The particle size distribution of the Portland limestone cements, as well as the fineness of clinker and limestone, is strongly connected with the limestone content and the fineness of the cement.
- The limestone cements indicate satisfactory strength and generally demand less water than the relative pure cements.
- The limestone addition improves the clinker reactivity and the exploitation of its hydraulic potential.
- The Portland limestone cements indicate competitive concrete properties and improve the durability of the concrete.

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