

## IMPACT OF DIFFERENT THERMAL ACTIVATED CALCINED CLAYS TO CONCRETE PROPERTIES: A REVIEW

Jelena Bijeljić<sup>1</sup>, MSc; Nenad Ristić<sup>2</sup>, PhD; Natalija Tošić<sup>3</sup>, MSc; Milan Protić<sup>4</sup>, MSc

<sup>1</sup>Collage of applied technical science, Niš, SERBIA, [jelena.bijeljic@vtsnis.edu.rs](mailto:jelena.bijeljic@vtsnis.edu.rs)

<sup>2</sup>Faculty of civil engineering and arhitecture, Niš, SERBIA, [nenad.ristic@gaf.ni.ac.rs](mailto:nenad.ristic@gaf.ni.ac.rs)

<sup>3</sup>Collage of applied technical science, Niš, SERBIA, [natalija.tosic@vtsnis.edu.rs](mailto:natalija.tosic@vtsnis.edu.rs)

<sup>4</sup>Collage of applied technical science, Niš, SERBIA, [milan.protic@vtsnis.edu.rs](mailto:milan.protic@vtsnis.edu.rs)

**Abstract:** Concrete is one of the most commonly used material in construction industry. It's already clearly that worldwide production of cement impact to environmental pollution and involves the emission of CO<sub>2</sub>. Various types of pozzolanic materials are purposed to improve that properties of concrete made of cement supplementary materials can be reached or made even higher. This paper is a review of the researchs of fresh and hardened properties of concrete made of different thermal activated calcined clays in the form of metakaolin (MK). The main goals of researchers are fresh and hardened properties of self-compacted concrete (SCC), consistency, enhanced strengths, deformational and durability properties of concrete.

**Keywords:** calcined clay 1, metakaolin 2, thermal activation 3, mechanochemical activatation 4, pozzolanic materials 5

### 1. INTRODUCTION

Due to energy consumption and existence of pollutants as CO<sub>2</sub> in cement production industry, some concrete adds have been researched to be used as a partial substitute for cement (to decrease cement) or aggregate and to be their alternative material [1]. How quantities of CO<sub>2</sub> pollution are on the really high level, about six billion tonnes per year, depending of previous construction type or goals of fresh and mechanical properties there are many mineral adds that can be used in the form of partial substitute of cement or aggregate. Environmental concern both in terms of damage caused by the extraction of raw material and CO<sub>2</sub> emission during cement manufacture have brought about pressure to reduce cement consumption by the use of supplementary materials [2]. Minimising impact to the environmental and energy consumption, for sustainable concrete production it's become clearly important, in addition to achieving, reductions in the use of natural materials and greenhouse gas emission [4]. To minimize negative effects, the requirement to increase powder content in some special types of concrete as self-compacting concrete – (SCC) is usually met by the use of additions. Some of the additions might be usually in the form of powders like limestone powder, basalt powder, fly ash, slag or calcined clay in the form of metakaolin [3]. Those pozzolanic materials might be used as effective cement replacement materials in concrete mixes [4].

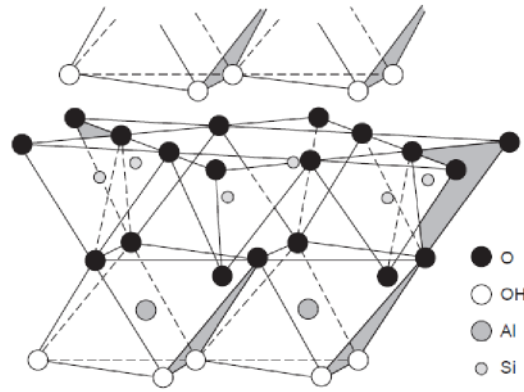
Calcined clays can be used as pozzolanic material in the form of kaolin (metakaolin - in literature MK). Calcined clay is obtained by calcination of kaolinitic clay at different temperatures, usually between 500-800°C. This white, fine particle size clay mineral has primary use in the manufacture of porcelain [5].

