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Metakaolin as a main cement constituent. Exploitation of poor Greek kaolins

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Abstract

In this work, the properties and the hydration procedure of cements containing metakaolin were monitored for periods up to 180 days. Four metakaolins, derived from poor Greek kaolins, as well as a commercial metakaolin of high purity were used. Cement mortars and pastes, with 0%, 10% and 20% replacement of cement with the above metakaolins, were examined. Strength development, water demand and setting time were determined in all samples. In addition, XRD and TGA were applied in order to study the hydration products and the hydration rate in the cement–metakaolin pastes. It is concluded that metakaolin has a very positive effect on the cement strength after 2 days and specifically at 28 and 180 days. The blended cements demand significantly more water than the relatively pure cement and the water demand increase is higher, the higher the metakaolin content. The produced metakaolins as well as the commercial one give similar hydration products after 28 days and the pozzolanic reaction is accelerated between 7 and 28 days, accompanied by a steep decrease of $Ca(OH)_2$ content. Finally, it is concluded that a 10% metakaolin content seems to be, generally, more favorable than 20%. The produced metakaolins, derived from poor Greek kaolins, as well as the commercial one impart similar properties with respect to the cement strength development, the setting and the hydration.

Keywords: Cement; Metakaolin; Strength; Setting; Hydration

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1. Introduction

The most common cementitious materials that are used as concrete constituents, in addition to Portland cement, are fly ash, ggbs and silica fume. They save energy, conserve resources and have many technical benefits [1]. Metakaolin, produced by controlled thermal treatment of kaolin, can also be used as a concrete constituent, since it has pozzolanic properties [2,3].

According to the literature, the research work on metakaolin is focused on two main areas. The first one refers to the kaolin structure, the kaolinite to metakaolinite conversion and the use of analytical techniques for the thorough examination of kaolin thermal treatment [4–12]. The second one concerns the pozzolanic behavior of metakaolin and its effect on cement and concrete properties [2,3,13–30]. Although there is a disagreement on specific issues, the knowledge level is satisfactory and is being continuously extended.

In this study, the properties and the hydration procedure of cements containing metakaolin were monitored for periods up to 180 days. Four metakaolins, derived from poor Greek kaolins, as well as a commercial metakaolin of high purity were used. This work forms part of a research project, which aims to exploit Greek kaolins in concrete technology.

2. Experimental

2.1. Materials

Four Greek kaolins (K1–K4), having varying chemical and mineralogical composition, are examined. In addition, a commercial metakaolin (MKC) of high purity was also used as a reference material. Table 1 presents the chemical composition of the samples. Concerning the commercial metakaolin, for comparison

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Table 1
Chemical composition of kaolins (% w/w)

	K1	K2	K3	K4	KC
SiO_2	73.45	72.47	38.92	65.92	47.85
Al_2O_3	18.04	18.40	35.38	22.56	38.20
CaO	0.40	0.35	0.54	0.36	0.32
MgO	0.03	0.03	0.06	–	–
Fe_2O_3	–	–	0.60	–	0.30
K_2O	0.80	0.80	2.51	0.57	0.27
L.O.I.	8.10	8.00	21.50	8.60	12.30
SO_3	3.00	3.12	10.03	2.00	–

reasons, the characteristics of the commercial kaolin (KC), instead of MKC, are given.

The semi-quantitative mineralogical estimation of the materials is presented in Table 2. The estimation is based on the characteristic XRD peaks of each mineral, in combination with the bulk chemical analysis of the samples, the details of which have presented previously [11]. The kaolins mainly consist of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and K-alunite ($KAl_3(SO_4)_2(OH)_6$). They also contain quartz and cristobalite. In addition, the sample KC contains detectable amounts of illite, while a trace amount of illite is also present in sample K4. K1 and K2 have the lowest kaolinite content, while K3 has the highest content of kaolinite and alunite. K4 has an average kaolinite content and the lowest alunite content.

Portland cement (PC: I/55) of industrial origin was used for the production of the mixtures. The chemical analysis of PC and the clinker characteristics are given in Table 3.

