



## Research paper

## Pozzolanic activity of thermally and mechanically treated kaolins of hydrothermal origin

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## ABSTRACT

This work investigates the effect of the mechanical treatment of kaolin on its pozzolanic activity. Three representative Greek kaolins and a commercial product were activated using thermal and mechanical treatment. The pozzolanic activity was evaluated on the basis of Chapelle test and was investigated by means of X-ray Diffraction, Differential Thermal Analysis and Infrared Spectroscopy. The results showed that mechanical treatment of kaolin results in gradual kaolinite distortion, amorphization and, accordingly, to a competitive pozzolanic activation to that of the respective thermally treated ones. The crystallinity of raw kaolinite adversely affects the pozzolanic activity of both metakaolinite and nanostructured kaolinite.

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## 1. Introduction

The incorporation of different supplementary cementing materials (SCMs) in concrete can have a considerable effect on both fresh and hardened properties (Ding and Li, 2002; Badogiannis et al., 2004; Kovler and Roussel, 2011). SCMs are known to be enhancing the engineering and performance properties of concrete, in terms of its mechanical characteristics and durability (Siddique, 2008; Siddique and Khan, 2011). Their high pozzolanic activity leads to a further particle packing enhancement that is achieved by the pozzolanic products (chemical action) and acts complementary to the physical action (Badogiannis et al., 2004; Cyr et al., 2006). The main SCMs are silica fume, fly ash, ground granulated blast furnace slag, natural pozzolan, metakaolin and other clays. The effect of clay in cement is not a new subject and most applications utilize calcined clay like metakaolin, e.t.c. (Badogiannis and Tsvilis, 2009; Siddique and Klaus, 2009; Sfikas et al., 2014).

At the same time, the apply of nanotechnology in concrete has been gradually developing, aiming to the improvement of the macroscale concrete properties by the use of nanoscale materials (Garboczi, 2009; Raki et al., 2009; Scrivener, 2009; Sanchez and Sobolev, 2010). The research on concrete nanotechnology is focused on the measurement and characterization of the nano and microscale structure of cement-

based materials (Constantinides et al., 2003; Garrault et al., 2004; Plassard et al., 2005; Beaudoin et al., 2009; Ulm and Vandamme, 2009), and how this structure affects the properties and the performance of concrete (Garboczi et al., 2000; Dolado et al., 2007; Pellenq et al., 2008). It is also concentrated on the treatment techniques of the structure of nanomaterials, which could lead to the development of new nano SCMs (Ji, 2005; Li et al., 2006; Qing et al., 2007). It is expected that the addition of these new nano SCMs, could lead to superior mechanical performance and durability of concrete (Sobolev and Ferrada-Gutiérrez, 2005; Scrivener and Kirkpatrick, 2008).

Recent studies focuses on the possibility of using natural nanosized and non-calcined clays, since their properties that are important as admixtures to cement, naturally exist on the nanoscale, too (Chang et al., 2007; He and Shi, 2008; Morsy et al., 2009). Kaolin is one of the most widely used industrial minerals due to its physical and chemical properties, crystal structure, and surface chemistry (Murray et al., 1993; Rashad, 2013). However, only the metakaolin (MK) produced from kaolin, is a widely known material, applicant as a pozzolanic material either in cement or as SCM in concrete (Sabir et al., 2001; Siddique and Klaus, 2009). Metakaolin ( $\text{Al}_2\text{Si}_2\text{O}_7$ ) is a thermally activated pozzolanic material that is obtained by the calcination of kaolinitic clay at moderate temperatures ranging from 650 to 800 °C (Grim, 1968; Kristof et al., 2002). The main difference of MK from other pozzolanic materials, is its high reactivity with calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ], and its ability to accelerate cement hydration. Due to the high levels of silica and alumina in metakaolin, the C/S ratio of the produced calcium silicate

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hydrates (C-S-H gel) is expected to be greater than of silica fume and fly ash, thus implying improved concrete microstructure and contributing to the enhancement of its durability performance, in terms of strength, porosity, permeability, chloride ion diffusivity and freezing-thawing resistance, etc. (Jones, 2002; Hubertova and Hela, 2007; Hassan et al., 2012).

These properties of metakaolin, generated from its thermal amorphization, could be also attained by its mechanochemical activation. Mechanical activation is generally achieved when grinding utilizes impact and friction forces among particles (vibratory, oscillating, planetary mills, etc.) (Burton, 1966; Miller and Oulton, 1972; Mingelgrin et al., 1978; Dynys and Halloran, 1981; Miyazaki et al., 2000). It has been found that mechanochemical activation (e.g., dry grinding) of kaolinites can considerably increase the surface area, ion-exchange capacity, crystal structural deformation and amorphization, and solubility in acid and results in a progressive lowering of dehydroxylation temperature and intercalation reactivity (Kelley and Jenny, 1936; Laws and Page, 1946; Gregg et al., 1954; Takahashi, 1959; Schrader, 1970; Kristof et al., 2002; Frost et al., 2003). More specific, mechanochemical activation of kaolin is considered to initially lead to a removal of adsorbed and coordinated water, which is attributed mostly to “gel–water” formed from the structural hydroxyl groups of the kaolinite (Mako et al., 2009; Hamzaoui et al., 2014). The increase of the level of mechanical activation, (further grinding, further size decrease to nano scale), leads to an increase of the level of amorphization and distortion of the kaolinite structure which means that Si and Al ions are chemically available. Several studies certify that the optimization of the grinding method and consumed energy, could be an additional tool for kaolin activation and metakaolin production (Miller and Oulton, 1970; Juhasz, 1980; Aglietti et al., 1986; Gonzalez Garcia et al., 1991; Sanchez-Soto et al., 2000; Horvath et al., 2003; Leonel et al., 2014).