### 2. PRODUCTION AND PROPERTIES OF METAKAOLIN

The behaviour of clay minerals heating usually depends of the mineral structure. The term Metakaolin (MK), and “meta“ prefix is used to denote that some change in material have been happened. Kaolin is phyllosilicate whose composition (equation 1) is Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH<sub>4</sub>), that consider layers of silica and alumina in tetrahedral and octahedral coordination [6]. Structure is consist of alternating sheets of SiO<sub>4</sub> tetrahedral (layer T) and alumina octahedral (layer O) joined by oxygen atoms, that are not shared by SiO<sub>4</sub> tetrahedral in the T layers (Figure 1). The figure shows a one sheet kaolinite structure. Figure 1b show post-heating amorphous phase deriving from kaolinite in to metakaoline [7].

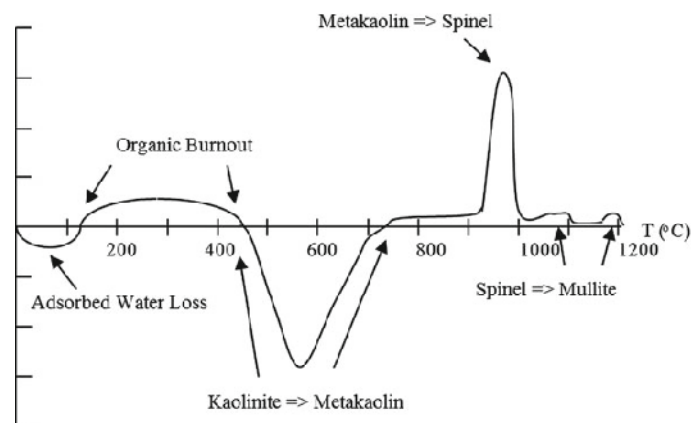
Δ 550°C





**Figure 1:** Structure of one kaolinite sheet [7]

Clay calcination leads to changed physical and chemical properties. The temperature between 100 and 250°C causes to liberation of inter-layer water (Equal 1). Process of dehydration began at 300-400°C and is accelerated at 500-600°C. Process of dehydration is completed when an atomic structure is destroyed [7]. Activation of Kaolin might be thermal or mechanochemical. Thermal activation is based on kaolin clays heating to the point of kaolin dehydroxylation. MK might be with pozzolanic properties, when dehydroxylation is reached. Thermal activation to the temperature that is less than it's needed for dehydroxylation leads to insufficiently reactive kaolinite material that containing residues. To the other way, heating up to the temperature higher that it's needed for observed material, effects of sintering and formation of non-active mullite are always expected [9]. Thermograf of kaolin is shown in Figure 2.



**Figure 2:** Thermogram of Kaolin [6].

Process of production is usually carefully controlled. Kaolinites are usually calcinated in rotary kilns by using a process that might reduce calcination time from hours to minutes. Process of calcination considers rapid subprocesses like heating, calcination and at the end cooling [7]. High MK quality usually depend applied calcining process, mineralogical and chemical composition of kaolin clay. Typical chemical MK composition usually consider SiO<sub>2</sub> in value 50–70 % by mass, Al<sub>2</sub>O<sub>3</sub> in value 17-45 % by mass, Fe<sub>2</sub>O<sub>3</sub> in value 0.2-5.5 % by mass. Others chemical compounds like CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and others are about 1% by mass or less.

**Table 1:** Typical chemical composition of MK detected at the Laboratory for Geochemistry, Faculty of Science Niš

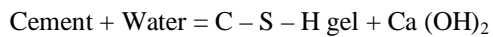
Ingredients	% by weight
SiO <sub>2</sub>	59.1
Al <sub>2</sub> O <sub>3</sub>	32.2
Fe <sub>2</sub> O <sub>3</sub>	5.0
CaO	0.9
MgO	0.6
Na <sub>2</sub> O	0.5
K <sub>2</sub> O	1.1
SO <sub>3</sub>	/
P <sub>2</sub> O <sub>5</sub>	0.5
TiO <sub>2</sub>	0.9

### 3. POZZOLANIC REACTIVITY

Pozzolanic material reactivity is ability of material to react with calcium-hydroxide when water is added. In that case, compounds might be divided to compounds of pozzolanic or hydraulic properties. Detecting pozzolanic reactivity methods might be used and divided to direct or indirect. Direct methods are based on measure reactive calcium hydroxide by using methods known as TG/DTA, XRD, FTIG, Chapelle method and many more. Indirect methods are based on compression strength measurements of mortar mixtures when pozzolanic material has been added [9].