Table 2
Mineralogical composition of kaolins (% w/w)

	K1	K2	K3	K4	KC
Kaolinite	38	39	65	52	96
Alunite	7	7	22	5	–
Quartz (mainly) + cristobalite	55	54	8	41	–
Illite	–	–	–	–	3

Table 3
Chemical analysis of PC and characteristics of clinker

Cement		Clinker	
Chemical analysis (%)		Mineralogical composition (%)	
SiO_2	21.54	C_3S	57.8
Al_2O_3	4.83	C_2S	18.1
Fe_2O_3	3.89	C_3A	6.2
CaO	65.67	C_4AF	11.8
MgO	1.71	Moduli	
K_2O	0.60	Lime saturation factor (LSF)	0.949
Na_2O	0.07	Silica ratio (SR)	2.47
SO_3	2.74	Alumina ratio (AR)	1.24
Cl^-	0.00	Hydraulic modulus (HM)	2.17

2.2. Metakaolin production

The optimum conditions for thermal treatment have been reported previously [10,31]. The kaolins K1, K2 and K4 were thermally treated in a pro-pilot plant furnace at 650 °C for 3 h. The sample with the higher percentage of alunite (K3), was heated at 850 °C, in order to remove the excess SO_3. The SO_3 content of the produced metakaolin MK3 is related to the treatment temperature as follows: (a) $T = 650$ °C, $SO_3 = 10.56\%$, (b) $T = 750$ °C, $SO_3 = 6.90\%$, (c) $T = 850$ °C, $SO_3 = 2.37\%$, (d) $T = 950$ °C, $SO_3 = 2.23\%$. The complete transformation of kaolinite to metakaolinite was confirmed by X-ray diffraction (Siemens D5000 diffractometer—nickel-filtered Cu Kα_1 radiation $\lambda = 1.5405$ Å). The metakaolins derived from K1, K2, K3 and K4 are referred as MK1, MK2, MK3 and MK4 respectively.

Table 4 presents the metakaolinite content of the metakaolins. The estimation is based on the chemical and mineralogical analysis of the kaolins (Tables 1 and 2).

The produced metakaolins MK1–MK4 were superfine ground, using the AJ100 Aerojet Mill Minisplit Classifier of British Rema. The fineness characteristics of the ground metakaolins as well as the MKC are given in Table 5.

2.3. Cement properties and hydration

Blended cements were produced by replacing PC with 10% w/w and 20% w/w of MK1, MK2, MK3, MK4 and MKC. The compressive strength of mortar samples, cured for up to 180 days (EN 196-1) as well as the water demand and the setting time (EN 196-3) was determined.

The hydration process of the cements containing MK4 and MKC was studied according to the following procedure (MK4 has been selected for the study of the hydration procedure, as K4 is the most typical kaolin

Table 4
Metakaolinite content in metakaolins (% w/w)

MK1	MK2	MK3	MK4	MKC
36	37	71	49	95

Table 5
Metakaolin fineness characteristics

Sample	Fineness characteristics			Rosin–Rammler parameters	
	d_{20} (μm)	d_{50} (μm)	d_{80} (μm)	n	pp (μm)
MK1	11.5	6.9	3.4	1.63	8.6
MK2	9.6	5.8	3.0	1.70	7.2
MK3	9.4	5.3	2.4	1.45	6.8
MK4	13.6	7.5	3.4	1.42	9.7
MKC	10.3	5.1	1.9	1.18	6.9

mineral in Greece). The cements were mixed with deionized water at a water-to-cement ratio (W/C) of 0.4 to produce pastes. The pastes were cast in cubic moulds (20 × 20 × 20 mm). The specimens were left in the moulds for 6 h, then were put in polythene containers, sealed hermetically and water-cured at 20 °C. Samples hydrated for periods of 1, 2, 7, 28, 90 and 180 days were crushed, subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum at laboratory temperature (approximately 20 ± 2 °C). The hydrated samples were ground to pass through a 54 μm sieve and were studied by means of XRD in order to identify the crystalline hydration products. In addition, TGA was used for the evaluation of the hydration rate. A Mettler Toledo TGA/SDTA 851 instrument was used. The samples were heated from 20 to 800 °C at a constant rate of 15 °C/min in an atmosphere of carbon dioxide free nitrogen, flowing at 50 cm^3/min.

