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Portland-limestone cements. Their properties and hydration compared to those of other composite cements

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Abstract

The new European Standard EN 197-1 emphasizes the development of composite cements. In Greece a variety of pozzolanic and/or hydraulic materials are used as cement main constituents. Until now, limestone could be used only as a filler (up to 3% w/w), but since 2001 (application of EN 197-1) it can also be used as a main cement constituent. In this work a comparison between limestone and some of the materials that are already used in Greece is presented. An ordinary Portland cement and three Portland-composite cements containing limestone, natural pozzolana or fly ash were produced. The grinding process was designed in order to produce cements of the same 28 day compressive strength. The mechanical and physical properties of the cements were measured and hydrated products, formed after 1–28 days, were identified by means of XRD. The composite cements present significant differences as far as the clinker fineness, the development of the strength, the water demand and the hydration rate is concerned. The production of Portland-limestone cements seems to be very challenging, due to the satisfactory properties of the limestone cements as well as the low cost and the high availability of limestone in Greece.

Keywords: Portland-limestone cement; Natural pozzolana; Fly ash; Cement properties; Hydration products

1. Introduction

The development of Portland-composite cements, using traditional and up-to-date mineral additions, is considered to be state of art on cement production. The initial aim was of course the reduction of cost but further objectives have been added, such as the improvement of performance, the energy saving, the use of conventional raw material or industrial by-products and the ecological benefits [1–3].

The European Standard EN 197-1 (2000) identifies type II cements that may contain various materials as main constituents, in percentages ranging from 6% to 35%. Pozzolana, fly ash, ground granulated blastfurnace slag (ggbs) and limestone are the main materials that are permitted by the EN 197-1 [4].

As far as the traditional composite cement properties are concerned, the literature review shows that the behavior of pozzolana, fly ash and ggbs has been thoroughly investigated. The principal hydration products in composite cements are almost similar to those found in pure Portland cement but the added constituents may affect either the hydration rate or the stoichiometry of hydration products [3,5].

In Greece a variety of pozzolanic and/or hydraulic materials are used as cement main constituents. The main constituents, used in Greece, are natural pozzolana and fly ash. Lastly, ggbs imported from Italy, is also used. Until now, limestone could be used only as a filler (up to 3% w/w), but since 2001 (application of EN 197-1) it can also be used as a main cement constituent.

The European Standard EN 197-1 identifies four types of Portland-limestone cement containing 6–20% limestone (types II/A-L and II/A-LL) and 21–35% limestone (types II/B-L and II/B-LL), respectively [4]. The use of Portland-limestone cements seems to have many benefits, both technical and economical [2,6,7]. 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.

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As far as the limestone cement is concerned, the research work is focused on three areas. The first one is the effect of limestone on the cement performance [7–12]. The second one deals with the participation of limestone in the hydration reactions of clinker [13–24], while the third one with the production process and specifically the intergrinding of clinker and limestone [8,25–27]. Although there is a disagreement on specific issues, 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 [12,28–32]. 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 [33–40].

In this study a comparison between limestone and some of the materials that are already used in Greece is presented. This work is a part of a project, developed in our laboratories, concerning the properties of limestone cement and concrete. The recent identification of Portland-limestone cements by the EN 197-1 is expected to change strongly the picture of the cement market in Greece during the next years. Therefore, it is very important to extend the knowledge concerning the effect of the available materials, as main cement constituents, in Greece, on the cement and concrete properties. In this paper the effect of limestone, fly ash and natural pozzolana on the cement properties and hydration is studied.

2. Experimental

One sample of reference Portland cement and three samples of composite cements containing limestone, natural pozzolana from the Milos Island and fly ash from the Megalopolis area, referred as PC, PLC, PPC and PFC respectively, are examined. The chemical composition of the used materials is shown in Table 1, while the Bogue potential composition and the moduli of the clinker are given in Table 2.

The cements have been produced by intergrinding clinker (85%), the 2nd main constituent (15%) and gypsum (5% of clinker by mass) in a pro-pilot plant ball mill. The grinding process was designed in order to produce cements having the same 28d compressive strength. It is decided to examine cements of the same 28d compressive strength instead of the same fineness, as this case is closer to the industrial practice. The main characteristics of the produced cements are given in Table 3.