#### 3.1. Pozzolanic activity of metakaolin

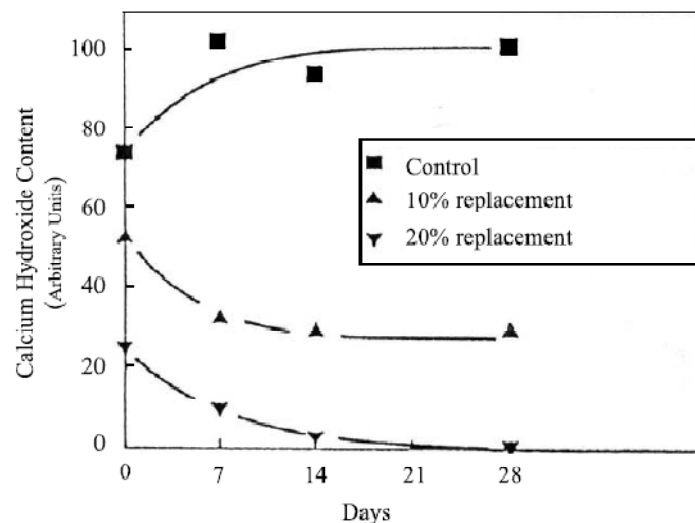
The calcination conditions and other characterizations of MK that have been investigated since the middle of 19<sup>th</sup> century and first able in the ceramic industry context [2]. There are several parameters influence pozzolanic activity of MK. The hydration reaction of MK usually depends of several factors like area surface, particles fineness, water amount, temperature etc. Calcium hydroxide (CH) is a by-product of cement hydration reaction. Cement, when is partially replaced by MK, forming reacts with calcium hydroxide results C-S-H gel [7][8]. In general, typical principal reaction is that  $Al_2O_3 \cdot 2SiO_2$  or  $(AS)_2$  react CH (that derived from cement hydration in the presence of water). The reaction form of cementations aluminium containing C – S - H gel [2]. The hydration reaction of MK depends of Portland cement (PC) type,  $AS_2/CH$  ratio, quantity of free water and the temperature of the mixture reaction. The chemical reaction is given in Equation 2 [7][8].



Many studies have been carried out to determine the hydration reaction and reactivity level of MK. By using the Chapelle test, some of the studies showed that MK is very effective pozzolan. In Table 2, reactivities of MK have been expressed as consumption rates of CH per gram of pozzolan, to Silica fume (SF) and Fly ash (FA). The total amount of CH has been measured by using thermograph analysis (DTA). Kostuch et al.'s reported that the results that 20% of MK might annul CH in concrete at 28 days. The effect of MK replacement level on the CH content has been shown in Figure 3. Oriols et al. reported that 30% and 40% of MK is required to annul all CH in MK-PC paste at the 28 days. [2].

**Table 2:** Pozzolanic activity of various pozzolans [2]

Pozzolan	SF	FA	MK
Reactivity Mg			
Ca(OH) <sub>2</sub> /g Pozzolan	427	875	1050



**Figure 3:** The effects of MK replacement level to the CH concrete content [2]

#### 4. FRESH PROPERTIES OF CONCRETE CONTAINING METAKAOLIN

Fresh properties of concrete with partial substitute of cement by MK might be measurements in well-known tests that help in determination parameters like slump-flow diameter, time  $T_{500}$  and many others.

Eva Vejmelkova et al. were investigating self-compacting concrete mixture (SCC) with partial substitute of cement. Mixture that contain MK (SCC-M) exhibited by using slump flow tests, that were compared to SCC that contain blast furnace slag (SCC-S). The loss of flowability over time was for SCC-M much faster than for SCC-S. This is related to higher surface area of the binder that contains MK. The results that are given in the paper are in qualitative agreement with previous studies. Used water/binder ratio was 0.32 [10].

Jae Hong Kim et al. were investigating the effects of mineral admixtures on workability of concrete. Three type of minerals were used: Silica fume (SF), MK, and wet-processed attapulgite clays. Mixtures were prepared by using of river gravel while cement/water ratio was constant. The mixtures prepared by using of MK were investigated with 1, 2, 5 and 10 percentage of MK adding. The average particle sizes are approximately  $1.2\mu\text{m}$ . The results given in there paper are also in qualitative agreement of based previous studies [11].

