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Compressive strength and microstructure of ordinary cured and autoclaved cement-based composites with mechanically activated kaolins

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HIGHLIGHTS

- Cement composites with two different mechanically activated kaolins are compared.
- Strength and microstructure of ordinary cured and autoclaved composites are determined.
- Higher strengths exhibited AKG composites containing high content of quartz.
- AKG composite strengths were higher when autoclaving was applied.
- Ordinary curing of composites caused substantial strength decrease.

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ABSTRACT

The effects of two different mechanically activated kaolins, AKV (61% kaolinite, 14% quartz and 16% mica) and AKG (51.6% kaolinite and 40.6% quartz) on the compressive strength of cement composites and microstructure of pastes were investigated. Composite mixtures, in which 10, 20, 30, 40 and 50% of ordinary Portland cement (OPC) was replaced by AKV or AKG, were prepared with w/b of 0.5, and exposed to different curing conditions (ordinary curing for 28 days and autoclaving). Factors affecting microstructure were investigated on pastes by X-ray diffraction (XRD), Differential thermal analysis/thermal gravimetry (DTA/TG) analyses, Mercury intrusion porosimetry (MIP) and Scanning electron microscopy with Energy-dispersive spectroscopy (SEM-EDS).

AKG composites exhibited higher compressive strengths under both curing conditions. Positive autoclaving effects on strengths were predominantly pronounced at the higher cement replacement levels. Comparison of the autoclaved and ordinary cured paste microstructure, revealed more intensive pozzolanic reaction during autoclaving conditions (CH content near zero) and higher total porosity. The negative effect of hydrogarnet on the strength was compensated by the formation of the crystalline tobermorite.

Obtained results revealed that mechanically activated kaolin, with high content of quartz, could be a promising pozzolanic addition, even at high cement replacement levels (30–50%), especially when autoclaving curing conditions were applied.

1. Introduction

Pozzolanic additions, as supplementary cementitious materials (SCMs), are widely used for substitution clinker in cement, or cement in mortars or concretes. They could be by origin natural or artificial [1]. There are two types of artificial pozzolanic additions: byproducts, such as fly ash and silica fume, and thermally activated clays, whereby the best known is metakaolin (MK).

Pozzolanic additions are used to improve technical characteristics of mortars and concretes, such as strength, durability, rheological and transfer properties. The enhancement of these properties is related to the reactivity (chemical pozzolanicity), as their additions lead to a formation of supplementary cementitious compounds (SCCs), but also to their fineness (physical pozzolanicity) [2]. Beside technical benefits, their use reduces energy consumption and has environmental benefits as a result of reduction in the carbon dioxide emission, compared to the manufacture of Portland cement [3,4].

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MK, commercially produced from 1990, is manufactured under stringent conditions from a selected naturally occurring kaolin. The industrial process generally comprises selection/grinding, then thermal activation/calcination of the raw kaolin for several hours in a rotary kiln, followed by grinding of the burned material. The quality and reactivity of MK is strongly dependent on the composition and structure of the kaolin used, and on the thermal activation efficiency to remove chemically-bound water, through dehydroxylation [5–7]. Complete dehydroxylation corresponds to the destruction of kaolinite crystallinity (amorphisation) resulting in an increase of pozzolanic activity.

Supplies of traditional SCMs (fly ash, blast furnace slag, silica fume) are quite limited compared to the worldwide production of cement. However, due to its high price, application of MK is limited to high-strength or high-performance concretes. Increased demand for additions, which might substitute traditional SCMs and might be produced at lower cost, led to many investigations of alternative pozzolanic additions. One of the alternative pozzolana is mechanically activated kaolin. Although many studies [8–11] have shown benefits of mechanical activation of kaolin, this process, as far as we know, has not been yet applied on the industrial scale. Several studies showed that the optimization of the milling method and consumed energy, could be an additional tool for kaolin modification and production [12–15].

MK is used in various types of ordinary cured concrete, such as high-performance concrete, high-strength and lightweight concrete, glass fibre reinforced concrete [16]. In order to improve properties of concrete with MK, at least 15–20% of cement has to be replaced. The optimum replacement level of cement with MK is dependent on the nature and proportion of different reaction products, temperature and reaction time. Literature review [17] shows that optimal performance of concrete is achieved by replacing 10%–15% of the cement with MK. While it is possible to use less amount, the benefits are not fully realized until at least 10% of MK is used. Compressive strength of concrete with MK after 28 days of curing could be 20% higher compared to the reference concrete.

Recent studies [18,19] have demonstrated that beside ordinary curing conditions, MK could be used under steam-curing, usually applied in the precast industry. Studies showed that it was possible to substitute up to 25% of cement with MK, whereby positive effects on the strength were still achieved.

Although the reactivity of mechanically activated kaolin is similar or slightly inferior to that of thermally activated kaolin, there are few publications [11,20,21] referring to its utilization in cement composites. Also, a general description of the effect of mechanochemically activated kaolin on the hydration reactions and properties of cement-based composites is lacking. Therefore, the investigation of strength, hydration products, microstructure and other performance parameters of cement-based composites containing mechanically activated kaolin is considered important.