The compressive strength of the samples (EN 196-1) as well as the consistency of the standard paste, the setting time and the soundness (EN 196-3) were determined. In addition, the linear shrinkage/expansion of cement mortars was measured (NF P 15-433).

Table 1
Chemical composition of materials (%)

Oxide	Clinker	Limestone	Natural pozzolana	Fly ash
SiO_2	21.99	0.54	59.18	49.33
Al_2O_3	5.28	0.35	16.12	20.72
Fe_2O_3	3.79	0.12	6.14	7.98
CaO	65.65	51.95	4.92	10.26
MgO	1.77	1.16	1.96	2.19
Na_2O*eq*	0.56	0.02	1.41	1.28
LOI	0.00	42.10	4.78	2.02

Table 2
Mineralogical composition (%) and moduli of clinker

Bogue potential composition (%)				Moduli			
C_3S	C_2S	C_3A	C_4AF	LSF	AR	SR	HM
59.25	18.37	7.57	11.54	93.42	2.42	1.39	2.11

Table 3
Characteristic properties of the cements

Cement	Grinding time (min)	Specific surface (Blaine) (m^2/kg)	28d Compressive strength (MPa)
PC	41	303	40.3
PLC	60	511	40.5
PPC	52	418	41.2
PFC	40	388	41.0

Pastes were prepared with water to solid ratio of 0.4 using carbon dioxide free distilled water. Cement and water were thoroughly mixed in sealed polyethylene containers and preserved at 20 °C. Samples hydrated for periods 1, 2, 7 and 28 days were subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum.

Powdered samples, with particle size less than 54 μ, were measured on a Siemens D5000 diffractometer and the data were evaluated using Siemens "Diffrac Eva" software in order to identify the hydrated products.

Calcium hydroxide content in dried cement pastes, hydrated for 28 days, was determined using the thermobalance TGA 2050 of TA Instruments. 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.

3. Results and Discussion

3.1. Properties of Portland-composite cements

As it was mentioned, the produced cements were designed to have the same 28 day compressive strength, which varies from 40.3 to 41.2 MPa (Table 3). The required grinding time and the specific surface (according to Blaine apparatus) of the tested cements are also given in Table 3. As it is seen the PLC requires the higher energy consumption for its grinding while the PFC the lower one. In Fig. 1 the Rosin–Rammler distribution of the produced cements is presented. Taking into account that (a) the fineness of the cements follows the decreasing order: PLC, PPC, PFC (Fig. 1) and (b) the grindability of the used materials follows the decreasing order: limestone, fly ash, pozzolana, clinker—the limestone is the easier ground material and clinker is the more difficult ground material [26,27], it is concluded that clinker has the higher fineness in PLC, while the clinker in PFC has the lower fineness. In order to clarify the above conclusion, a simple example is given. From Fig. 1 it is resulted that the material with particle size less than 8 μm is 30.9% and 34.0% for PFC and PPC respectively. As both fly ash and pozzolana are easier ground than clinker, their concentration in the fine fractions (for example <8 μm) is greater than the initial one (15% w/w). As fly ash is also easier ground than pozzolana, it is concentrated in the fine fractions in a higher degree. If (a%) is the content of fly ash in the fine fraction and (b%) is the content of pozzolana in the same fraction, then $a > b$. The clinker content in the fine fraction is $0.309 \cdot (100 - a)$ and $0.340 \cdot (100 - b)$ for the PFC and PPC respectively. As $a > b$, it is obvious that the clinker content in the fine fraction is lower in the case of PFC and thus the clinker has a lower fineness.

It must be noticed that the particle size distribution of PLC is wider than PPC and PFC as resulted from the uniformity factor of the Rosin–Rammler curves of the cements (Fig. 1).