Rahmat Mandandoust et al. were investigating fresh and hardened properties of SCC that containing MK as a partial substitute for cement (0-20% of cement was replaced by MK, also tests were conducted with different water/binder ratio - 0.32, 0.38 and 0.45). The slump-flow test values of different concrete mixtures were measured in a range of 660-715mm, and all categorized as class 2, according to used standard. The flowability of mixtures was reduces with the higher proportion of MK replacement. Results of the test where water/binder ratio was 0.32 are shown in Table 3 [3].

Bijeljčić et al. were also investigating influence of MK to fresh properties of concrete. In that major, a test of flowability and workability of the mix design containing 80% cement and 20% MK was conducted. The results of the slump-flow test show that the designed mixture satisfies the criteria set forth by the EN 206-9:2010. Using the same equipment as for the conventional concrete, the slump-flow test was conducted. After the lifting of the conus, the housed concrete collapsed and spreaded under by it own weight and the two perpendicular diameters of the casting were measured. The obtained results were 700 mm in one, and 720 mm in the other direction. According to EN 206-9:2010 this SCC classifies as SF2 (concretes of plastic consistency, with spread diameter within limits of 660 mm and 750 mm). Hence, the first condition was satisfied [12][15].

**Table 3:** Resulting of testing fresh SCC mixtures

Type of the measuring	Authors	Vejmelkova et al.		Jae Hong Kim et al.			Rahmat Mandandoust et al.				Bijeljčić et al.	
		40%	10%	5%	2%	1%	20%	15%	10%	5%		
Slump flow diameter (mm)		MK	MK	MK	MK	MK	MK	MK	MK	MK	MK	20%
		730	711	622	616	578	670	690	675	680	720	MK
$T_{500}$ (sec)		8	-	-	-	-	6.56	4.88	4.32	2.88	5	

#### 5. COMPRESSIVE STRENGTH PROPERTIES OF CONCRETE THAT CONTAIN METAKAOLIN

During the past several studies have done to investigate the strength development properties of concrete that contain MK. Those studies show how MK as a partial substitute of cement could help in getting better results of concrete properties.

Wild et al. were investigating influence of MK to the hardened properties of concrete. The authors gave conclusion about few elementary factors. Filler effect that is based to PC hydration, which occurs in first 24h, and pozzolanic reaction with maximum effect in first 7-14 days when using MK in portion between 5 and 30% [13].

Brooks et al. were investigating compressive strength of concrete containing 0 to 15% of MK. Water/binder ratio was 0.28. On the 28 days compressive strength was the lowest for etalon concrete - 87MPa, 91.5MPa for concrete when contain 5% of MK, highest 104MPa for concrete when contain 10% of MK, and high compressive strength of concrete when contain 15% of MK - 103.5MPa [14].

Badogiannis et al. studied the effects of MK to compressive strength of concrete when MK replaces cement in portion of 10 to 20%. Positive effects to concrete started but after 2 days. Other their investigations were on Greek kaolins. Cement was replaced by 0, 10 and 20% of MK. They concluded that MK had positive effect on concrete strength but after 2 days, and then 28 to 180 days. Finally, it concluded that 10% of MK seemed to be favourable than 20% [5].

Eva Vejmelkova et al. were investigating properties of SCC containing MK and blast furnace slag. Compressive strength of the concrete made of MK that increased in inertial time of 2 days is much faster than to concrete made of blast furnace slag. This is related to higher reactivity of the blended binder when MK. The compressive strength that measured where 9.5 MPa, 37.8 MPa, 62.8 MPa and 72.0MPa at 2, 7, 28 and 90 days respectively [10].

## 5. CONCLUSION

According to many researchers, using of calcined clay in form of MK might be used as an excellent partial substitute of cement. How pozzolanic reactivity has been improved, as a result it's presented that MK might be good choice in to concrete mixtures. Researches of set of properties of fresh and hardened properties demonstrated that material that is analysed is a really good material that for sure can respond to now a days required requests and can find the application in building industry. It has been improved that fresh and hardened properties of concrete mixtures depend on of MK and water/binder ratio.

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