3. Results and discussion

3.1. Cement properties

Fig. 1 shows the compressive strength development of metakaolin cements in relation to the metakaolin type and cement replacement level. For 10% replacement of PC with MK, the blended cements exhibit higher strength than the PC at all ages up to 180 days (with the exception of MK1 at 2 days). Strength enhancement, due to the MK, is greatest between 2 and 28 days. Concerning 20% replacement, blended cements, depending on the metakaolin type, exhibit similar or lower strengths than the PC at 2 days of curing. In contrast, strength after 7 days is influenced in a positive manner by the metakaolin and blended cements show significantly increased strength compared to the PC strength (with the exception of MK1 at 7 days).

Fig. 2 shows the relative strength of metakaolin cements in relation to curing age, the metakaolin type and the cement replacement level. Relative strength is the ratio of the strength of the metakaolin cement to the strength of the PC at each particular curing time. The rate of strength development in PC is mainly dependent on the hydration rate of clinker, while in PC-MK systems it is dependent on the combination of PC hydration and the pozzolanic activity of metakaolin. Therefore, the relative strength–time plots provide an insight into the rates of reaction in the blended system relative to the plain PC system [28]. According to the literature, the main factors that affect the contribution of metakaolin in strength are: (a) the filler effect, (b) the

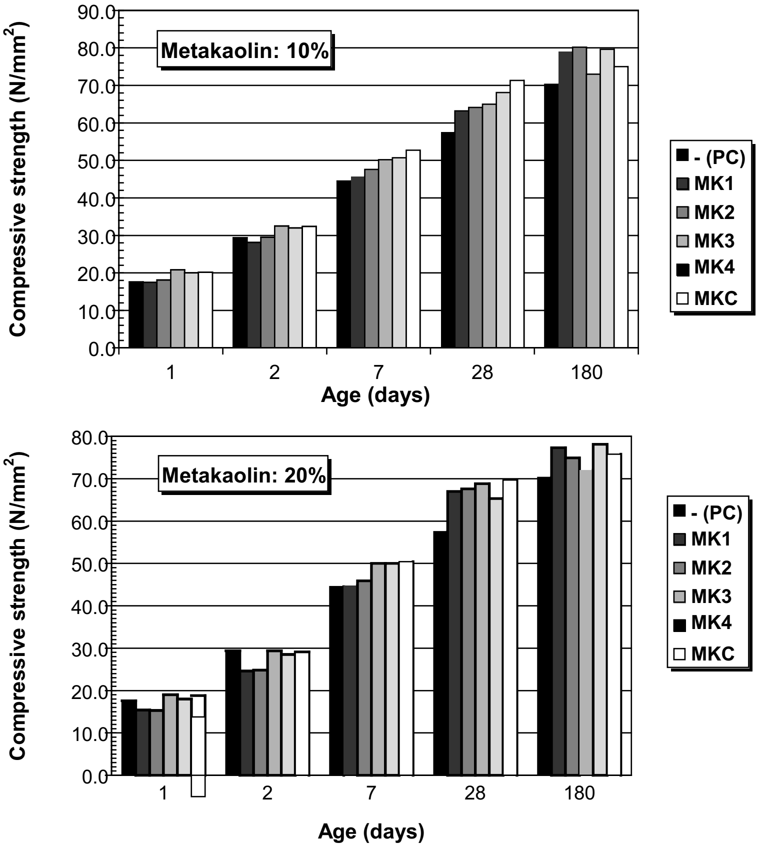

Fig. 1. Compressive strength development of metakaolin cements in relation to the metakaolin type and the metakaolin content.