This research is the continuation of our previous investigation [20,22,23] with the main objective to enlarge the use of mechanically activated kaolin in cement-based systems. Its main objective is to show how the use of two different mechanically activated kaolins affects strength and microstructure of cement composites, cured under different conditions.

2. Materials and methods

2.1. Raw materials

Two different mechanically activated kaolins, AKV and AKG, were used for cement replacement. Their main physical and chemical properties are presented in Table 1. The complete details about activation conditions can be obtained elsewhere [20,24]. AKV was obtained from kaolin having 61% of kaolinite, 14% of quartz and 16% mica, while major minerals in AKG were kaolinite 51.5% and quartz 40.6%.

Table 1
Properties of AKV and AKG.

	AKV [20]	AKG [24]
Pozzolanic activity, MPa	13.7	14.0
Reactive silica content, %	29.52	33.00
Specific surface area, m^2/g	49.76	21.75
Particle size (d_{50}), μm	5.913	6.346

Ordinary Portland cement (OPC), CEM I 42.5R, produced by Lafarge BFC, Beočin Serbia with a Blaine fineness of 4120 cm^2/g, and the following chemical composition (mass%): SiO_2 20.86, Al_2O_3 5.59, Fe_2O_3 2.49, CaO 62.40, MgO 2.50, K_2O 0.77, Na_2O 0.22, SO_3 3.63 and LOI 1.74, was used.

CEN Standard sand, distilled water, superplasticizer Sika ViscoCrete TECHNO 20S and hydrated lime were also used.

2.2. Design, mixing, curing and testing

2.2.1. Composite mixtures

Composite mixtures, where 10%, 20%, 30%, 40% and 50% of cement was replaced with AKV or AKG, were prepared with the water-to binder ratio 0.50, and the sand to binder ratio 3.0. For the purpose of comparison, also a reference mix (Ref. C) having only OPC as the binder was studied. The workability was adjusted using superplasticizer. Hydrated lime was added at higher cement replacement levels −30% to 50% (designation CH) in order to secure enough CH for pozzolanic reaction. For estimation of the hydrated lime quantity it was assumed that 20% of CH was released during the cement hydration, and that the best mechanical properties could be achieved when MK was reacted with CH in the ratio MK/CH = 2 [1,25].

Composite mixture proportions are presented in Table 2.

The specimens were cast in moulds (three prisms size 40 × 40 × 160 mm) using vibration table.

2.2.2. Curing

In order to examine the effects of curing conditions on the mechanical properties of composites, ordinary and autoclave curing were applied.

Samples were stored in the mould in the moist atmosphere for 24 h and thereafter hardened samples were ordinary cured in water under standard curing conditions until the testing age of 28 days, or autoclave cured at constant temperature and pressure of 216 °C and 2 MPa for 4 h. Then the autoclave heater was turned off and the chamber was allowed to cool naturally.

2.2.3. Compressive strength test

Compressive strength measurements were carried out according to EN 196-1.

2.2.4. Cement paste

Representative pastes with 20% (AK 20) and 30% and 50% of AKV or AKG, with the addition of appropriate hydrated lime quantity (AK 30 CH and AK 50 CH), were prepared, with water-to-binder ratio (w/b) of 0.4, for determination of hydration products and for measurements of porosity and pore size distribution. Ordinary cement paste (without AK) was prepared as the reference (Ref. P).

Paste samples were cast in cubic moulds (50 mm × 50 mm × 50 mm), and cured in the same way as composite mixtures. The hydration reaction was stopped at 28 days by immersing crushed particles in acetone for 24 h to replace free water. Afterwards, the samples were subjected to drying at 65 °C in an oven for 24 h. The pretreated fractured samples were analyzed by MIP and SEM-EDS.

Samples for determination of hydration products were additionally milled for 60 s in the oscillatory Herzog HSM 100 mill, to pass 45 μm sieve.

2.2.5. Microstructure testing

The following techniques were used for the evaluation of microstructure of pastes:

- XRD analysis for the identification of crystalline phases in pastes (Philips PW 1050 diffractometer, with 40 kV and 30 mA, using Cu-Kα graphite-monochromatized radiation (λ = 1.5418 A)). Data were recorded from 5° to 60° 2θ, with the step size of 0.05° and time per step of 10 s. Crystalline phases were identified using EVA software package v.9.0 and PDF-2 database.
- DTA/TG analyses (SDT Q600 simultaneous TG/DTA instrument (TA Instruments)) were performed under dynamic (100 cm^3 min^{-1}) N_2 atmosphere, with a heating rate of 20 °Cmin^{-1}, from ambient temperature up to 1100 °C, in order to investigate the $Ca(OH)_2$ consumption and to determine the hydration reaction products.
- MIP tests for the microstructural determination of total porosity and pore size distribution were performed on the AutoPore IV 9500 mercury porosimeter with a maximum 228 MPa injection pressure.
- The morphology of hydration products of selected pastes was observed by SEM-EDS using a JEOL JSM-6460 LV coupled with EDS detector (LINK AN 1000 EDS microanalyzer). The samples were coated with gold and the SEM-EDS analysis was carried out at an accelerating voltage of 20 kV.