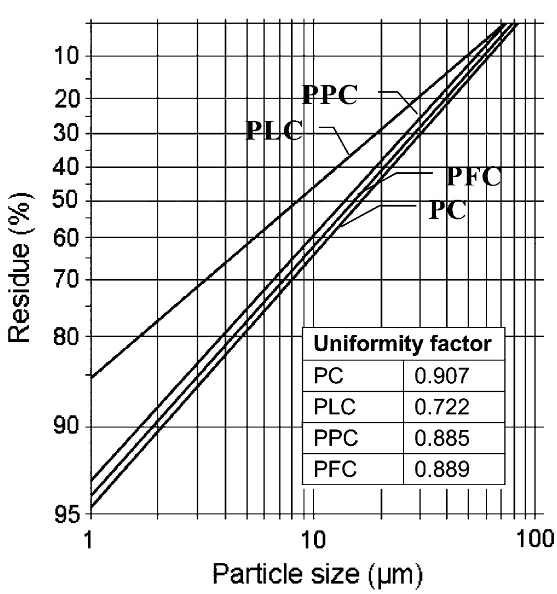

Fig. 1. Rosin–Rammler distribution of the cements.

The strength development of the tested cements is illustrated in Fig. 2. As all the cements have the same 28 day compressive strength, the interesting point is the strength development rate before and after 28 days. Up to 7 days, it is clearly observed that limestone cement exhibited the highest value of compressive strength, while the fly ash cement showed the lowest value of strength. The reasons behind the above behavior are the filler effect of the fine particles of limestone, the higher clinker fineness in PLC and the low rate of the pozzolanic reaction. The strength development between 7 and 28 days seems to be good in all cements. However, the strength development is higher in PFC than the rest studied cements. For the period 28–540 days, the strength development is very significant in the case of PPC and PFC, while PLC showed the lowest rate of strength development.

The physical properties of the cements are given in Table 4. The PLC (despite its higher specific surface) demands less water than the PPC and PFC. The wider particle size distribution of the PLC is a significant reason for the lower water demand [8,10]. The initial and final setting of all cements do not indicate any important differences. The soundness of the cements (expansion according to Le Chatelier process) is satisfactory excluding the PFC that reaches the limit value prescribed by the EN 197-1.

The results of the shrinkage/expansion tests are presented in Table 5. The linear shrinkage of the tested cement mortars is satisfactorily low. In addition, the linear expansion is low in all samples, with PFC indicating the higher value.

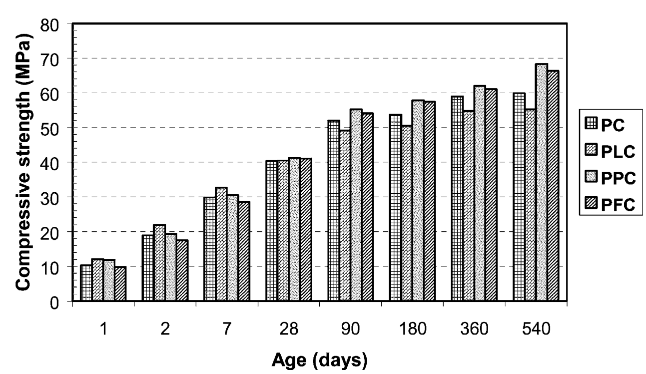

Fig. 2. Strength development of the cements.

Table 4
Physical properties of the cements

Sample	Paste water demand (%)	Setting time (min)		Expansion (mm)
		Initial	Final	
PC	24.3	125	170	1
PLC	24.5	90	170	2
PPC	26.2	95	140	3
PFC	26.4	100	160	10

Table 5
Linear shrinkage/expansion of the samples

Sample	Shrinkage (10^{-6})				Expansion (10^{-6})			
	3d	7d	14d	28d	3d	7d	14d	28d
PC	50	80	170	200	10	20	30	40
PLC	20	100	150	210	35	45	45	50
PPC	30	100	130	230	15	20	25	40
PFC	10	80	140	190	35	40	45	75

3.2. Hydration of Portland-composite cements

As it is known, the principal hydration products in composite cements are essentially similar to those found in pure Portland cement. Of course, in composite cement pastes, $Ca(OH)_2$ content is lowered, both by the dilution of clinker and the pozzolanic reaction. Fig. 3 presents, indicatively, the X-ray patterns of PFC pastes after 1, 2 and 28 days of hydration. Despite the gradual decrease of the anhydrous compounds of clinker, there is no increase of $Ca(OH)_2$ content since it is consumed in the pozzolanic reaction. In the pastes containing fly ash, there are, also, indications of C_2AH_8 formation, probably due to the release of Al_2O_3 from the fly ash.