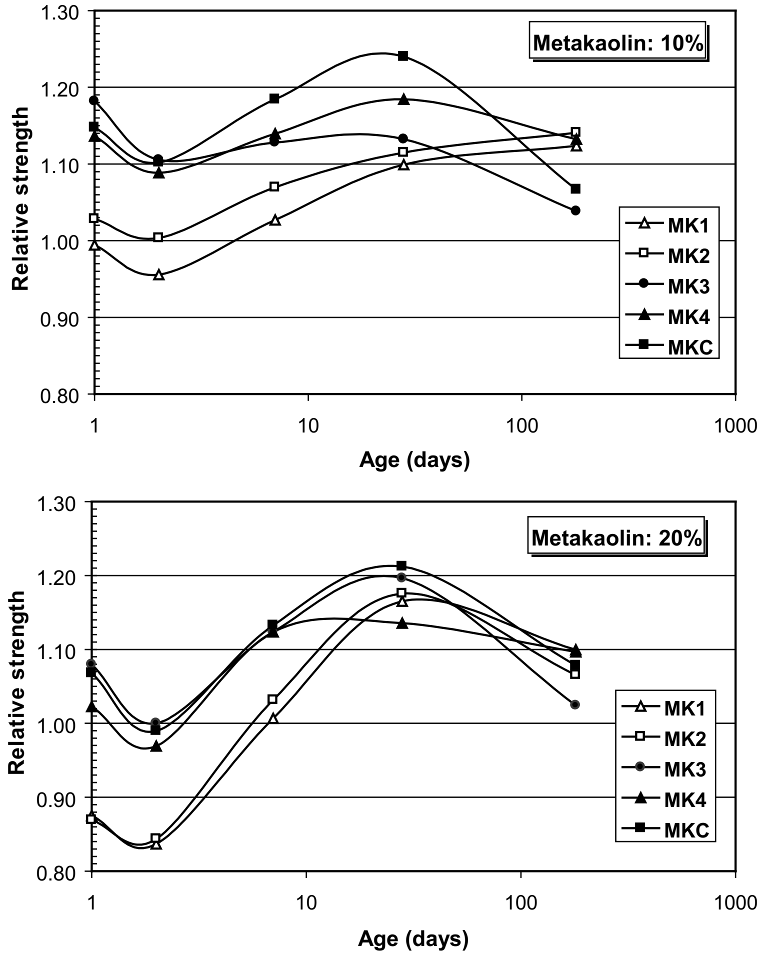

Fig. 2. Relative strength of metakaolin cements in relation to curing age, the metakaolin type and the metakaolin content (relative strength: ratio of the strength of the metakaolin cement to the strength of the PC).

dilution effect and (c) the pozzolanic reaction of metakaolin with CH [28]. As the studied Greek metakaolins have significant differences in their metakaolinite content (Table 4), the metakaolinite content is a further factor that influences the strength development of metakaolin cements.

For 10% replacement of PC with MK, the increased relative strength at 1 day (Fig. 2) is mainly attributed to the filler effect that leads to an initial acceleration of PC hydration. For 20% replacement of PC with MK, at 1 day, the filler effect is surpassed by the dilution effect and this leads to lower relative strength than that observed in the case of 10% metakaolin. Also, cements containing MK1 and MK2, that have the lowest metakaolinite contents (Table 4), exhibit the lowest relative strengths at 1 day. This suggests that the reaction of metakaolin with CH affects the strength even at very early ages.

The decrease of relative strength between 1 and 2 days is attributed to the dilution effect and the decrease is greater in the case of 20% replacement of PC with metakaolin (Fig. 2). Between 2 and 28 days the relative strength shows a clear increase, due mainly to the pozzolanic reaction of the metakaolin. The increase in the relative strength is greater in the case of 20% replacement of PC with metakaolin. The acceleration of the pozzolanic reaction between 7 and 28 days is also confirmed by TGA measurements (see Section 3.2). For 10% replacement of PC with MK3, relative strength reaches a maximum value between 7 and 28 days. In addition, cement with 10% MK3 gives a lower value of relative strength at 180 days, compared to the other metakaolin cements. The different behavior of MK3 is attributed to its low reactivity, which has been reported in a previous work [11].

Between 28 and 180 days, in most cases, there is a decrease of the relative strength, due to the cessation of the pozzolanic reaction. In the case of cements containing 10% MK1 and 10% MK2, relative strength continues to increase after 28 days. This phenomenon needs more investigation and may be attributed to differences in metakaolinite content and reactivity.

It must be noticed, that in all metakaolin cements, with 10% or 20% metakaolin content, the relative strength at 180 days is greater that 1, which confirms

Table 6
Physical properties of metakaolin cements

Sample	Metakaolin (% w/w)	Water demand (% w/w)	Setting time (min)	
			Initial	Final
PC	–	27.5	105	140
MK1-10	10	29.0	75	130
MK2-10	10	29.0	85	130
MK3-10	10	32.0	105	160
MK4-10	10	32.5	155	180
MKC-10	10	31.0	95	130
MK1-20	20	32.0	105	160
MK2-20	20	31.5	110	165
MK3-20	20	38.5	120	160
MK4-20	20	41.0	205	230
MKC-20	20	37.5	140	170

that even long-term cement strength is affected by the metakaolin in a positive way.

