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Exploitation of poor Greek kaolins: Durability of metakaolin concrete

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ABSTRACT

In this paper the effect of metakaolin on concrete durability is investigated. A Greek kaolin of low kaolinite content was thermally treated at defined conditions and the produced metakaolin was finely 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 10% or 20% by weight of the control cement content. Durability of metakaolin concrete was evaluated by means of resistance to chloride penetration, air permeability, sorptivity, porosity and pore size distribution. Metakaolin concrete exhibits significantly lower chloride permeability, gas permeability and sorptivity. The addition of metakaolin refines the pore system of concrete, leading to a decreased mean pore size and improved uniformity of the pore size distribution. The produced metakaolin, derived from the poor Greek kaolin, imparts similar behavior to that of the commercial metakaolin, with respect to the concrete durability.

1. Introduction

Metakaolin is the most recent mineral admixture to be commercially introduced to the concrete construction industry [1–3]. Unlike other pozzolans, it is a primary product, not a secondary product or by-product, produced by controlled thermal treatment of kaolin. This allows manufacturing process of metakaolin to be optimized, ensuring the production of a consistent pozzolanic material.

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 [2,4,13–33].

Concrete durability depends mainly on the chemistry (cement hydration process), and the microstructure of the concrete. Metakaolin addition affects positively both factors; Metakaolin consumes rapidly and effectively the $Ca(OH)_2$ that is produced from the cement hydration process and additional to CSH, phases like C_2ASH_8 (stratlingite), C_4AH_{13} and C_3ASH_6 (hydrogarnet) are produced. These pozzolanic products contribute to a total pore refinement [13,18,32]. The refined pore system results in a more compact concrete, through which transportation of the water and other aggressive chemicals is significantly impeded and therefore a decrease in the diffusion rate of harmful ions is reported [17,27,33,34].

This work forms part of a research project, which aims towards to the exploitation of poor Greek kaolins in concrete technology. Up to now, the optimization of the kaolin to metakaolin conversion [10,29,35], the study of the CH–metakaolin system [36], the effect of the crystallinity of the original kaolinite on the pozzolanic activity of metakaolinite [11,29], the properties and behavior of metakaolin cements [37], the effect of metakaolin on the corrosion behavior of cement mortars [30] and the evaluation of strength development of metakaolin concrete by means of *k*-value [38] have been carried out. In the present work, two metakaolins, a produced metakaolin originated from poor Greek kaolin and a commercial one of high purity, are examined and their effect on concrete durability is investigated.

2. Experimental

2.1. Materials

A poor Greek kaolin (K), originated from Milos Island, was used. In addition, a commercial (from Imerys Minerals) metakaolin (MKC) of high purity was also used as a reference material. The chemical analysis of the materials is given in Table 1. Concerning the commercial metakaolin, for comparison reasons, the characteristics of the commercial kaolin (KC), instead of MKC, are given. As can been seen from Table 1, K is a poor kaolin as it contains only 52% kaolinite.

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Table 1
Chemical and mineralogical analysis of kaolins.

Material	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	L.O.I.	SO_3
Chemical analysis (%)[a]							
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

Material	Kaolinite	Alunite	Quartz[b]	Illite
Mineralogical analysis (%)				
KC	96	–	–	3
K	52	5	41	–

[a] EN-450, EN-196 and EN-451.
[b] Quartz (mainly) + cristobalite.

The semi-quantitative mineralogical estimation of the materials is presented in Table 1. The estimation is based on the characteristic 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 [11]. 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. In previous work [11] has also found that the contained kaolinite in Greek kaolin K is less ordered than the kaolinite in the commercial KC and this has a positive effect on MK reactivity (MK is the metakaolin originated from K).

Ordinary Portland cement (PC: I/55) of industrial origin was used for the production of the mixtures. The chemical analysis of PC and the characteristics of clinker are given in Table 2.

2.2. Metakaolin production

The optimum conditions of thermal treatment have been reported in previous works [35,36]. The kaolin K was thermally treated in a pro-pilot plant furnace at $T = 650\ ^{\circ}C$ for 3 h. The complete transformation of kaolinite to metakaolinite was confirmed by X-ray diffraction. The metakaolinite content of the used metakaolins is 49% w/w and 95% w/w for MK and MKC, respectively (Table 3). The estimation is based on the chemical and mineralogical analysis of the kaolins (Table 1). In Table 3, 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 finely ground, using the AJ100 Aerojet Mill Minisplit Classifier of British Rema. The fineness characteristics of the ground metakaolin as well as the MKC are given in Table 4.

2.3. Concrete preparation and properties

The concrete production was carried out in a mixer of 50 l capacity. In addition to the control concrete mixture, four concrete mixtures were prepared for each metakaolin, where metakaolin replaced either cement or sand in percentages 10% or 20% by weight of the control cement content. The water content (tap water at 20 °C) for all specimens was kept constant (175 kg/m^3). Normal graded calcareous aggregates, including fine (37%), medium (21%) and coarse (42%) aggregates, were used. The coarse aggregate maximum size was 31.5 mm. For the control specimen, the water-to-cement ratio (W/C) was 0.5 and the aggregate-to-cement ratio (A/C) was 5.5. A common superplasticizer (CHEM SLP P by Domylco Ltd., type E and F of ASTM C494/C494M-08a) was used at appropriate percentages in order to retain the slump of the fresh concrete between 50 and 90 mm (class S2 of EN 206). The mixture proportions of all concrete specimens are summarized in Table 5 for cement and sand replacement, respectively. The main properties of fresh and hardened concrete are summarized in Table 6. For each age, three specimens (cubes of 150 mm) were tested for compressive strength and the mean value of these measurements is reported. The density of the fresh concrete varies from 2427 to 2453 kg/m^3.

The specimens for the durability tests were cast in steel cylinders of 100 mm diameter and 200 mm height. The molds were stripped after 24 h and the specimens placed under lime-saturated water at 20 °C for 90 days. This long-term curing period under water ensures an advanced degree of both Portland cement hydration and pozzolanic reaction.

Table 2
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	LSF	0.949
Na_2O	0.07	SR	2.47
SO_3	2.74	AR	1.24
Cl^-	0.00	HM	2.17

Table 3
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

Table 4
Metakaolin fineness characteristics.

d (μm)	Residue (%)	
	MK	MKC
Particle size distribution		
22.0	4.7	2.4
18.2	9.3	4.9
15.1	16.1	8.6
12.4	24.4	13.7
8.5	43.2	27.0
5.8	60.7	42.4
3.3	79.7	63.8
1.8	90.4	79.5
1.0	95.8	89.5
0.6	98.4	95.6
Fineness characteristics		
d_{20} (μm)[a]	13.6	10.3
d_{50} (μm)	7.5	5.1
d_{80} (μm)	3.4	1.9
Rosin–Rammler parameters		
n	1.42	1.18
pp (μm)	9.7	6.9

[a] d_i: The diameter where i % w/w of the particles (powder) are coarser.

2.4. Durability tests

The AASHTO T277 rapid test method was followed to rank the chloride penetration resistance of concrete by applying a potential of 60 V (DC) and measuring the charge passed through the specimen. The tested concrete cores are slices 51 mm thick, cut from the middle of the initially 200 mm specimens and coated with watertight tape on the cylindrical surface.

The air permeability tests were applied to a concrete cylinder of 100 mm diameter and height varied between 45 mm and 50 mm. The specimens were oven-dried at 105 °C, until a weight change