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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

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