It is apparent from Figs. 1 and 2 that between 28 and 180 days an increase in metakaolin content from 10% to 20% has a positive effect on cement strength only in the case of MK3. It seems, that 10% is the optimum content for MK1, MK2, MK4 and MKC. MK3, which is the least reactive material [11], produces its greatest influence on strength at 20% cement replacement level.

Table 6 gives the water demand and the setting times of the cement pastes. The "water demand" is the quantity of water that is required in order to prepare a cement paste of standard consistency as specified in EN 196-3. The blended cements demand significantly more water than the relatively pure cement. With a metakaolin content of 10%, the water demand varies from 29.0% to 32.5%, while the PC has a water demand of 27.5%. With a metakaolin content of 20%, the water demand varies from 31.5% to 41.5%. Metakaolins MK1 and MK2 show the best behavior and increase the water demand less. The increase in water demand is mainly attributed to the high fineness of metakaolin (Table 5, $d_{50} = 5.1\text{–}7.5\ \mu\text{m}$) as well as to their narrow particle size distribution (Table 5, n: 1.18–1.70) [32].

The initial and final setting time of metakaolin cements is affected by the metakaolin content. Cements with 10% metakaolin, generally, exhibit similar setting times to that of PC, while for 20% metakaolin content there is a delay in the setting (Table 6). MK4 shows the greatest effect on the setting delay of the cements.

3.2. Hydration rate of metakaolin cement pastes

Pastes of PC, MK4-10, MK4-20, MKC-10 and MKC-20 were studied by means of a TG analyzer. The weight loss up to 550 °C, which corresponds to the total water incorporated in the cement paste (total combined water), was determined. The $Ca(OH)_2$ content, which for PC is directly related to the hydration of silicate compounds, was also measured. When pozzolanic materials are combined with PC, the $Ca(OH)_2$ content (when compared to that of PC alone), also provides an indication of the pozzolanic reaction. The weight loss in the range 600–700 °C, if any, corresponds to the decomposition of $CaCO_3$ and it has to be converted to the equivalent $Ca(OH)_2$. The carbonation of the pastes may take place during the preparation of the paste or during the grinding of the paste previous to the TG measurement. The water combined in the hydration products (other than calcium hydroxide) corresponds to the weight loss up to 300 °C. Any changes of this value indicates that the quantity, type and relative proportions of the hydration products are changing.

Fig. 3 gives the calcium hydroxide content, total combined water and water in the hydration products at 7 days. There is a significant decrease of calcium hydroxide content in samples containing metakaolin, relative to the PC control, due to the pozzolanic reaction. Also the pozzolanic reaction is more rapid in samples containing the commercial metakaolin MKC. This phenomenon is related to the higher fineness of

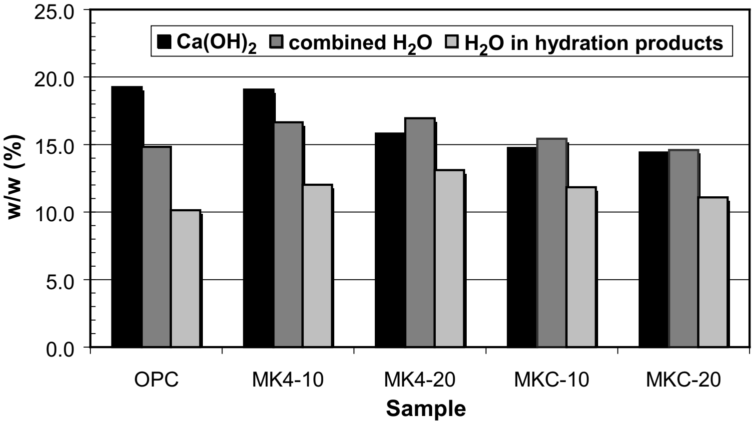

Fig. 3. Calcium hydroxide, total combined water and water in the hydration products for a hydration age of 7 days.