In limestone cement pastes, carbonate ions incorporated in calcium aluminate hydrates and carboaluminates are formed. Fig. 4 presents the XRD patterns of limestone cement pastes at different ages. As it is observed, a detectable amount of $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$ has already been formed after 24 h of hydration and its amount continues to increase up to 28 days. The peak next to carboaluminates is associated with Ca–Al–Si hydrates, probably in the form of gismondine.

Fig. 5 presents the XRD patterns of the samples after 7 days of hydration. Ettringite (AFt) and Ca–Al–Si hydrate have been formed in all samples. However, differentiations are observed as far as the formation of calcium monosulfate hydrate (AFm) is concerned. It seems that fly ash accelerates the transformation AFt to AFm, while natural pozzolana and limestone act as retarders.

Table 6 presents the content of $Ca(OH)_2$, measured by means of thermogravimetry, in pastes hydrated for 28 days. The higher content of calcium hydroxide is found in PC paste while the lower one is found in PFC paste. The limestone addition does not affect the amount of CH formed. It must be noticed that it is not possible, based on the CH measurements, to draw clear conclusions concerning the reactivity of the cement mixtures, as the clinker fineness also affects the CH content. Comparing the three composite cements and taking into account that (a) PFC has the lower fineness (Fig. 1), (b) clinker has the lower fineness in PFC (Section 3.1) and (c) all the cements have the same 28 day compressive strength (Table 3), it is strongly indicated that the addition of fly ash leads to more reactive cement mixture.

Taking into consideration the above results, it is concluded that the intergrinding of the additives with the clinker causes important variations of the clinker fineness, especially in the case of fly ash and limestone. Consequently, composite cements containing the

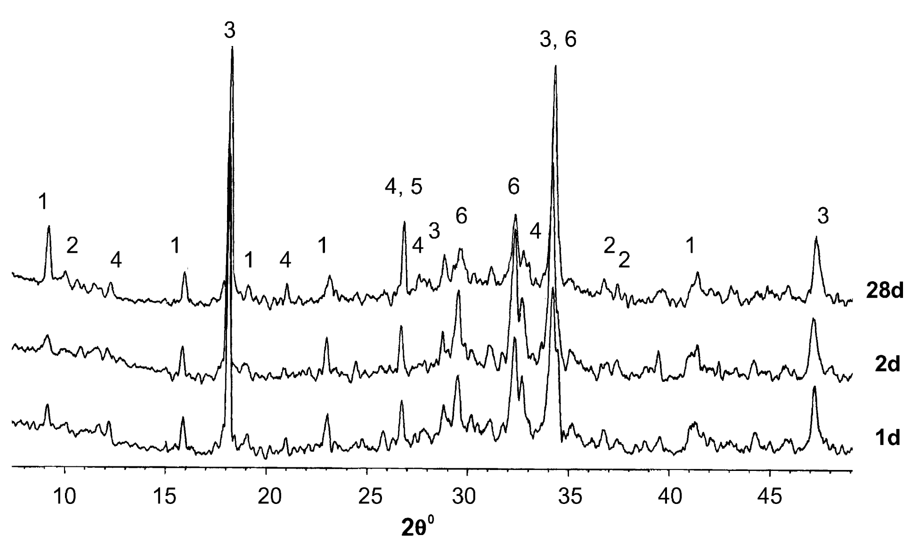

Fig. 3. XRD patterns of PFC pastes (1: ettringite, 2: calcium monosulfate hydrate, 3: portlandite (C–H), 4: gismondine$_2$ ($CaAl_2Si_2O_8{\cdot}4H_2O$), 5: quartz, 6: anhydrous compounds of clinker).