The production of a mechanochemical activated kaolin will gain the interest of the concrete industry, only if this activation is also chemical, and if it could be translated to pozzolanic activity. There are few studies showing that mechanical activation of kaolin is considered mechanochemical and that it is possible to obtain an active pozzolan with activity similar to that of commercial metakaolin. More specific, it has been shown that pozzolanic index of the resulting material is a function of the mineralogical composition of the raw kaolin and of the grinding process. The mechanochemical process increases the surface area of the material as well as its pozzolanic reactivity (Vizcayno et al., 2010; Mitrovic and Zdujic, 2014).

Additionally to the performance enhancement of concrete, through its improved durability, metakaolin is also considered as a sustainable and environmental-friendly material, due to the limited CO<sub>2</sub> emissions during its production process (compared to cement production). Thus, when it is used in concrete as a replacement material of cement, a significant reduction of the total CO<sub>2</sub> emissions is achieved (Aitcin, 1998). Apparently, the reduction of the CO<sub>2</sub> emissions becomes greater, if the production of metakaolin is achieved without thermal treatment. According to industrial data (pers. comm.) the energy required for the thermal decomposition of kaolinite is approximately 1600 kWh/t. Depending on the grinding method (wet or dry), the required energy for the mechanical treatment of kaolinite, is expected to be in the range of 200–1000 kWh/t.

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

	K1	K2	K4	KC
SiO <sub>2</sub>	73.45	72.47	65.92	47.85
Al <sub>2</sub> O <sub>3</sub>	18.04	18.40	22.56	38.20
CaO	0.40	0.35	0.36	0.32
MgO	0.03	0.03	–	–
Fe <sub>2</sub> O <sub>3</sub>	<0.10	<0.10	<0.10	0.30
K <sub>2</sub> O	0.80	0.80	0.57	0.27
Na <sub>2</sub> O	0.20	0.20	0.20	0.10
SO <sub>3</sub>	3.00	3.12	2.00	–

**Table 2**  
Grinding conditions of mechanically treated kaolins.

Sample	Mass (g)	Grinding balls size (mm)	Grinding time (h)
GK1	7.6	0.5	2.5
GK2	10.0	1.0	2.0
GK4	10.0	1.0	2.0
GKC	7.5	0.5	1.5

In this work, three representative Greek kaolins and one commercial product were studied concerning their pozzolanic activity after thermal and mechanical treatment. The pozzolanic activity was evaluated on the basis of Chapelle test. X-ray Diffraction, Differential Thermal Analysis and Infrared Spectroscopy are used for the characterization of the raw materials, the thermally and the mechanically treated kaolins and the Chapelle products.

## 2. Materials & methods

### 2.1. Materials

Three kaolin samples of hydrothermal origin (Kelepertsis et al., 1990) and varying chemical and mineralogical composition, were extracted from the kaolin quarry of Rallaki, Chalakas in NW part of Milos Island, Aegean Sea, Greece. K1 and K2 are typical samples with an average kaolinite content and low SO<sub>3</sub> content and K4 has higher and lower content of kaolinite and alunite, respectively. In addition, a commercial kaolin sample of high purity, KC, is also examined. The detailed characterization of raw kaolins is given in Section 2.4. Table 1 presents the chemical composition of the samples.

### 2.2. Experimental procedure

Thermal treatment of the kaolins was carried out in a laboratory programmable furnace. The samples ( $m = 140$  g) were thermally treated at a constant rate (10 °C/min) from ambient to 650 °C, where they remained for 3 h. The optimum conditions of thermal treatment were determined in a previous work (Kaloumenou et al., 1999; Kakali et al., 2001; Badogiannis et al., 2005). The thermally treated kaolins are referred as MK1, MK2, MK4 and MKC, respectively.

Mechanical treatment of kaolins was carried out in a Planetary Micro Mill. The samples, ( $m = 7.5–10$  g), were ground in a water suspension, using different sizes of ZrO<sub>2</sub> balls and the necessary grinding time, in order to produce samples with  $d_{50}$  of 0.5 μm, approximately. Details of the grinding conditions are listed in Table 2. The fineness characteristics of raw and treated kaolin samples, as determined by Malvern Mastersizer and Fritsch Analysette 22 Nano Tec, are presented in Table 3.

The pozzolanic activity of thermally (650 °C, 3 h) and mechanically treated samples was measured according to Chapelle test (Largent,

**Table 3**  
Fineness characteristics of raw and treated kaolin samples.

Sample	Fineness characteristics		
	$d_{20}$ (μm) *	$d_{50}$ (μm)	$d_{80}$ (μm)
K1	46.8	17.5	4.6
K2	36.8	14.0	3.8
K4	38.3	15.6	4.7
MK1	11.5	6.9	3.4
MK2	9.6	5.8	3.0
MK4	13.6	7.5	3.4
MKC	10.3	5.1	1.9
GK1	2.8	0.7	0.2
GK2	0.5	0.3	0.2
GK4	0.7	0.4	0.2
GKC	1.4	0.5	0.1

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