Exploitation of poor Greek kaolins: Strength development of metakaolin concrete and evaluation by means of *k*-value

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Abstract

In this paper, the effect of metakaolin on concrete properties is investigated. A poor Greek kaolin was thermally treated at defined conditions, and the produced metakaolin was superfine ground. In addition, a commercial metakaolin of high purity was used. Eight mixture proportions were used to produce high-performance concrete, where metakaolin replaced either cement or sand in percentages of 10% or 20% by weight of the control cement content. The strength development of metakaolin concrete was evaluated using the efficiency factor (*k*-value). The produced metakaolin as well as the commercial one imparts a similar behavior with respect to the concrete strength. Both metakaolins exhibit very high *k*-values (close to 3.0 at 28 days) and are characterised as highly reactive pozzolanic materials that can lead to concrete production with an excellent performance.
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1. Introduction

The worldwide demand for high-performance, cement-based materials has increased, and predictions are that it will reach a major industrial dimension during the early 21st century. Economics and environmental considerations have had a role in the mineral admixture usage as well as better engineering and performance properties.

The cementitious materials that are widely used, as concrete constituents, are fly ash, ggbs, and silica fume [1]. Metakaolin, produced by controlled thermal treatment of kaolin, is the most recent mineral admixture to be commercially introduced to the concrete construction industry. It has been claimed that concrete containing metakaolin exhibits premium-level engineering properties comparable to silica fume concrete [2–4].

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 [5–13]. The second one concerns the pozzolanic behavior of metakaolin and its effect on cement and concrete properties [3,4,14–32]. Although there is a disagreement on specific issues, the knowledge level is satisfactory and continuously extended.

The concrete performance depends mainly on the environmental conditions, the microstructure, and the chemistry of the concrete. The two latter factors are strongly affected by the concrete components. It is obvious that the metakaolin presence affects the concrete performance. In particular, this effect on concrete properties can be practical, approached by the supplementary cementing materials (SCM) efficiency factor (*k*-value).

The *k*-value is defined as the part of the SCM in a pozzolanic concrete which can be considered as equivalent to Portland cement, having the same properties as the concrete without SCM (obviously, $k = 1$ for Portland cement) [33]. The quantity of the SCM in the mix can be multiplied by the *k*-value to estimate the equivalent cement content, which can be added to the cement content for the determination of the water–cement ratio, minimum required

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Table 1
Chemical analysis of kaolins (%)

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	LOI	SO_3
KC	47.85	38.20	0.03	0.04	1.29	12.30	–
K	65.92	22.56	0.36	0.02	0.90	8.60	2.00

The methods specified by EN 450, EN 196, and EN 451 were followed.

cement content, etc. The property used for the estimation of k-values is the compressive strength [33,34]. However, durability properties can also be used, and relative k-values can be calculated. Knowing these k-values, the mix design for the preparation of the building product can be easier and more accurate.

In previous publications, a simplified scheme describing the activity of silica fume and fly ash (of low and high calcium) in terms of chemical reactions was proposed, yielding quantitative expressions for the estimation of the final chemical and volumetric composition of such SCM concretes [35–38]. Furthermore, a practical approach to the effect of SCM on the strength of Portland cement systems and on their resistance against carbonation and chloride penetration was presented using the concept of the SCM efficiency factor [39,40].

This work forms part of a research project, which aims towards the exploitation of poor Greek kaolins in concrete technology. Up to now, the optimization of the kaolin to metakaolin conversion [11,30,41], the study of the CH– metakaolin system [30], the effect of the crystallinity of the original kaolinite on the pozzolanic activity of metakaolinite [12,30], and the properties and behavior of metakaolin cements [42] have been carried out.

The present work deals with the behavior of two meta-kaolins: a produced metakaolin that originated from poor kaolin and a commercial one of high purity. More specifically, the strength development of metakaolin concrete, the evaluation of metakaolin activity according to accepted quantitative criterion (k-value), and the comparison of the produced metakaolin with the commercial one are studied.

2. Experimental

2.1. Materials

A poor Greek kaolin (K), which originated from Milos Island, was used. In addition, a commercial metakaolin (MKC) of high purity was also used as a reference material. The chemical analysis of the materials is given in Table 1.

Table 2
Mineralogical analysis of kaolins (%)

	Kaolinite	Alunite	Quartz	Illite
KC	96	–	–	3
K	52	5	41	–

Quartz (mainly) + cristobalite.

Table 3
Chemical analysis of OPC 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	LSF	0.949
Na_2O	0.07	SR	2.47
SO_3	2.74	AR	1.24
Cl^-	0.00	HM	2.17

Concerning the commercial metakaolin, for comparison reasons, the characteristics of the commercial kaolin (KC), instead of MKC, are given.

The semiquantitative mineralogical estimation of the materials is presented in Table 2. The estimation is based on the characteristic X-ray diffraction (XRD) peaks of each mineral, in combination with the bulk chemical analysis of the samples and has been presented in details in a previous work [12]. The Greek kaolin K mainly consists of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and quartz. K also contains K-alunite [$KAl_3(SO_4)_2(OH)_6$]. KC contains kaolinite and a detectable amount of illite.

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

2.2. Metakaolin production

The optimum conditions of thermal treatment have been reported in previous works [11,30]. The kaolin K was thermally treated in a propilot plant furnace at $T = 650$ °C for 3 h. The complete transformation of kaolinite to meta-kaolinite was confirmed by XRD. The metakaolin that originated from K is referred to as MK. The metakaolinite content of the used metakaolins is 49% and 95% w/w for MK and MKC, respectively (Table 4). The estimation is based on the chemical and mineralogical analysis of the kaolins (Tables 1 and 2). In Table 4, the SiO_2 content (estimated from Table 1 data) and the active SiO_2 (measured according to EN 196-2) of the metakaolins are also given. The active silica is defined as the fraction of the SiO_2 that is soluble after treatment with hydrochloric acid and with boiling potassium hydroxide solution (EN 197-1).

The produced metakaolin MK was superfine ground, using the AJ100 Aerojet Mill Minisplit Classifier of British

Table 4
Metakaolinite, SiO_2, and active SiO_2 content of metakaolins

	Metakaolinite (%)	SiO_2 (%)	Active SiO_2 (%)
MKC	95	54.6	53
MK	49	72.1	30