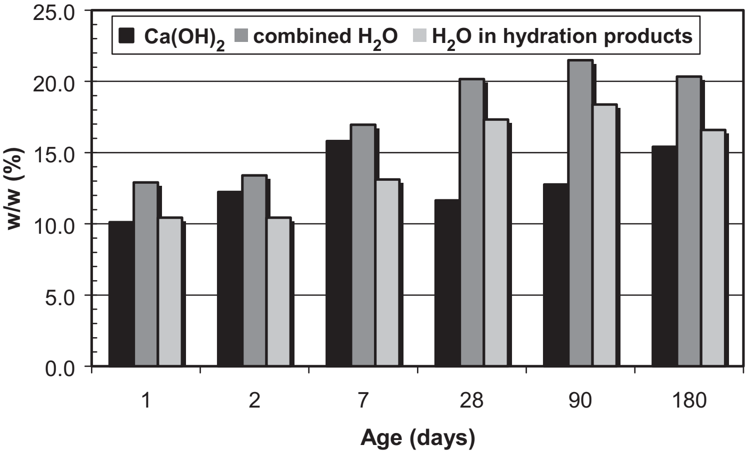

Fig. 4. Calcium hydroxide, total compound water and water in the hydration products in relation to the hydration age for the sample MK4-20.

MKC (Table 5) as well as to its higher metakaolinite content (Table 4). In contrast, pastes containing MK4 exhibit higher values of total combined water and water in the hydration products than the MKC pastes, due probably to the different hydration products.

Fig. 4 gives the calcium hydroxide content, total combined water and water in the hydration products for the sample MK4-20 in relation to the hydration age. A steep decrease of $Ca(OH)_2$ content is observed between 7 and 28 days, due to the acceleration of the pozzolanic reaction. At the same period, the change of the water combined in the hydration products (other than calcium hydroxide) is attributed to the change of the quantity, type and relative proportions of the hydration products.

3.3. XRD studies of metakaolin cement pastes

The exact identification of hydration products in cement paste, by means of XRD, is difficult due to their low degree of crystallinity and/or their small amounts. In all metakaolin–cement pastes, XRD patterns indicate a decrease of $Ca(OH)_2$ content, in comparison with pure cement pastes. This is due to the pozzolanic reaction, as well as to the dilution of the clinker.

According to the literature, the main hydration products in metakaolin–$Ca(OH)_2$ are C_2ASH_8, C_4AH_{13} and C_3AH_6 [33,34]. However, according to our knowledge, these compounds have not been clearly identified in metakaolin–cement pastes. Our measurements showed that the main peaks in the XRD patterns of metakaolin–cement pastes correspond to $Ca(OH)_2$ and the anydrous clinker phases. After 1 day of hydration, ettringite was also present in all samples. In addition, a small amount of monosulfate was formed in pure cement pastes. Monosulfate was also present in metakaolin–cement pastes after 2 days of hydration. It seems that the transformation of ettringite to monosulfate is retarded in samples containing metakaolin.

XRD patterns of metakaolin–cement pastes showed some indications of Ca–Al–Si hydrates (probable ratio Ca:Al:Si = 1:1:1–2; d:3.34, 4.21 and 4.08, 2.89) but they did not permit a safe identification. In general, the XRD patterns of pastes containing MKC and MK4 were quite similar.

All the above results show that metakaolin cements containing the metakaolin derived from poor Greek kaolins, show some similarities in behavior with cements containing a commercial metakaolin of high purity, with respect to strength development, setting times and hydration. Although a more thorough investigation is required, their exploitation seems to be very promising.

4. Conclusions

The following conclusions can be drawn from the present study:

- The produced metakaolins derived from poor Greek kaolins, when combined with PC to produce blended cements, impart similar behavior to that of commercial metakaolin, with respect to cement strength development, setting times and hydration.
- The studied metakaolins have a very positive effect on the cement strength after 2 days and specifically at 28 and 180 days. The blended cements demand significantly more water than the relatively pure cement and the water demand increase is higher, the higher the metakaolin content.
- The pozzolanic reaction of metakaolins is accelerated between 7 and 28 days, accompanied by a steep decrease of $Ca(OH)_2$ content. The hydration products, after 28 days, are similar in all samples.
- Based on the mechanical and physical properties of metakaolin cements, a 10% metakaolin content seems to be, generally, more favorable than 20%.

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