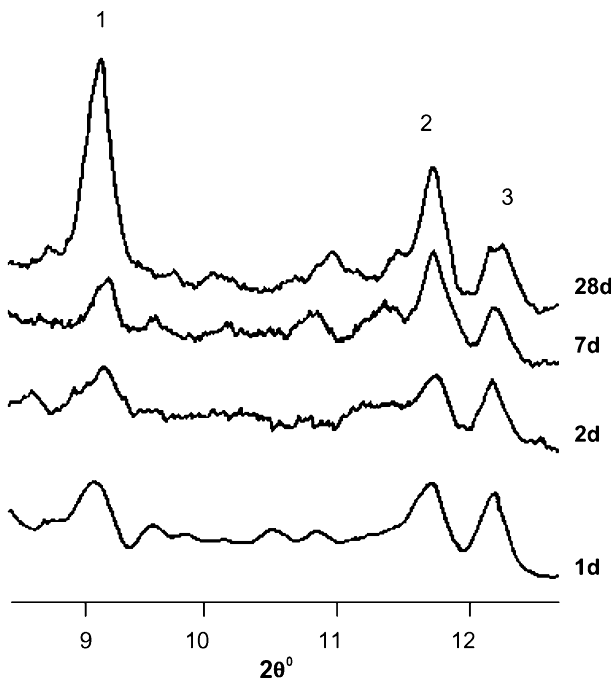

Fig. 4. XRD patterns of PLC pastes (1: ettringite, 2: monocarboaluminate hydrate, 3: Ca–Al–Si hydrate).

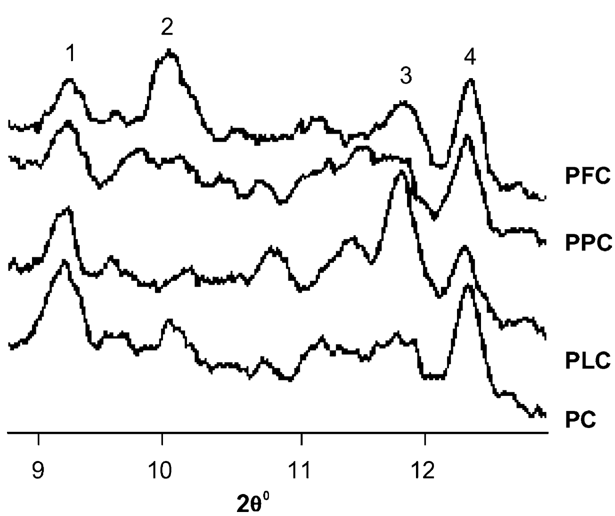

Fig. 5. XRD patterns of composite cement pastes at 7 days (1: ettringite, 2: calcium monosulfate hydrate, 3: monocarboaluminate hydrate, 4: Ca–Al–Si hydrate).

Table 6
$Ca(OH)_2$ content in pastes hydrated for 28 days

Sample	PC	PLC	PPC	PFC
$Ca(OH)_2$ (%)	21.37	18.57	19.13	17.22

examined materials present significant differences as far as the development of the strength, the water demand and the hydration rate is concerned. Taking into account the satisfactory properties of the limestone cements as well as the low cost and the high availability of limestone in Greece, it is concluded that the production of Portland-limestone cements seems to be very challenging.

4. Conclusions

The comparative study, on the behavior of composite cements, having the same 28 day compressive strength and containing limestone, natural pozzolana or fly ash, leads to the following conclusions.

- The intergrinding process affects the fineness of the clinker and therefore the properties of the cements. In our case, cements with fly ash and limestone have the coarser and finer clinker respectively.
- The cement containing limestone exhibits higher early strength. The opposite effect is caused by the addition of fly ash. At 90 days and up to 540 days, cements with natural pozzolana or fly ash exhibit significantly higher compressive strength than the Portland cement and the Portland-limestone cement.
- The cement containing limestone demands less water than cements with pozzolana and fly ash.
- Although the principal hydration products in composite cements are almost similar to those found in pure Portland cement, the added minerals affect the ettringite transformation to monosulfate hydrate. In limestone cements, $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$ is formed from the first days of hydration and is still present after 28 days.
- The production of Portland-limestone cements seems to be very challenging, due to the satisfactory properties of the limestone cements as well as the low cost and the high availability of limestone in Greece.

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